Advanced Surface Engineering
Room 209 F W - Session SE-WeM

Advanced Surface Engineering Oral Session
Moderator: Diana Berman, University of North Texas

8:00am SE-WeM-1 Tools for High-Throughput Autonomous Materials Discovery and Development for the Surface Engineer, *Christopher Muratore,* University of Dayton **INVITED**
The talk highlights automated experimental tools enabling synthesis and characterization of hundreds of samples per day. This approach, where experimentation is much faster than simulation has the potential to flip the traditional 'order of operations' for materials discovery where experiment feeds model during initial iterationsOne high-throughput format relies on scanning lasers with broad ranges of power, scan rates, and focal positions to induce physical and chemical transformations within materials. Laser heating parameters may be set to approximate quasi-equilibrium heating as in a furnace, or induce extreme heating and cooling rates, thereby broadening the range of accessible compositions and crystal structures dictated by kinetics of both chemical reactions and crystallization. Deposition tools, such as our magnetron sputtering system outfitted with 36 different source materials may also be used to create a broad range of compositions on the sample surface. Once a combinatorial sample with a desired range compositions and laser illumination conditions is processed, it can be manually or autonomously subjected to the combination of high-throughput characterization tools required for evaluation of the properties specified by the user. Autonomous systems enable users to specify a desired property and the system iterates processing and characterization data to 'make decisions' about optimization of conditions to realize the user-specified input.For example, an automated Raman spectroscopy system enables rapid collection of key data points (grain size, defect density, thickness, etc.) for technologically important optical, electronic, and energy materials.Some specific case studies include fundamental kinetics studies showing migration-limited crystallization kinetics amorphous materials can be directly observed.Pre-cursor materials for downstream processing can be converted directly into reaction intermediates with the appropriate non-equilibrium laser energy input to reduce process activation energy and process temperature required for high-quality materials. For photocatalysis materials rapid, non-equilibrium process conditions were identified demonstrating optimized performance with mixtures of phases.

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8:30am SE-WeM-3 Hydrophobic and Hydrophilic Metallic Coatings: Their Sputter Depositions and Applications, *Jinn P. Chu,* National Taiwan University of Science and Technology, Taiwan
The talk will cover two types of metallic coatings with extreme properties: hydrophobicity and hydrophilicity.

First, an introduction to a low-friction hydrophobic metallic glass (MG) coating and its applications will be provided. This amorphous multicomponent coating, fabricated via sputter deposition, exhibits typical glass characteristics, such as a glass transition temperature upon heating. The MG coating has been successfully applied in various fields, including medical tools. This non-stick MG coating is intended to replace easily peeled-off teflon coatings, such as polytetrafluoroethylene (PTFE).

On the other hand, for the superhydrophilic coating, a 316 stainless steel layer is sputtered onto various substrates, resulting in a water contact angle of approximately 10 degrees on the coated surface. This coating also demonstrates antifouling and underwater superoleophobic properties, making it advantageous for use in separation membranes for oil/water emulsions. Moreover, it has proven highly effective in enhancing electrochemical responses in electrodes used for electrochemical sensors and supercapacitors.

8:45am SE-WeM-4 Surface Engineering of Organic Nm-Thick PEDOT:PSS Films for Enhanced Electrical Conductivity, *Aaron DiFilippo,* Virginia Tech*; Amrita Chakraborty,* Virginia Tech, United States Minor Outlying Islands (the)*; Marius Orlowski,* Virginia Tech
We report on enhancing the electrical conductivity of Poly(3,4-ethylenedioxythiophene) Polystyrene Sulfonate (PEDOT:PSS) using various surface engineering methods, including acid treatment, topical doping with Cu and Ag nanoparticles, multilayer PEDOT:PSS deposition, and graphene incorporation. Our investigations reveal that optimizing multilayer deposition combined with nitric acid surface treatment yields superior results compared to alternative methods involving metal nanoparticles and graphene. This approach not only significantly enhances conductivity but also offers improved stability, reduced errors, and cost-effectiveness. Key optimization parameters, such as spinning speed, etchant concentration, and etching time, were identified as critical to achieving these outcomes. From all acids tested, nitric acid-treated multilayer PEDOT:PSS demonstrated a remarkable reduction in sheet resistance, from 1 MΩ/sq to 7 Ω/sq, corresponding to an increase in electrical conductivity from 0.18 S/cm to 15,699 S/cm—an improvement of over 10^5 times. Topical doping with Cu and Ag nanoparticles (30-90 nm) also improved conductivity, though less effectively than nitric acid treatment. Notably, Cu nanoparticles were as effective as Ag in topical doping, unlike bulk doping, where Cu oxidizes in aqueous solutions. This makes topical doping a versatile and cost-effective alternative, particularly for applications requiring surface metal nanoparticles, such as conductive dendrites for resistive RAM.

