MEMS and NEMS Technical Group
Room 302 - Session MN+AS+NS+QS+SE-MoM

Dynamics and Engineering of MEMS/NEMS

Moderators: Jürgen Brugger, EPFL, Switzerland, **Eva Weig**, University of Munich, Germany

9:00am **MN+AS+NS+QS+SE-MoM-3 MEMS-Based Surface Nanoengineering Using Thermal AFM Probes: 30 Years and Counting**, ***Jürgen Brugger,*** École Polytechnique Fédérale de Lausanne, Switzerland **INVITED**

Soon after the first publication in 1985 of the atomic force microscope (AFM) attempts were made to extend AFM-based surface probing from microscopy to lithography [reviewed in 1]. The potential applications in writing and reading for data storagein the early years served as technology driver and showed remarkable performances [2]. One of the variants of AFM-based writing (and reading) operates a heated nano-tip to perform thermally induced phase changes of materials. The three-fold combination of nano-scale heat localization (30 nm scale), high temperature (~ 500 °C)and particularly fast heating/cooling cycles (10E-6 s) is unique and opens new opportunities for surface engineering and material conversion using heat.In the meantime, nano-tips and cantilevers were further perfected as nanotools to locally induce phase changes in materials for a wide range of exploratory studies. Today, thermal scanning probe lithography (t-SPL) has matured into turn-key systems that can be compared to some extend to electron beam lithography, but without the useof charged particles and without the need for development. The full grasp of potential applications in R&D and production is still growing as the technique is still emerging.

In this talk, we will give first some background how heated AFM probes were initially designed and fabricated that led to today's advanced thermo-mechanical probe design of micro-cantilevers and nano-tips. The paper will then review some main achievements up to date [3] and then present recent results on t-SPL utilized for 2D materials by our own work [4, 5], and will conclude with some outlook on further challenges in hot-tip nanoengineering.

References:

[1] R. Garcia, et al. Nature Nanotechnology (2014)

[2] H. J. Mamin et al. Applied Physics Letters (1992)

[3] S. T. Howell et al. Microsystems & Nanoengineering (2020)

[4] X. Liu et al. Advanced Materials (2020)

[5] X. Liu et al. Nano letters (2020)

10:40am **MN+AS+NS+QS+SE-MoM-8 Atomically-Thin MoS_2 Nanoelectromechanical Resonators**, *R. Yang,* Shanghai Jiao Tong University, China*; **Jaesung Lee,*** University of Texas at El Paso **INVITED**

With the development of the Internet of Things (IoT), new sensors and signal processing elements that consume *near-zero* power to operate on resonance, have high tunability and small form factor are necessary.The ultralow mass and large resonance tunability make resonant 2D nanoelectromechanical systems (NEMS) suitable for ultrasensitive mass, force and biomolecular sensing, radio-frequency (RF) front end, and strain-tunable devices.Further, molybdenum disulfide (MoS_2) resonators only require picowatt level of power for sustaining the strong and stable resonance operations due to their ultralight weight.This opens an opportunity to explore new sensors and signal processing elements for IoT applications that really require near-zero power to operate on resonance, and at the same time, have wide dynamic ranges and tuning ranges. In this talk, we summarize our most recent advances in 2D MoS_2 NEMS resonators.

11:20am **MN+AS+NS+QS+SE-MoM-10 Can a Single Nanomechanical Mode Generate a Frequency Comb?**, ***Eva Weig,*** Technical University of Munich, Germany **INVITED**

Doubly-clamped nanostring resonators excel as high Q nanomechanical systems enabling room temperature quality factors of several 100,000 in the 10 MHz eigenfrequency range. Dielectric transduction via electrically induced gradient fields provides an integrated control scheme while retaining the large mechanical quality factor [1]. Dielectrically controlled nanostrings are an ideal testbed to explore a variety of dynamical phenomena ranging from multimode coupling to coherent control [2]. Here I will focus on the nonlinear dynamics of a single, resonantly driven mode. The broken time reversal symmetry gives rise to the squeezing of the string's fluctuations. As a result of the high mechanical Q factor, the squeezing ratio is directly accessible from a spectral measurement [3]. It is encoded in the intensities of the two spectral peaks arising from the slow dynamics of the system in the rotating frame. For stronger driving, an onset of self-sustained oscillation is observed which leads to the generation of a nanomechanical frequency comb. The effect is a consequence of a resonantly induced negative effective friction force induced by the drive. This is the first observation of a frequency comb arising solely from a single mode and a single, resonant drive tone [4].

[1] Q. P. Unterreithmeier et al., Nature 458, 1001 (2009)

[2] T. Faust et al., Nature Physics 9, 485 (2013)

[3] J. Huber et al., Phys. Rev. X 10, 021066 (2020)

[4] J. Ochs et al., in preparation

Applied Surface Science Division
Room 320 - Session AS+CA+EL+EM+LS+SE+SS-MoA

Quantitative Surface Analysis

Moderators: Jordan Lerach, PPG Industries, **Hong Piao**, FUJIFILM Electronic Materials USA., Inc.

1:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-1 Hard Targets: Developing Tools for Quantitative HAXPES*, David Cant,*** National Physical Laboratory, UK **INVITED**

'Soft' x-ray based XPS, using aluminium or magnesium anodes, has been a workhorse of surface analysis labs for decades. Over this time, substantial efforts have been made in the development of tools such as sensitivity factors, transmission function corrections, physical parameter databases, simulation software, interpretation methods, and more. Thanks to the existence of such tools, the data obtained from 'soft' XPS, with careful analysis, can provide a strong, quantitative understanding of samples in terms of the relative concentration of elements and their chemistry within the topmost ~10 nm of material. Nevertheless, sometimes 10 nm is not enough.

Until recently, XPS of materials beyond this topmost region of the surface would require either destructive depth profiling of the sample or the use of synchrotron light sources; the former carries its own metrological challenges, as well as ruining a sample, while the latter introduces a plethora of complexities which render calibration difficult. However, recent developments in the design of instruments utilising higher-energy x-ray anodes have begun to make HAXPES instruments more readily available in the lab. This allows far more analysis of samples that previously might have been restricted to synchrotron studies; for example in non-destructive depth-profiling of coated samples with overlayers beyond the ~10 nm limit of 'soft' XPS. Yet with new instruments come new issues; transmission function calibrations that work for the 0 - 1400 eV energy range are not much use for spectra that stretch some KeV beyond, and relative sensitivity factors for each new photon energy and instrument geometry are needed, particularly given the cornucopia of new core levels made available, and the breadth of sensitivity at higher photon energies.

Here we discuss progress towards more quantifiable XPS and HAXPES measurements. A method for the calculation of theoretical sensitivity factors is described, applicable to instruments of any geometry for x-ray sources in the energy range 1.5 - 10 keV, and their validity for depth-profiling of samples well beyond the depths achieved by aluminium sources is demonstrated. We discuss developments in straightforward transmission-function calibrations of standard aluminium sources by the use of a mathematically-defined reference spectrum, as well as progress towards transmission calibration of higher energy sources for which reference spectra do not yet exist. From these developments, the possibility of a 'universal' calibration and sensitivity scheme for both lab- and synchrotron-based HAXPES systems at a range of energies is proposed.

2:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-3 Process-Induced Reactions in Interfaces of High-K/Metal Gate Stacks Studied Using HAXPES*, Thierry Conard*,** *A. Vanleenhove, F. Mascarenhas, I. Hoflijk, I. Vaesen,* IMEC, Belgium

While high-energy photoemission has been in use for decades, it has remained mostly confined to synchrotron radiation facilities. Synchrotron beamlines allow a large flexibility regarding measurement conditions and set-up but are inconvenient in the framework of technological developments, where routine analysis of material systems is needed. The recent availability of performant lab-scale high-energy photoemission spectrometers [1,2,3] alleviate these beamline limitations and thus allow to investigate technological relevant models.