While each method individually enhanced conductivity, combining them did not yield significant additional improvements. The optimized nitric acid treatment, involving nine PEDOT:PSS layers, achieved the highest conductivity enhancement. However, acid-treated PEDOT:PSS exhibits a modest, self-limiting degradation in conductivity over time, stabilizing after a few days. This behavior suggests that while the initial enhancement is substantial, long-term stability requires further investigation.The study underscores the importance of optimization parameters and highlights the potential of these methods for advancing PEDOT:PSS-based technologies in flexible electronics, energy devices, and beyond. The surfaces have been characterized with Atomic Force Microsopy (AFM)X-ray diffraction (XRD), and optical microscopy in terms of surface roughness and surface composition. We also address film aging to mitigate reliability issues induced by ambient conditions.

9:00am SE-WeM-5 Atomic Oxygen-Resistant Metal Oxide Coatings for Space Operations in Low-Earth Orbit, *Joslin S. Prasanna, Javier Meza-Arroyo, Minglei Sun, Chase Hazboun,* Department of Materials Science and Engineering, University of Texas at Dallas*; Fernando Quintero-Borbon,* Centro de Investigación en Materiales Avanzados S.C. (CIMAV), Unidad Monterrey, Mexico*; William Vandenberghe, Julia Hsu, Robert M. Wallace, Rafik Addou,* Department of Materials Science and Engineering, University of Texas at Dallas
Space operations in low-earth orbit (LEO) are hindered by the effect of atomic oxygen (AO) on spacecraft [1]. Coatings on spacecraft suffer loss of material due to erosion from attack by AO, thereby increasing drag and causing vehicles to drift from their operational orbit. Consequently, frequent thrust maneuvers are required to correct this position, consuming fuel, and ultimately limiting the duration of service. This raises the need to develop low-drag coatings for spacecraft that are resistant to AO and extend the life of space missions. Atomic-layer deposition (ALD) is an effective technique to deposit extremely conformal coatings of high quality and free from pinholes [2]. It also gives exceptional control over thickness down to the angstrom scale. Solution synthesis performed by the sol-gel method can scale the deposition process to deposit thicker films over larger areas.

In this work, we investigated the use of metal oxides (Al_2O_3 and TiO_2) deposited by ALD and sol-gel techniques as AO-resistant, low-drag coatings to protect conventionally used materials like Kapton and other polymers. SiO_2 and Kapton films were also studied alongside the metal oxide films for reference. Two different ALD recipes were tested for growing TiO_2, and one recipe for Al_2O_3. The films were characterized, both as deposited and after O_2 plasma exposure, by X-ray photoelectron spectroscopy (XPS) for chemical analysis, ellipsometry for thickness measurement, and atomic force microscopy (AFM) for surface roughness measurement. This investigation is further assisted by theoretical modeling of drag using experimentally determined surface structures. The drag simulations will be used to identify the key parameters influencing drag performance. Our study showed that Al_2O_3 deposited by ALD and sol-gel techniques displayed excellent resistance to O_2 plasma. The TiO_2 films showed more degradation but still far outperformed the Kapton and SiO_2 reference films, proving to be promising materials for AO-resistant coatings in LEO.

This work is supported by DARPA Materials Investigation for Novel Operations in Space (MINOS).