In this presentation, we will demonstrate the potential of HAXPES lab-scale systems regarding application in the semiconductor industry, and more specifically regarding the chemical analysis of interfaces. We will demonstrate the investigation of modifications in layer chemistry of buried layers in multi-layer high-k/metal gate stacks upon thermal treatments. Annealing is one of the critical stages during manufacturing of gate stacks and chemical modification at interfaces play a major role in device performance. With this presentation we will present results on simple stacks such as TiN/HfO_2/SiO_2/Si as well as more complex stacks such as TaN/TiAl/TiN/HfO_2/SiO_2/Si or W/TiN/HfO_2/SiO_2/Si. Results will be presented obtained both with Cr Kα (5.4 keV) and Ga Kα (9.25 keV) HAXPES. The respective advantages of these two energies will be discussed in terms of chemical identification, sensitivity and quantification.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the HAXPES Lab instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

References

[1]https://www.ulvac-phi.com/en/products/xps/quantes/

[2]https://www.kratos.com/products/axis-supra-xps-surface-analysis-instrument

[3]https://scientaomicron.com/en/system-solutions/electron-spectroscopy/HAXPES-Lab

2:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-4 Quantification and Reporting of XPS Data Taken Under Near Ambient Pressure Conditions – Chances and Challenges in Acquision Speed, Beam Damage, Sensitivity, Reliability, Reproducibility and Repeatability***, P. Dietrich,* ***Andreas Thissen,*** SPECS Surface Nano Analysis GmbH, Germany

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But even more, data quality becomes transparent also in times of open source publications and open data repositories.

For the last ten years XPS under near ambient pressure conditions (NAP-XPS) has gained significant attention in the XPS community. The technique allows for standard analysis of samples under pressures up to about 50 mbar. This opens XPS to liquids, solid-liquid interfaces, gas-solid-interfaces, gas-liquid-interfaces. New fields like operando studies on electrochemical systems, corrosion experiments, analysis of food samples, but also studies of biological samples have been added to the XPS portfolio. The background gas pressure in such experiments is beneficial for the analysis of materials, because it avoids beam damages and degradation due to UHV conditions and also enables true non-destructive analysis of all types of degassing samples and insulators. On the other hand, the absorption of X-rays in the gas atmosphere, the emitted electrons from the gas molecules and inelastic electron scattering in the gas influences the spectral distribution of photoelectrons significantly strongly influencing elemental identification, quantification and detection sensitivity. This presentation summarizes the special challenges in the interpretation of NAP-XPS data and uses several reference samples (mostly published in Surface Science Spectra) from different fields of application. Basic concepts for identification and quantification of spectral features are demonstrated. Finally an outlook is presented how close NAP-XPS is to be a routine metrology technique.

3:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-5 The Modern Spectrometer – Reliable, Repeatable and Relatable***, S. Coultas, J. Counsell,* Kratos Analytical Limited, UK*;* ***Christopher Moffitt,*** Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Limited, UK

The outlook of the XPS community has changed significantly in the last decade. The technique has seen constant steady growth due to the rise in surface-based material research – energy storage and harvesting are two such disciplines. This growth of new first-time users needs to be considered, as does the way in which faculties manage centralised analytical facilities. This has led to a change in the philosophy of the workflow of an XPS spectrometer and how the user interacts with the "tool". In this modern era of devolved data and non-expert users the spectrometer itself needs to be reliable, repeatable and relatable. Reliable

– delivers on the promise, Repeatable – consistency with data acquisition and processing, Relatable – simple, easy-to-use, non-expert. This new philosophy creates new challenges for manufacturers who need to deliver the best spectrometer for this new market whilst at the same time maintaining the expectations and beliefs of the traditional analyst.

The discussion will focus on defining the issues of the current XPS outlook and providing practical, workable solutions. The following topics, when combined together, will illustrate the holistic design principles of a modern spectrometer: Simplified workflow, standard methods, automated routines, parameter logging, calibrated and up-to-date sensitivity factors, processing operators, data output and report generation.

3:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-6 Modulation with Atomic Number of the Shirley Background of the Photoemission Spectra of Transition Metals***, **Alberto Herrera-Gomez**, D. Guzman-Bucio,* CINVESTAV-Queretaro, Mexico*; D. Cabrera-German, M. Mayorga-Garay, O. Cortazar-Martinez, J. Torres-Ochoa, A. Carmona-Carmona,* CINVESTAV-Unidad Queretaro, Mexico*; M. Gonzalez Reyna ,* UNAM-Mexico*; V. Crist,* XPS Library*; C. Ospina-Ocampo,* Cinvestav-Unidad Queretaro, Mexico

The 2*p* photoemission spectra of the first-row pure transition metals are similar enough to each other to display a meaningful progression, through the row, of the characteristics of the peaks and background [1]. The same goes for the 3*d* spectra of the second-row pure transition metals [2]. In addition, there are similarities between the behavior of the peak and background parameters of these two rows, such as the dependence of the intensity of the Shirley background with atomic number. The Shirley background is largest for the first column (3B column of the periodic table), decreases to a local minimum to then rise again to a local maximum on the seventh column (8B). The large value of the Shirley background for the first column elements is correlated with the large asymmetry of the main peak and the presence of strong intrinsic plasmons. This correlation might be due to a similar physical origin [3] The local maximum in the 8B column coincides with the maximum of permutations of the valence band, as previously pointed out by Castle and Salvi [4]. The physical mechanism of these phenomena will be discussed.

[1] D. Cabrera-German, G.-B. Dulce-Maria, M. Mayorga-Garay, O. Cortazar-Martinez, J.-A. Torres-Ochoa, A. Carmona-Carmona, A. Herrera-Gomez, Peak and background parameters of the 2p core level of the pure first row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[2] D.-M. Guzman-Bucio, A. Carmona-Carmona, M.A. Gonzalez-Reyna, A. Herrera-Gomez, Peak and background parameters of the 3d core level of the pure second row transition metals, J. Vac. Sci. Technol. A. (2022) (in progress).

[3] A. Herrera-Gomez, D. Cabrera-German, A.D.A.D. Dutoi, M. Vazquez-Lepe, S. Aguirre-Tostado, P. Pianetta, D. Nordlund, O. Cortazar-Martinez, A. Torres-Ochoa, O. Ceballos-Sanchez, L. Gomez-Muñoz, L.G.M. Herrera-Gomez, Alberto., Dagoberto Cabrera-German., Anthony D. Dutoi., Milton Vazquez Lepe., Servando Aguirre-Tostado., Piero Pianetta., Dennis Nordlund., Orlando Cortazar-Martinez., Alejandro Torres-Ochoa., Oscar Ceballos-Sanchez., Intensity modulation of the Shirley background of the Cr 3p spectra with photon energies around the Cr 2p edge, Surf. Interface Anal. 50 (2018) 246–252. https://doi.org/10.1002/sia.6364.

[4] J.E. Castle, a. M. Salvi, Interpretation of the Shirley background in x-ray photoelectron spectroscopy analysis, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 19 (2001) 1170. https://doi.org/10.1116/1.1378074.

4:00pm **AS+CA+EL+EM+LS+SE+SS-MoA-8 Thin Film Analysis by XPS: Quantitative Modeling of Sputtering and Depth Profile Data***, **Lev Gelb**, A. Walker,* University of Texas at Dallas

We present progress in the simutaneous quantitative extraction of both compositional profiles and sputtering parameters from XPS depth-profiles of multilayer films. Depth-profile data are routinely processed to provide “fractional composition vs ion dose” profiles, but such profiles suffer from significant drawbacks: they are constructed assuming that the sample is homogeneous in the probed region, which is not true near interfaces, and it is not normally possible to precisely convert between units of ion dose and depth.

Our approach is to first construct analytical models for both the sample structure and for the erosion process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) most consistent with the observed apparent fractional composition profiles. This is done numerically, by comparing simulated and observed apparent composition profiles in a maximum-likelihood framework using an evolutionary optimization algorithm. The only required inputs to the calculation are the “fractional composition” profiles (above) and models for the inelastic mean free paths (IMFPs) for each tracked peak.

We demonstrate the basic idea by analysis of using synthetic data. The resolution of the extracted depth profiles improves when additional peaks are incorporated in the analysis. Small deficiencies in the structure or sputter model do not strongly affect the extracted compositional profiles, while errors in the IMFPs used have much larger effects. We then discuss promising results obtained from the analysis of experimental data from some well-characterized samples. Finally, we discuss improvements and extensions of this modeling/analysis framework. The sputtering model can be extended to include in-sample mixing and chemical reactions. The scheme can also be extended to use complete spectra as input.

4:20pm **AS+CA+EL+EM+LS+SE+SS-MoA-9 Understanding and Controlling Sample Degradation on Modern XPS Spectrometers***, **David Morgan**,* Cardiff University, UK

As XPS systems become ever more user-friendly, with “load-point-click-report” type automated analysis possible, the expertise in understanding samples, their handling and ultimately identifying and dealing with experimental artefacts is slowly eroding.

It has been previously shown that developments in the charge compensation methodology employed, especially the use of dual electron-ion compensation systems, can cause significant damage to a range of inorganic and organic materials [1,2] and in some cases a synergistic effect from the x-rays on the degradation rates can be observed.

Herein, the degradation effect using x-rays and a dual beam neutraliser are explored and discussed, and a delineation of the effects from both neutraliser and the x-rays on a series of polymeric, organic and inorganic materials are presented, together with methodologies to mitigate, or at the very least minimise, such analysis induced damage and propose that which we believe to be a better way of estimating sample damage on a per-system basis than those previously published [3].

[1] L. Edwards, P. Mack and D. J. Morgan, “Recent advances in dual mode charge compensation for XPS analysis”. Surface and Interface Analysis, 51 (2019) 925-933

[2] R. McLaren, G. Owen and D. J. Morgan, “Analysis Induced Reduction of a Polyelectrolyte”, Results in Surfaces and Interfaces, (2021) 100032

[3] G. Beamson and D. Briggs, “High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database,” Wiley, Chichester, 1992.

4:40pm **AS+CA+EL+EM+LS+SE+SS-MoA-10 XPS Intensity Calibration and Validation Using Polyethylene and Ionic Liquids***, **Benjamen Reed**,* National Physical Laboratory (NPL), UK*; J. Radnik,* Bundesanstalt für Materialforschung und -prüfung (BAM), Germany*; A. Shard,* National Physical Laboratory (NPL), UK

For quantitative X-ray photoelectron spectroscopy (XPS) analysis, it is necessary to know the *energy-dependent spectrometer response function* ('transmission function') of the XPS instrument. There is a huge variability of transmission functions between different laboratories and instruments, as well as different acquisition parameters for the same instrument. For comparable and reproducible analyses, there is a necessity for a standardised method of intensity calibration and validation.

For intensity calibration, the simplicity of polyethylene’s inelastic background can be described by a mathematical function that can be easily reproduced, is continuous, and noise-free. Instrument geometry must be considered due to the anisotropic emission of photoelectrons and the polarization of monochromated x-rays in many commercial XPS instruments. We therefore present geometry-corrected reference spectra of polyethylene for Al Kα instruments which are traceable to gold, silver, and copper reference spectra from the National Physical Laboratory (NPL). Polyethylene does not require in-situ sample preparation needing only to be scraped with a scalpel before measurement, making it a suitable method for instruments without an ion-sputtering source. VAMAS study A27 determined that over a kinetic energy range of 180 eV to 1500 eV, intensity calibration with polyethylene deviates by ±6.5% compared to previous NPL method using precious metals. Deviations less than 5%, and as low as 1%, are attainable with careful data acquisition from well-maintained instruments. This intensity calibration method is now being developed as an international standard under the auspices of ISO TC201 “Surface Chemical Analysis”.

Once an instrument has been intensity corrected, it is good practice to validate the calibration by measuring a homogeneous sample of known composition. Ionic liquids have several notable properties that make them an ideal material for XPS analysis. Ionic liquids exhibit a high degree of lateral and depth homogeneity, are UHV compatible, and have well-defined stoichiometries. When deposited in recessed sample holder, the meniscus of an IL will be perfectly flat meaning that there are no contributions from sample topographic effects. 1-propyl-3-methyl-imidazolium-bis(trifluoromethyl sulfonyl)imide (Solapur®) is one such IL candidate, with core levels up to ~800 eV binding energy, making it apt for verifying the quantification of light elements, especially for organic materials. Here we present spectra for Solapur® ionic liquid and discuss how they may be used to validate an XPS intensity calibration.

Biomaterial Interfaces Division
Room 318 - Session BI1+AS+EM+NS+SE+TF-TuM

Bioanalytics, Biosensors and Diagnostics

Moderators: Caitlin Howell, University of Maine, **Laura Mears**, TU Wien, Austria

8:00am **BI1+AS+EM+NS+SE+TF-TuM-1 Understanding and Employing Adhesion Forces in Microfluidic Channels for Cell Separation***, **Avi Gupta**, F. Chrit, A. Liu, A. Alexeev, T. Sulchek,* Georgia Institute of Technology, USA

Rapid advancements in microfluidic technologies during the past few decades have significantly aided advancements in the field of BioMEMS. These technologies can facilitate development of easily scalable tools that can be translated to point-of-care healthcare products. Researchers have capitalized on these tools to create differential separation techniques that rely on adhesion forces. The adhesive interactions play a significant role in governing the trajectory of cells in microfluidic channels as well as the reliability of these devices, however, a concise model explaining cell interactions with chemically coated surfaces is yet to be developed. This research describes studies using microfluidic flow at different flow regimes to study dynamic cell adhesion. APTES, P-selectin, and Pluronic were used as models for non-specific adhesion, specific adhesion, and adhesion-free surfaces, respectively. A microfluidic device with slanting ridges was used to provide forced contact and to visualize the effect of these chemistries on cell trajectories using a microscope and a high-speed camera. Parameters of the channel that were studied include ridge angle, gap size, channel width, and flow rate. It was found that adhesive forces modulate the interaction time of cells during contact points with the slanting ridges. At an average flow velocity of 3.1 cm/sec we observed higher interaction time for APTES coatings and lower for Pluronic coatings. Higher adhesion on APTES coated surface of the channel leads to more deflection of cells towards the streamlines leading them to go opposite to the ridge direction. In contrast, lower surface adhesion on Pluronic coated surface made cells deviate along the ridge perpendicular to streamlines. Narrow channel widths and acute ridge angles helped in exaggerating the differences in trajectories of cells going along or under the ridge. Atomic force microscopy (AFM) was used to quantify the adhesion forces. This knowledge was used to develop a predictive model employing Lattice Boltzmann techniques along with Morse potential and Bell model to represent interaction between cells and device surface. This improved understanding of adhesion forces in microfluidic devices opens new avenues for developing separation techniques that don't employ specific molecules like P-selectin but rely upon the inherent geometry and surface interaction of the cells with a microfluidic channel.

8:20am **BI1+AS+EM+NS+SE+TF-TuM-2 Wafer-Scale Metallic Nanotube Arrays with Highly Ordered Periodicity for SERS Application***, **Jinn Chu**,* National Taiwan University of Science and Technology, Taiwan

This paper reports on the wafer-scale fabrication of ultrahigh sensitivity SERS substrates using metallic nanotube arrays (MeNTAs) with highly ordered periodicity. Various metals and alloys have been used to prepare MeNTAs via sputtering over a contact-hole array template created in photoresist. These include ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au). The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 10 µm) in a variety of shapes, including tall cylinders and dishes. In addition, over this is deposited a uniform coating of Au nanoparticles to form a high-sensitivity AuNP@MeNTAs 3D-SERS substrate. Systematic micro-Raman spectroscopic analysis reveal that the fabricated array could function as a SERS-active substrate with crystal violet (CV) and folic acid as analytes (a minimum detection limit of 10^{-13} M CV). Enhancement factor of 1.06×10^9 is obtained from our triangular Ag MeNTA. This work is the first to fabricate wafer-scale metallic nanotube arrays with SERS properties, which represents an important step toward realizing the large-scale fabrication of ultrasensitive SERS-active materials.