[1] S.W. Samwel et al., Space Res. J., 7(1), 1-13, (2014)

[2] T.K. Minton et al., Appl. Mater. Interfaces, 2(9), 2515-2520, (2010)

9:15am SE-WeM-6 Reducing Tribological Run-in Through Morphology Control: A Dual-Layer Approach for Improved Environmental Insensitivity and Tribological Performance, *Steven Larson, Alex Mings, Tomas Babuska, Ping Lu, Jon Vogel, Michael Dugger, John Curry,* Sandia National Laboratories

Molybdenum disulfide (MoS_2)-based composite coatings are widely utilized in the aerospace and defense industries to reduce friction, prevent galling, and enhance wear resistance. These coatings are often grown as composites with various metals (Ni, Ti, Al, Pb, Au, WSe) and nonmetals (Sb_2O_3, PbO, C). A commonly used composition incorporates antimony oxide (Sb_2O_3) and gold (Au) into the MoS_2 matrix to promote increased density and improve wear life by amorphization. However, these additions significantly compromise the aging resistance of MoS_2, resulting in increased friction during both run-in and dwell-time phases.

In this presentation, we demonstrate a dual-layer MoS_2 sputtered coating designed to mitigate the effects of oxidation during long-term storage and short-term exposure to highly oxidizing environments, effectively transforming the traditionally water-sensitive MoS_2 into an environmentally insensitive coating. In addition to enhancing oxidation resistance, these structures facilitate a reduction in run-in friction, reducing initial cycle friction to near run-in levels (zero run-in coatings). We correlate deposition parameters with plasma probe measurements (retarding field energy analyzer), thin film material properties (density, crystallinity, hardness, modulus, and stoichiometry), and tribological performance (friction, run-in behavior, and wear rate) of the films. The resulting thin film stacks reduce initial friction after aging by nearly 300%, exhibiting negligible transient friction behavior (run-in) while maintain ultra-low wear rates.

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9:30am SE-WeM-7 Optimizing Low-temperature MAX-phase Ti_2AlN Synthesis in Reactive TiAlN Multi-layer Thin Films, *Moses Nnaji, David Tavakoli,* Georgia Institute of Technology, USA*; Dale Hitchcock,* Savannah River National Laboratory*; Eric Vogel,* Georgia Institute of Technology, USA

$M_{n+1}AX_n$ phases are a class of layered nanolaminates where M represents a transition metal, A represents a group 12-16 element, and X represents carbon or nitrogen. These $M_{n+1}AX_n$ phases, or "MAX-phases", often boast a novel combination of metal and ceramic properties, including thermal and electrical conductivity, machinability, thermal shock resistance, and high-temperature integrity. Consequently, MAX-phase thin films have attracted interest for use in high-temperature protective coatings, Ohmic contacts, and low friction systems. However, the high temperatures (>700 °C) needed to form their complex crystal structures serve as a persistent bottleneck for meaningful adoption of MAX-phase coatings on sensitive substrates. Reducing the substrate temperature needed to form MAX-phase films is necessary to improve their viability in select applications, and thus improve the performance of said applications.

Magnetron sputtering is a common technique for MAX-phase thin film synthesis, and MAX-phase synthesis via low-temperature sputtering of reactive multi-layers and subsequent high-temperature annealing has also been reported. In this context, reactive multi-layers are thin film structures which can exploit exothermic reactions as a form of stored chemical energy. These reactions are not spontaneous at low substrate temperatures, but become favorable at higher temperatures and provide additional energy to the film. This phenomenon effectively results in phase transitions at decreased substrate temperatures. Thus, tailoring the thin film deposition process to yield multi-layers with high reactivity may help in forming MAX-phases at desirably low temperatures.

MAX-phase synthesis via reactive multi-layers is established, but work explicitly addressing the impact of the reactive multi-layer mechanism and phase composition on MAX-phase formation temperature is limited. Thus, comparing the behavior of composite multi-layers with different reactivities (e.g., containing constituent materials with different free energies and enthalpy) can provide insight towards minimizing the annealing temperature needed for MAX-phase synthesis. In this work, various techniques, including *in-situ* X-ray diffraction and differential scanning calorimetry, will be used to extensively characterize the evolution of MAX-phase Ti_2AlN as a function of annealing temperature in sputtered composite Ti-Al-N films. *In-situ* analysis of Ti/AlN, TiN/TiAl, and single-layer TiAlN thin film morphologies will aid optimization of processes that yield Ti_2AlN films at especially low temperatures.