8:40am **BI1+AS+EM+NS+SE+TF-TuM-3 Customizing Silk Film Surface Properties Using Plasma-Enhanced Chemical Vapor Deposition***, A. Devore, G. Reyes, **Morgan Hawker**,* California State University, Fresno

Silk fibroin (silk) is a naturally-derived polymer with high utility in biomedical contexts, notably in tissue engineering. Silk bulk properties can be tuned to mechanically match a range of biological environments, including soft and hard tissues. As with other naturally-derived polymers, silk constructs degrade via surface-mediated enzymatic hydrolysis into non-toxic amino acid byproducts. Because tissue engineering relies on the underlying scaffold to degrade as the healthy tissue forms, controlling silk scaffold degradation kinetics is essential to maximize silk's utility. Notably, prior work to control silk degradation kinetics relies on either altering silk matrix properties (i.e., manipulating the secondary structure), or through creating silk-containing blends such as copolymers. Although both strategies effectively control degradation, doing so is often at the expense of mechanical properties. Any mechanical mismatch induced through controlling degradation can hinder scaffold function. Developing a strategy to program silk degradation - without altering bulk mechanical properties - is required to enhance their efficacy as biomaterials.

This talk will highlight recent efforts to develop a radio-frequency plasma-enhanced chemical vapor deposition (PECVD) approach with the potential to modulate silk degradation. The long-term objective of this work is to control the rate of surface-mediated enzymatic hydrolysis by customizing silk surface properties. Surface properties are thought to be paramount in controlling silk construct/enzyme interactions, so tuning silk film surface properties using PECVD was a logical first step. Silk films were first dropcasted, and were then subjected to PECVD. Plasma feedgas composition was tuned using two unique precursors: acrylic acid (to produce thin films with polar functional groups on the silk surface), and pentane (to produce thin films with non-polar functional groups on the silk surface). Plasma polymerization using mixed precursor conditions was also explored. Contact angle goniometry was utilized to evaluate the wettability of all plasma-modified and control silk films. Changes in surface chemistry were evaluated using high-resolution x-ray photoelectron spectroscopy. Collectively, findings demonstrated that surface properties depend on both feedgas composition and position of the silk film in the plasma reactor. In sum, PECVD represents a promising approach to customize silk surface properties.

9:00am **BI1+AS+EM+NS+SE+TF-TuM-4 Biopotential Sensing Using Flexible, Reusable Smart Textile-Based Dry Electrodes***, **Jitendra Pratap Singh**,* Physics Dept IIT Delhi, India

Biopotential signals are used to assess organ function and make diagnoses. Biopotential electrodes are used to monitor and record biopotentials by acting as an interface between biological tissue and electrical circuits. The accurate detection of physiological signals from the human body is essential for health monitoring, preventive care, and treatments.

Wearable bioelectronics developments applied directly on the epidermal surface provide a promising future biopotential sensing option. Wearable textile electrodes for biopotential sensing are a promising candidate for long-term health monitoring. Wearable health-monitoring devices should be simple to use, stigma-free, and capable of delivering high-quality data. Smart textiles, which incorporate electronic elements directly into the fabric, offer a seamless way to incorporate sensors into garments for a variety of purposes. This work describes different types of flexible and reusable textile-based dry electrodes for biopotential monitoring. This work also describes the direct writing of laser-induced graphene (LIG) on a Kevlar textile for the production of reusable dry electrodes for long-term ECG monitoring. The electrode as-prepared has a high electrical conductivity and skin contact impedance of 100 ± 1 kΩ to 7.9 ± 2.7 kΩ for frequencies ranging from 40 Hz to 1 kHz, which is comparable to conventional Ag/AgCl wet electrodes.

The outcomes demonstrate comparable performance with significantly reduced electrode-skin impedance for clinical-grade devices. Even after several hours of usage, these electrodes do not irritate the skin and are effective without any skin preparation. As a result of their flexibility and a better match to the modulus of the skin, it is anticipated that the suggested dry electrodes will provide comfort for long-term biopotential monitoring. A simple, cost-effective, and scalable fabrication approach enables the fabrication of flexible electrodes of arbitrary shape for long-term biopotential monitoring.

1. Y. Maithani, B. Choudhuri, B. R. Mehta, and J. P. Singh: Self-adhesive, Stretchable, and Dry Silver Nanorods Embedded Polydimethylsiloxane Biopotential Electrodes for Electrocardiography. *Sensors Actuators A Phys.***332**, 113068 (2021).
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long - term ECG monitoring. *IOP Publ. Ltd 2020***2**(chapter 8), 1 (2020).

9:20am **BI1+AS+EM+NS+SE+TF-TuM-5 Functional Plasma Polymers for Biosensing Applications***, Melanie McGregor,* University of South Australia **INVITED**

Materials with intricate nanostructures display wetting properties that modern technologies already use to lubricate engines or waterproof clothing. Yet, their full potential in applications for sustainable catalysis, air purification or biosensing cannot be realised until we understand how nano-objects adsorb to surfaces with features of comparable size. Indeed, controlling or even predicting how proteins, antibodies, exosomes, surfactant or nanoparticles stick to nano-engineered surfaces is a challenge because key aspects of the wetting phenomenon remain poorly understood at this scale. In this talk, I will briefly review what we currently know about “nanowetting”.[1] I will then introduce the concept of plasma polymerisation as a technique to control both surface chemistry and surface topography. I’ll use the example of plasma deposited polyoxazoline (POx) to highlight this technique’s attributes, drawbacks and recent progress made in understanding the unique chemistry and reactivity of POx films, using both plasma in-situ and post deposition spectroscopic analysis.[2]Plasma deposited Polyoxazoline thin films share many valuable properties with polyoxazoline prepared via conventional organic chemistry: they are biocompatible, non-cytotoxic and low fouling.[3] What is more, they bind biomolecules covalently, support cell adhesion, and are generated in a solvent free, single step process, which makes them particularly attractive for industrialization. For these reasons, plasma deposited polyoxazoline are used in applied biomedical research, from in vitro stem cell culture to controlling immune responses.[4]

I’ll conclude this presentation with tangible outcomes of the translational research projects I’ve conducted with various industries, where we used nanoengineered plasma polymers, to create materials for cancer diagnosis and growing organoids.[5]

[1]**M. MacGregor** and K. Vasilev. *Advanced Materials Interfaces,4*, 1700381.,2017**;M. MacGregor** et al., *Nanoscale*, 8(8),4635-4642, 2016

[2] **M. Macgregor***et al.*Chemistry of Materials, 29(19)8047-51,* 2017; **M. N. MacGregor**-Ramiasa et al., *J. Mat. Chem. B*, 3, 6327-6337, 2015

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[5]**M. MacGregor***et al. *Biosensors and Bioelectronics,* 171: 112699,2020; K.M. Chan […]**M. MacGregor****Cancers* 13(21), 5544 2021

Chemical Analysis and Imaging Interfaces Focus Topic
Room 302 - Session CA+AS+SE+SS-TuM

Progress and Challenges in Industrial Applications

Moderators: Alex Tselev, University of Aveiro, Portugal, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

8:00am **CA+AS+SE+SS-TuM-1 Progress on Commercializing Doped Diamond Materials and Devices***, Anna Zaniewski,* Advent Diamond **INVITED**

Diamond has long been recognized as a potentially transformative material for power, sensor, and quantum applications. However, realizing the potential of diamond has depended upon a series of breakthroughs in the growth, design, and fabrication of diamond for electronics. Most notably, CVD growth of doped diamond has been a catalyzing breakthrough for realizing next-generation diamond components. Advent Diamond will present progress on achieving commercialization of diamond components and outline future targets for semiconducting and quantum devices.

8:40am **CA+AS+SE+SS-TuM-3 Advanced in Situ Transmission Electron Microscopy: A Powerful Tool for Materials Science, Catalysis, Energy Storage & Lifescience Applications***, Hugo Pérez-Garza,* DENSsolutions, Netherlands **INVITED**

We introduce our technology for in situ studies inside transmission electron microscope (TEM), where next to heating and biasing studies, also environmental studies (i.e. in gaseous or liquid environments) are made possible. The systems rely on a Micro Electro-Mechanical System (MEMS)-based device as a smart sample carrier, which contains an integrated set of biasing electrodes or an integrated microheater, to enable in situ electrochemistry, catalytic studies, failure analysis and biomedical studies, among others. As a result, the system provides users with the capability to visualize exciting dynamics in vacuum or liquid/gas environments as a function of different stimuli. In order to provide meaningful results and address historical challenges, our MEMS device controls the flow direction and ensures the gas/liquid will always pass through the region of interest. Thereby, the developed systems offer the opportunity to define the mass transport and control the kinetics of the reaction. Furthermore, the systems allow to control the liquid thickness, enabling resolutions that can go even down to 2.15 Å (for a 100nm liquid thickness). We believe that our developments will play a fundamental role in addressing many of the research questions within battery optimization, fuel cells, (electro)catalysis, as well as for advanced (bio)materials and nanomedicine. Furthermore, it will the unique possibility to visualize biological processes in real time, without the need of vitrifying the biological specimen.

Keywords: Transmission electron microscopy, in situ, MEMS, environmental studies, stimuli

9:20am **CA+AS+SE+SS-TuM-5 Chemical Analysis Using Laboratory-Based Hard X-Ray Photoelectron Spectroscopy: The Binding Energy Reference Challenge***, A. Vanleenhove, F. Mascarenhas, **Thierry Conard**,* IMEC, Belgium

XPS is a well-established technique used for non-destructive analysis of the chemical composition of thin layers and interfaces and is most commonly performed using Al Kα radiation (1486.6 eV), which limits the analysis to the top 5-10nm. The recently developed laboratory-based hard X-ray photoelectron spectroscopes (HAXPES) provide new analysis options. They enable the analysis of thicker film structures and interfaces buried down to 20-50 nm depending on the photon energy and facilitate the analysis of fragile buried layers without ion-induced chemical damage.

This new in-lab technology however comes with new challenges. By the increase of effects which were less pronounced or did not play a role in the analysis with soft X-ray photoelectron spectroscopy the exact binding energy determination and hence analysis of chemical bonding inside layers and at interfaces is more challenging. The recoil effect for instance, which is related to preservation of momentum, resulted in electron energy shifts well within the error bar of peak position determination for XPS spectra. For HAXPES, the recoil effect has to be taken into account, especially when examining low Z materials. Charging effects play a bigger role as well. While charging has to be taken into account for XPS, the analysis of most XPS spectra is quite straightforward as long as the surface charge is stable and the lateral distribution of surface charge is uniform within the area of analysis. For HAXPES however vertical charge distribution comes into the game for a large group of structures whose development can benefit from HAXPES analysis. Vertical charge build up can be complex, especially if examined structures exist of multiple layers and hence multiple interfaces, containing a large variety of materials. But even in ‘simple’ non-conducting one-layer structures a vertical charge gradient builds up when exposed to X-rays and small changes in the parameters of standard surface charge neutralization techniques - as the use of e-beam flood guns - can influence the nature of the charge gradient.

HAXPES spectra of technologically relevant samples will be discussed to demonstrate the challenge of determining exact binding energy values. The set of examined samples comprises complex oxide layers with varying thickness on Si samples and metal/high-k/Si stacks including high-k materials as HfO_2. All experiments are performed in a PHI *Quantes* system and/or a Scienta Omicron *HAXPES Lab*, both equipped with two monochromatic X-ray sources: an Al Kα (1486.6 eV) and a Cr Kα (5414.8 eV - *Quantes*) or Ga Kα (9252.1 eV – *HAXPES lab*) X-ray source.

Acknowledgement

We are grateful to the Research Foundation Flanders (FWO) for funding the *HAXPES Lab* instrument within the HERCULES program for Large Research Infrastructure of the Flemish government. Project I014018N.

11:00am **CA+AS+SE+SS-TuM-10 Integrating Spatial Multiomics Using Giant Cluster Imaging Mass Spectrometry at the Single-Cell Level***, Hua Tian,* University of Pittsburgh **INVITED**

Tissue is highly organized with diverse cells that interact and communicate. Together with numerous biomolecules (e.g. metabolites and lipids) of cellular processes, the multilevel heterogeneities drive the biological function and disease-associated discoordination[1-2]. This spatial complexity is often ignored by traditional tissue assay. Mass spectrometry imaging holds the potential to visualize the heterogeneous cell organization and biomolecules in their context. However, it is challenging to achieve high spatial resolution and high chemical sensitivity toward different biomolecules. Moreover, the correlation of spatial omics in a single sample is impossible due to the difficulty of preserving the fast-changing metabolites.

To overcome these analytical hurdles, innovative technology and methodology are developed for omics imaging in single cells. On the same frozen-hydrated tissue, successive $(H_2O)_{n\ (n>28k)}$-GCIB-SIMS and C_{60}-SIMS imaging are employed to profile untargeted metabolites/lipids and targeted proteins by lanthanides antibodies (~ 40 in one acquisition) at 1 µm resolution. The novel ion source, $(H_2O)_{n(n>28k)}$-GCIB enhances chemical sensitivity, improves beam focus, reduces matrix effect, and extends detection ranges up to *m/z* 6000 [3-12]. Coupled with cryogenic analysis, the tissue is analyzed at near nature state, retaining the spatiotemporal distribution of metabolites and lipids. The AI-aided computational processing is used to register the omics in different cell types for further discriminant analysis.

With the new development, a number of tissues are imaged. On breast cancer tissue, the high population of macrophages (CD68) and less infiltration of immune cells (CD45, CD4) are observed, as well as the variation of the metabolic state in different cells. Several phosphatidylinositol species are concentrated in the epithelial tumor cells (pan-cytokeratin), along with desaturated lipids and GSH, indicating the mechanism of immune resistance and antioxidation for tumor survival [27]. Eight ganglioside GM3s correlate with the Ki-67 expressing cells, likely the markers of neoplastic transformation of breast tissue[37]. On liver tissue, distinct lipid clusters colocalize with periportal and pericentral proteins, and metabolic and lipidomic signature varies in distinct liver cells (*e.g.,* sinusoidal, Kupffer, hepatocytes, Ito stellate, immune cells). Similar to protein markers, further clustering analysis shows that metabolites and lipids classify the cell types for the first time. The multimodal SIMS imaging opens broad applications for exploring various biological phenomena of cellular/biomolecular interactions in health/disease.

11:40am **CA+AS+SE+SS-TuM-12 Atom Probe Tomography Using Wavelength-Tunable, Femtosecond-Pulsed Coherent Extreme Ultraviolet Radiation***, **Ann Chiaramonti**, B. Caplins, J. Garcia, L. Miaja-Avila, N. Sanford,* National Institute of Standards and Technology (NIST) **INVITED**

Laser-pulsed atom probe tomography (LAPT) is a powerful tool for materials characterization due to its desirable combination of high spatial resolution and analytical sensitivity. In state-of-the-art LAPT, the thermal pulse resulting from a near-ultraviolet (NUV) laser (E=3.5 eV to 3.6 eV; λ=355 nm to 343 nm) incident on the sample provides the energy to overcome the activation barrier for field ion evaporation.LAPT has been used successfully to characterize a wide range of materials including metals, semiconductors, insulators, biological materials, and even liquids. However, the thermal process is not without drawbacks. LAPT data quality can be degraded due to for example: thermal tails that limit sensitivity; the formation of cluster ions that may have isobaric overlap with elemental species; undetected neutral species which can adversely influence composition measurements; and unresolvable multiple hits which result in a loss of information. Data loss due to multiple hits and neutral species is particularly problematic for many ionic and covalent materials; it can limit the recovery of bulk stoichiometry or composition to a narrow range of experimental conditions, if at all [1,2].

Ionizing radiation in the extreme ultraviolet (EUV) region of the electromagnetic spectrum (E=10 eV to 100 eV; λ=124 nm to 12 nm) offers potential new field ionization pathways (e.g. direct photoionization and Auger decay) for atom probe tomography.Much of the EUV photon energy band is above the work function and ionization potential of any naturally occurring element, and photoionization cross-sections peak in the EUV band across the entire periodic table [3]. EUV is also highly absorbed within only the first few nm of the sample surface.

Instrument design and results from the world's first EUV radiation-pulsed atom probe microscope are presented. This instrument uses tunable wavelength (photon energy) femtosecond-pulsed coherent EUV radiation from phase-matched high harmonic generation in a hollow waveguide. Initial experiments demonstrate successful EUV (E=41.85 eV; λ=29.6 nm) radiation-pulsed field ion emission in a variety of materials systems. Time-independent background levels, delayed evaporation tails, peak widths, charge state ratios, multiple hit counts, and the relative number of cluster ions will be compared to NUV LAPT experiments on the same samples and specimens.