9:45am SE-WeM-8 Design of 2D Material-Based Coatings for Superlubricity in Sliding and Rolling Contacts, *Diana Berman, Ali Macknojia, Aditya Ayyagari,* University of North Texas

Friction and wear-related failures remain the greatest problems in today's moving mechanical components, from microelectromechanical devices to automotive assemblies and to biological systems. The critical need to reduce and eliminate the tribological failures constitutes the necessity for continuous search of novel materials and lubrication solutions. In this presentation, we demonstrate an experimental pathway to yield superlubricity in rolling-sliding contact conditions using MXene-based solid-lubricant materials. The material's compression and inter-layer shearing result in material reconstruction to pose superlubricity. High-resolution transmission electron microscopy analysis, complemented by multi-scan Raman spectroscopy showed the formation of a robust amorphous tribolayer. This demonstration is expected to not only advance the applied aspects in the development of oil-free solid lubricants but also push the boundaries of fundamental understanding of materials' structure-property relations across physical states.

11:00am SE-WeM-13 Physics of Sample Charging During X-Ray Photoelectron Spectroscopy: Insights from Experiments with Thin Film Insulators, *Grzegorz (Greg) Greczynski,* Linköping University, Sweden **INVITED**

Sample charging during X-ray photoelectron spectroscopy (XPS) measurements of poorly conducting samples is a widely recognized concern that seriously complicates analysis of chemical bonding. The high complexity owing to many instrument- and sample-determined variables involved in the process is likely responsible for the fact that no comprehensive theory of charging exists. The present study aims to describe the development of charging for the case of thin insulating films supported on conducting substrates. Such systems are particularly well suited for studies of charging phenomena as they provide unique opportunity to separate effects that operate on different length scales and allow to investigate the role of charge supplied from the bottom contact. Two inherently insulating oxides, SiO_2 and WO_3, with the thickness varying by more than three orders of magnitude (from 1 to 5000 nm) are chosen to serve as model systems for insulators with respectively low and high X-ray-induced conductivity. The key role of low-energy secondary electrons (SE), X-ray penetration depth, sample work function, and the insulator SE yield in the development of surface charging is demonstrated. Based on these findings, a conceptual model is presented to serve as a starting point for the interpretation and discussion of charging phenomena in specific cases. Although the study is based on thin films the conclusions give insights into critical factors that govern charging phenomena in any other types of insulating samples.

11:30am SE-WeM-15 Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling for Surface Engineering, *Mark Baker, Charlie Chandler,* University of Surrey, U.K.*; Simon Bacon, Dhilan Devadasan,* Thermo Fisher Scientific, UK*; Oliver Parlour, Steve Hinder,* University of Surrey, U.K.*; Tim Nunney, Richard White,* Thermo Fisher Scientific, UK

For corrosion and wear resistance applications, XPS depth profiling is the most widely used analytical technique for chemical analysis of thin films, coatings and other surface treatments. The technique also provides important chemical information on corrosion and wear products, important in understanding degradation mechanisms. Traditional XPS sputter depth profiling has its advantages, such as good depth resolution, but leads to incorrect chemical compositions and chemical state information being recorded in the profile for many materials, due to ion beam induced damage. Sputtering is also a relatively slow process and the profiling depth is limited to approximately 5 μm for practical purposes. A new approach has recently been developed in which XPS depth profiles are generated through femtosecond laser ablation (fs-LA) rather than sputtering. This new methodology avoids chemical damage and has the ability to profile to much greater depths (many 10s microns) due to the effective instantaneous ablation process and the ability to easily vary the amount of material removed per pulse through changing the laser energy [1]. Using a 1030 nm wavelength, 160 fs pulsed laser, fs-LA XPS depth profiles will be shown for: (i) single and multi-layer thin films, coatings and other surface engineering processes employed to enhance corrosion and wear resistance; (ii) oxidised/corroded surfaces, demonstrating the capabilities of this new technique for surface engineering applications.