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Applied Surface Science Division
Room 320 - Session AS+EM+SE-TuA

Surface Analysis Using Complementary Techniques

Moderators: Samantha Rosenberg, Sandia National Laboratory, **Carl A. Ventrice, Jr.**, SUNY Polytechnic Institute

2:20pm **AS+EM+SE-TuA-1 Origins of the Emergent Phenomena at Oxide Interfaces Studied with Complementary X-Ray Spectroscopic and Scattering Techniques***, **Alexander Gray**,* Temple University **INVITED**

Atomic-level design of complex-oxide heterostructures that exhibit functional electronic and magnetic phenomena has become a diverse and vibrant subfield of condensed matter physics and material science. Of particular interest are the material systems wherein rich physics and intricate interplay between various degrees of freedom at the interface give rise to functional properties not observed in the constituent materials. Detection and characterization of these interfacial properties present a unique practical challenge due to the lack of direct yet non-destructive techniques that are capable of probing minute changes in the electronic and magnetic states at a buried interface with element specificity and Ångstrom-level spatial resolution. In this talk, I will discuss several recent studies in which we utilized a combination of complementary x-ray spectroscopic and scattering techniques to understand the origins of the emergent low-dimensional ferromagnetic states in $LaNiO_3$/$CaMnO_3$ and $CaRuO_3$/$CaMnO_3$ superlattices. Depth-resolved standing-wave photoemission spectroscopy was used to probe the depth-dependent changes in the electronic states, while soft x-ray resonant magnetic scattering was used to extract the element-specific magnetic profile of the interface. The results of the experiments were compared to and interpreted using state-of-the-art first-principles theoretical calculations.

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences, and Engineering Division under Award DE-SC0019297.

3:00pm **AS+EM+SE-TuA-3 Multi-Technique Forensic Analysis by Co-Incident XPS & Raman Imaging***, **Robin Simpson**, P. Mack,* Thermo Fisher Scientific, UK

For more than 100 years fingerprint analysis has been ubiquitous in the forensic sciences and is still a core method for identifying individuals in forensics. The techniques used to analyze fingerprints are either structural, for identifying the features of the fingerprints, or chemical, characterizing the composition of the deposited material. Many of these chemical characterization techniques are destructive to the sample preventing any further analysis from being performed or the sample from being preserved as evidence for a later date. Here we show the benefits of using XPS to analyze fingerprints, where the elemental and chemical state composition of a sample can be acquired non-destructively from the top 10 nm of the surface.

In this investigation, we build on our previous work investigating fingerprint analysis. In that study, XPS and XPS mapping techniques were utilized to identify and characterize the contamination of fingerprints. Fingerprints contaminated with $TiO\text{-}_2$, and PbO deposited on the silicon wafer can be chemically mapped and visualized using XPS using principal component analysis, PCA.

In this study, we also discuss other examples of forensic analysis including the identification of pharmaceutical substances using complementary XPS and Raman analysis. To achieve this an “over the counter” multi-component analgesic tabletwas crushed to a powder form and deposited onto the substrate. The powder is mapped rapidly using XPS imaging and the data is processed by PCA. This information was used to identify areas for further analysis by high-resolution XPS and Raman. Further Raman analysis was used to characterize the composition of the 3 areas of the sample and identify the compounds contained in them. These are shown to be aspirin, paracetamol, and caffeine through comparison with known sample spectra in the OMINC Raman spectral database.

In the final two examples of forensic analysis workflows in this presentation, we discuss the identification and differentiation between overlapping ink and paint samples deposited on paper or fabric substrates. Raman mapping is used to differentiate between two paint samples that have virtually identical chemistry when analyzed via XPS, and rapid XPS imaging is used to identify the order of events between the deposition of computer-printed ink and handwritten ink from a ballpoint pen.

3:20pm **AS+EM+SE-TuA-4 Comparison of Methods to Quantify Silicone on Hair***, **Michaeleen Pacholski**, B. Johnson, T. Case, T. Powell, D. Carsten, J. Stratton,* The Dow Chemical Company*; C. Ji,* The Dow Chemical Company, China*; M. McIvor, N. Goodman, S. Yusuf, M. Upshur,* The Dow Chemical Company

Silicone has been used as a conditioning agent on hair for a long time.Silicone deposition can produce numerous benefits in reducing the coefficient of friction, improving combability and decreasing frizz.It can be delivered in multiple ways such as conditioning shampoo, rinse off conditioners, leave in conditioners and detangling products.Regardless of how it is delivered to the hair surface, the quantification of silicone on hair is an important metric for R&D product development and marketing.In a large analytical group there are many techniques that can be used including XPS, XRF, ICP, GC and IR.Each has different limits of detection, amount of sample required, time involved to both acquire and analyze the data, etc.A set of samples was generated using both shampoo and rinse off conditioner on both brown and bleached hair for a comparison study.The amount of silicone varied from low to high levels.Comparison of the techniques showed general agreement between all techniques within expectations.These experiments can now guide internal work based on the needs of the specific project and what instrumentation is available within that region.

4:20pm **AS+EM+SE-TuA-7 Progress Towards Atomic Scale Analytical Tomography***, **Brian Gorman**,* Colorado School of Mines*; T. Kelly,* Steam Instruments, Inc*; M. Holtz,* Colorado School of Mines **INVITED**

Atomic-Scale Analytical Tomography (ASAT) has been recently defined as the ability to identify every atom in its place. Specifically, ASAT is the ability to determine the isotopic identity and sub-Angstrom position of 100% of the atoms in a specific volume. Taking this a step further, ASAT should also be able to determine the local electronic structure of these atoms, thus giving rise to true 3-D atomic structure / electronic property relationships. ASAT datasets of semiconductor nanostructures will reveal the 3-D position of individual dopant atoms with pm spatial resolution, the 3-D position of nuclear spin isotopes, nanometer scale changes in strain due to structural defects and lattice mismatch, the 3-D position of point defects such as vacancies, and any electronic band structure changes at all these atomic-scale features.

Undoubtedly, ASAT is a lofty metrology goal but is nearly within reach. Contemporary metrology techniques such as (Scanning) Transmission Electron Microscopy ((S)TEM) are not currently capable of ASAT. (S)TEM can image atomic positions with better than 0.01 nm resolution in some specimens and tilt-series tomographic imaging can give 3-D information, sometimes at atomic resolution. Analytical STEM can be performed at atomic resolution in some cases, although identifying a single atom in 3-D is only possible in limited specimens and with poor depth resolution. Atom Probe Tomography (APT) can provide mass spectral information on individual atoms, however, 3-D image reconstruction methods are constrained by multiple empirical assumptions and lack of information about the specimen that limit the spatial resolution.

Recently, it was demonstrated that correlative TEM and APT on the same specimen can approach ASAT. We used (S)TEM imaging of the specimen before and after APT to define the analyzed 3-D volume. 4-D STEM diffraction was used to define atom positions within that volume (a dataset known as the specimen function) using information about the crystal space group, orientation, and lattice parameters. Individual isotopic nuclear spins are accurately placed within a semiconductor quantum do to within 0.05 Anstroms.

More work needs to be done using correlative TEM and APT to achieve ASAT, including demonstrating the ability to capture structural features such as interfaces and defects as well as 100% efficiency ion detectors. In the near future, ASAT will be achieved through integration of 100% efficiency ion detectors, improved data handling algorithms, and integration of TEM and APT into a single instrument.

5:00pm **AS+EM+SE-TuA-9 Investigating 2d-Materials Using Correlative Spectroscopy & Microscopy***, **Tim Nunney**, R. Simpson, P. Mack, H. Tseng,* Thermo Fisher Scientific, UK

Across a wide range of application areas, understanding the chemistry and structure of surfaces and interfaces is crucial. In the last fifty years, X-ray photoelectron spectroscopy (XPS) has become established as a one of the key techniques for measuring surface and interface chemistry, and advances in instrumentation have enabled it to keep pace with the requirements for both academia and industry. XPS can deliver quantified surface chemistry measurements, and by using depth profiling, an understanding of layer and interfacial chemistry, but the limit on spatial resolution for XPS can prevent it from determining how the surface structure is related to the measured chemical properties. For example, how the changing morphology of the surface during a depth profile could influence the measured composition would be challenging to determine using just XPS.