[1] M.A.Baker et al, *Applied Surface Science* **654** (2024) 159405

11:45am **SE-WeM-16 In Situ SEM Study of Graphene Rheotaxy: Growth on Molten Metals**, *Kristýna Bukvišová,* CEITEC; Thermo Fisher Scientific, Czechia*; Radek Kalousek,* Brno University of Technology, Czechia*; Jakub Zlámal,* CEITEC; BUT, Czechia*; Marek Patočka,* BUT, Czechia*; **Suneel Kodambaka**,* Virginia Tech*; Jakub Planer,* CEITEC, Czechia*; Vojtěch Mahel,* Thermo Fisher Scientific; BUT, Czechia*; Daniel Citterberg,* CEITEC, Czechia*; Libor Novák,* Thermo Fisher Scientific, Czechia*; Tomáš Šikola, Miroslav Kolíbal,* CEITEC; BUT, Czechia

Rheotaxy -- growth of crystalline layers on liquid substrates -- has been used to grow spatially-periodic self-assembled domains of graphene on molten metals such as Cu [1]. While earlier studies of graphene rheotaxy have identified the optimal growth parameters required for the growth of highly ordered domains, the mechanisms leading to self-assembly are not well understood [2,3]. Here, we present *in situ* scanning electron microscopy (SEM) studies of graphene growth via chemical vapor deposition of ethylene on molten Cu and Au surfaces at temperatures T between 1073 K and 1390 K.

The graphene layers are grown on solid and molten Cu ($T_{m, Cu}$ = 1357 K) in an ultrahigh vaccum (UHV) SEM and on solid and molten Au ($T_{m, Au}$ = 1336 K) in an environmental SEM equipped with a microReactor [4]. We observe *in situ* the nucleation and growth of graphene domains, changes in their shapes and sizes as a function of deposition time, ethylene pressure, and the metal composition (Au or Cu), its state (solid or liquid), and temperature. From *ex situ* Raman spectroscopy data, we confirm that the as-deposited layers are graphene. Using *in situ* high-temperature atomic force microscopy (AFM) operated at ~1300 K, we measure the surface curvature of graphene. *In situ* SEM images acquired during the deposition of graphene reveal that graphene domains oscillate and self-assemble. We follow the dynamics of graphene domains on molten metal surfaces, measure amplitudes of domain fluctuations, and quantitatively determine the rate-limiting mechanisms controlling the graphene growth on solid and liquid Au and Cu surfaces. From the data, in combination with density functional theory (DFT) calculations and continuum modeling, we show that the graphene domain oscillations lead to self-assembly and are due to Casimir-like effect of surface undulations of the liquid metal [5].

References:

[1] Geng, D. et al. PNAS 2012, 109, 7992-7996.

[2] Tsakonas, C.; Dimitropoulos, M.; Manikas, A. C.; Galiotis, C. Nanoscale 2021, 13, 3346-3373.

[3] Jankowski M. *et al.*, ACS Nano 2021, 15, 9638-9648.

[4] Novák, L., Wandrol, P., Vesseur J. R. Micr.&Microanal. 2020, 26 (S2), 1144-1145.

[5] Bukvišová, K. *et al.* arXiv:2503.04327.

12:00pm **SE-WeM-17 Optical Metasurfaces in Iridium for High-Temperature Applications**, *Zachary Kranefeld, T. Pan Menasuta, Kareena Guness, Kevin Grossklaus, Thomas Vandervelde,* Tufts University

Optical metasurfaces are gaining attention as a new technology because they can perform the tasks of several traditional optical elements simultaneously, while at a fraction of the size and weight. Their performance is dictated by the sub-wavelength structured surface, which also makes them extremely sensitive to morphology changes after fabrication. Oxidation and plastic deformation (edge rounding) are two dominant types of surface changes that occur in high-temperature environments, which limits optical metasurfaces from being a useful technology for those applications. We have pioneered a method of fabricating an optical metasurface into iridium films. Iridium is a refractory metal which is stable in these types of environments. The lack of reactivity, extremely high melting temperature, and high hardness are what makes iridium the best choice for the application. However, these features also present major challenges for lithographic pattern transfer at the nano-scale. The optical metasurface fabricated in our work was a selective emitter in the MWIR for a thermophotovoltaic system. The design process and all of the fabrication techniques we attempted are described, as well as the characterization of the final device.

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