Other experimental techniques which are unable to match the surface selectivity of XPS are able to provide complementary information to extend the data from XPS. Electron microscopy can provide high resolution imaging, with elemental composition provided by energy dispersive X-ray microanalysis, but without the same surface selectivity seen with XPS or Auger electron spectroscopy (AES). This can be a perfect complement to XPS analysis, so long as the same points of interest can be identified. Molecular spectroscopy, such as FTIR or Raman, can also provide complementary information to XPS, albeit with different sampling depths, which can be extremely useful to validate measurements or confirm particular molecular structures using the wide range of spectral libraries available for those techniques.

In this presentation, we will describe how a correlative approach using both surface analysis instrumentation and scanning electron microscopy can be used to characterize 2D nanomaterials. Samples of MoS_2 grown on Si substrates have been investigated using XPS, Raman and SEM to determine their composition and structure. To facilitate co-alignment of the analysis positions when moving between the instruments, special sample carriers and software alignment routines have been developed.

5:20pm **AS+EM+SE-TuA-10 Surface Analysis in Fujifilm Electronic Materials Research & Development Laboratory: Applications on Chemical Mechanical Planarization***, **Hong Piao,*** FUJIFILM Electronic materials USA., Inc.*; Y. Liang, K. Huang, B. Duong, J. McDonough, Y. Zhang, H. Lee, B. Hu,* FUJIFILM Electronic materials USA., Inc.

Chemical mechanical planarization (CMP) is a chemical reaction assisted polishing process in the semiconductor manufacturing industry. It has played a key role on integrated circuit (IC) manufacturing to anisotropically remove overburden material or specific layers in the film stacking and to planarize the topography at the wafer surface. Specific slurry formulations have been designed towards to the device structure and materials to be polished. The surface chemical processes at the interface of the wafer/slurry/pad have significant influence on the CMP performance. As device geometries are continuously shrinking as well as the introduction of new interconnect materials, the technological requirements on CMP performance have become more stringent. Thus, in-depth understanding of surface chemical processes which occur during polishing remains essential to the improvement of slurry design, the development of next-generation CMP processes and post-CMP cleaning applications.

Investigations aimed at understanding fundamental mechanisms usually employ electrochemical techniques. Surface analysis methods remain rather under-utilized in this field, especially when taking into account the explosive growth of these surface techniques for the analysis of "nano-structured" materials in other fields.Surface analysis tools (XPS, Tof-SIMS and AFM) at FUJIFILM Electronic Materials U.S.A., Inc. combined with other complementary testing methods have already shown great promise as a means of achieving fundamental knowledge to the mechanisms involved in CMP processes [1].

This review continues to highlight the promising role that surface chemical analysis methods can and should play in understanding the complex interplay that drives design of CMP slurry formulation for contributions to the CMP technology. Examples describing the CMP characterization have been given in several aspects that are growing in importance: (1) Cu, Co and Ru CMP, (2) Defects (organic residues,metal contaminants and particles) removal in a post-CMP cleaning process and (3) CMP consumables: root cause analysis of pad stains.

[1]Hong Piao, Yannan Liang, James McDonough, Tawei Lin, Hyosang Lee, Carl Ballesteros, Eric Turner, Abhudaya Mishra and Richard Wen, "*Industrial Applications of Surface Science in Chemical mechanical Planarization*", The AVS 65th International Symposium, Oct. 21-26, 2018, Long Beach, California.

5:40pm **AS+EM+SE-TuA-11 Investigating GeTe as an Ovonic Threshold Switch with Spectroscopic and Electronic Techniques***, **Melissa Meyerson,** M. Kalaswad, M. King, D. Adams, J. Custer, P. Kotula, M. Rodriguez, S. Rosenberg,* Sandia National Laboratories

Ovonic threshold switches (OTS) are a class of two or three terminal devices that exhibit a sharp transition between resistive and conductive operating regions. This transition is temporary, with the device reverting to a resistive state once bias is de-asserted from the device. The volatile resistive behavior makes OTS devices very attractive as select devices for phase change memory, voltage controlled tunable filters, and other applications. Metal telluride thin films show unique temperature dependent characteristics that may make them good materials for OTS devices. In this study, we examine the effect of annealing temperature on the chemical, physical, and electronic properties of GeTe thin films including exploring changes in crystallinity, chemical composition, and switching behavior. More specifically, X-ray photoelectron spectroscopy shows a chemical transition that occurs between 125 °C and 150 °C that results in an increase in metallic Ge and decrease in metallic Te relative to the concentration of GeTe present. Similarly, X-ray diffraction shows a transition from amorphous to crystalline GeTe around 160 °C. The films are further characterized with transmission electron microscopy, energy dispersive X-ray spectroscopy, and surface electronic measurements including ultraviolet photoelectron spectroscopy and inverse photoelectron spectroscopy to determine the band gap.

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6:00pm **AS+EM+SE-TuA-12 Multi-Technique Analysis of Organic and Inorganic Semiconductors for Composition and Electronic Information***, **Paul Mack,*** Thermo Fisher Scientific, UK*; M. Modreanu,* Tyndall National Institute-University College Cork, Ireland

Photoelectron spectroscopy has been used for many years to analyse the elemental and chemical composition of a broad range of industrially relevant materials, from polymers to semiconductors.In recent years, with the development of novel organic and inorganic semiconductors, there has also been an increasing demand to measure electronic parameters alongside the elemental and chemical state information.

In this work, complementary electron spectroscopic techniques were used to comprehensively characterise organic and inorganic semiconductors for composition and electronic properties.X-ray photoelectron spectroscopy (XPS) was used to analyse the elemental and chemical composition of the organic semiconductor, P3HT, and a range of ferroelectric films with the general formula, $Hf_xZr_yO_z$.Ultraviolet photoelectron spectroscopy (UPS) and reflection electron energy loss spectroscopy (REELS) were then used together to measure the ionisation potential, band gap and electron affinities of those samples.

Applied Surface Science Division
Room 320 - Session AS+BI+CA+HC+LS+PS+SE+SS-WeM
Analysis of Surfaces and Interfaces Related to Energy and the Environment

Moderators: Kateryna Artyushkova, Physical Electronics, **Tony Ohlhausen**, Sandia National Laboratory

8:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-1 Adhesion Properties of Industrial Steel Samples***, **Lukas Kalchgruber**, M. Hahn, L. Mears, M. Valtiner,* TU Wien, Austria

Solving industrial questions is of utmost importance to improve material properties, developing industrial applications and understanding fundamental processes. One of these questions is how different pre-treatments alter the adhesion process between steel and polymers.

To study the effect of the pre-treatment on the subsequent adhesion process, steel was treated either thermally or via plasma.

To characterize adhesion, the surface force apparatus (= SFA) was utilized in reflection mode. In the SFA experiment, the steel is brought into contact with another surface which is prepared on a fused silica optical disc. Before the optical discs can be used in SFA, a semitransparent, reflective layer needs to be deposited on the curved surface. Additionally, they were spin coated with few µm thin, homogeneous, smooth layers of SEBS polymer. Afterwards, a suitable particle free contact was established between the polymer and the steel sample in the SFA, which generated the following data types:

1. Newton rings à Provide information about the contact area
2. Force data à Adhesive pressure (referenced to contact area)
3. Fringes of chromatic order (= FECO) à Time-Distance-Curves

The main selling points of this technique are as follows: firstly, the model system is very close to the actual problem, as the steel sample in question can be used directly. Secondly, direct information about the adhesive pressure can be obtained. Thirdly, considerably more information about the adhesive behavior of the system is available beyond just one number.

The SFA results achieved are promising. We have a method that allows us to quantify the adhesive pressure in a model system and differentiate between differently treated steel samples. We have further put our adhesion results into context with the support of XPS characterization of the surface. Thermally treated samples have a hydroxide/oxide ratio of roughly 50/50 while samples treated with plasma show a ratio of 90/10. The hydroxide to oxide ratio correlates with the adhesion measured by SFA, which emphasizes the role of hydroxide in preventing adhesion.

8:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-2 An Electrochemically Polymerized Protective Layer for Magnesium Metal Anode***, Y. Wang,* University of Maryland College Park*; **Alexander Kozen,*** University of Maryland

Rechargeable magnesium (Mg) batteries are promising beyond Li-ion technologies due to their high volumetric capacity (3832 mAh cm^{-3}) and high natural abundance. Nonetheless, Mg metal anode is incompatible with most conventional electrolytes which leads to the formation of an ionically passivating layer. Mg also suffers from growth of dendrites similar to Li, which causes failure of the cells. In this study, we electrochemically polymerized 1,3-dioxolane (DOL) to form a thin Mg^{2+}-conducting elastomeric artificial solid electrolyte interphase (ASEI) layer by electrochemically pretreating Mg metal anodes. We found that this protective ASEI layer enables excellent cyclability of Mg-Mg symmetric cells at high current density (0.5 mAcm^{-2}) over 400 hours at a stable low overpotential (0.50 V vs. Mg^{2+}/Mg) without cell short-circuiting, while untreated pristine Mg symmetric cells quickly failed. The formation of this ASEI also significantly lowered the impedance of the cells, which proved its capability of conducting Mg^{2+} ions. Comprehensive surface chemistry analysis was done by X-ray photoelectron spectroscopy (XPS) which showed that an ASEI mainly consists of poly-DOL was formed, along with various Mg salts which are instrumental to the conductance of Mg^{2+} ions. More importantly, poly-DOL component in the elastomer was well preserved post-cycling, which contributed to the long-term cyclability and low voltage hysteresis of pretreated Mg-Mg cells, as compared to the pristine ones. Focused ion beam (FIB) – scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping showed that a generally uniform layer was formed on the surface and this ASEI is roughly 200 µm thick and was able to suppress the growth of Mg dendrites after cycling for 400 hours at 0.03 mA cm^{-2} current density, as compared to the rampant sphere-shaped dendrites on the surface of pristine Mg anodes after cycling. This is the first ever report on the successful formation of poly-DOL ASEI on Mg metal anodes as a protective layer and by electrochemical polymerization method that effectively enhanced the electrochemical cycling performance of the Mg metal anodes.

8:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-3 Analysis of Surfaces and Interfaces in Polymer Electrolyte Membrane Fuel Cell and Electrolyzer Devices***, **Svitlana Pylypenko**,* Colorado School of Mines **INVITED**

Implementing a hydrogen-based infrastructure depends on developing electrochemical energy conversion devices such as fuel cells and electrolyzers. Polymer electrolyte membrane fuel cells (PEMFCs) have been the focus of research for lightweight renewable transportation applications such as motor vehicles for years, but they also offer the potential to fuel stationary applications, including residential power, due to their potential to produce industrial amounts of energy via a renewable route. Polymer electrolyte membrane water electrolysis (PEMWE) is a promising strategy to produce and store renewable energy in the form of hydrogen for subsequent use in either manufacturing processes, or to run a fuel cell, which can generate electricity on demand.

Great improvements have been made in the development of catalysts and electrodes for PEM systems, improving their activity and stability while reducing the amount of precious metals used. The properties of the electrodes used in these devices are influenced by multiple parameters: the chemical identity of the catalyst and the ionomer; the morphological properties of the catalyst (e.g. shape and surface area); ink formulations; and the various processing parameters used to prepare the electrode. Due to the breadth of possible variable combinations and the inherent complexity of electrode materials, it is unsurprising that PEM electrodes are both morphologically and chemically heterogeneous. Characterization of relevant surfaces and interfaces in these devices, therefore, represents a challenge that requires a multi-technique approach that evaluates all relevant scales and properties and brings a better understanding of the evolution of surfaces and interfaces under more realistic conditions. This talk will discuss the progress towards the comprehensive characterization of the most critical surfaces and interfaces in PEM devices using a combination of X-ray and electron spectroscopy and microscopy methods. Several challenges related to the characterization of catalyst-gas and catalyst-ionomer interactions in these systems will be covered along with results obtained with near-ambient pressure x-ray photoelectron spectroscopy (nAP-XPS). The development of characterization strategies to enable the exploration of a large processing parameter space will be presented, which can then be used to fabricate optimized electrodes with state-of-the-art catalysts as well as electrodes that integrate novel catalysts, all made with scalable routes. And finally, the development of novel approaches toward the characterization of other components of PEM devices such as porous transport layers will also be briefly discussed.

9:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-5 XPS Analysis of Battery Materials***, **Sarah Zaccarine**, B. Schmidt, K. Artyushkova,* Physical Electronics USA*; A. Baniya, Q. Qiao,* Syracuse University

Lithium-ion batteries (LIBs) have experienced success including rechargeability and long lifetimes but their limited energy density restricts applications moving forward. Lithium metal batteries (LMBs) offer similar benefits but with much higher achievable energy densities, making them a promising future battery technology. Both LIBs and LMBs are multi-layered, complex systems with many materials and interfaces that each play a critical role in performance and stability. Tuning the composition and morphology of these materials is necessary to create stable, high-performing devices, but the multi-component interfaces, interactions, and dynamic nature of these systems makes characterization challenging. In order to optimize materials properties and improve battery lifetimes, there is a pressing need for physicochemical characterization approaches with high spatial resolution, chemical and morphological analysis, and correlation of synergistic properties.

X-ray photoelectron spectroscopy (XPS) is commonly used to characterize the chemical composition of battery materials, and the depth resolution (~10nm) is ideal for analyzing thin layers and interfaces. However, modern XPS instruments have a variety of operating modes and analytical accessories that enable characterization across a variety of lateral and vertical size regimes. Small and large spot comparisons can track overall composition and local features and changes, with scanning microprobe analysis allowing for spatial resolution down to a few microns. X-ray induced secondary electron imaging (SXI), including high-resolution mosaic imaging over a wide sample area, can be used for easy identification of important features and morphological imaging of various battery component materials to complement chemical information. Chemical mapping can visualize distribution of individual elements or chemical species to understand how materials are distributed and change with testing. Additional options address stability concerns associated with Li materials, including a cooling stage to preserve battery chemistry during extended experiment times, where time-resolved profiles are used to compare chemical degradation under controlled temperatures, and incorporating Al Kα and Cr Kα X-rays for non-destructive XPS and hard X-ray photoelectron spectroscopy (HAXPES) analysis of surface (up to ~10nm, Al) and subsurface (up to ~30nm, Cr) composition. Combined, these powerful capabilities enable thorough characterization of battery materials properties for micro- and large-area spectroscopic analysis of surfaces and interfaces and how these properties change under various analytical and operating conditions.

9:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-6 Novel Battery Material Analysis with High-Resolution and High-Throughput XPS***, J. Counsell, S. Coultas,* Kratos Analytical Inc., UK*; C. Moffitt,* Kratos Analytical Inc.*; C. Blomfield,* Kratos Analytical Inc., UK*; **Adam Roberts**,* Kratos Analytical Limited, UK

Several material systems will be discussed to give an overview on how XPS can yield information regarding the distribution and chemical speciation of battery materials.

Na-ion batteries are considered to be environmentally favourable alternatives to Li-ion batteries, particularly in the extremely large-scale application of grid storage, given the abundance of Na. However, to date, the battery performance has not been competitive, and promising ternary materials have been plagued by poor stability in air and unsatisfactory long-term cycling. Herein, air/moisture stability is effectively and systematically investigated with XPS, paving the way for material stability to be modified through rational design. Chemical assignments were correlated with performance and oxidation degradation [1]

The significance of sensitivity and detection limit, comparisons of surface and bulk and an approach for pragmatic peak fitting of difficult elemental lines will be discussed along with considerations such as etch artefacts and degradation.

[1] Shipeng Jia *et al*., J. Mater. Chem. A, 2022,10, 251-265

11:00am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-10 Multimodal Analysis and Imaging of the Boehmite Layer on AA6061***, **Lyndi Strange**,* Pacific Northwest National Lab*; X. Yu,* Oak Ridge National Laboratory*; V. Shutthahandan, M. Song, Q. Miller, M. Bowden, J. Gao, Y. Zhang, J. Son, R. Shimskey, R. Prabhakaran,* Pacific Northwest National Lab*; V. Joshi,* Pacific Northwest National Laboratory

Low-enriched uranium (LEU) alloyed with 10% Mo (U-10Mo) is being considered as a promising alternative to oxide-based dispersion fuel with high-enriched uranium for use in research reactors. The configuration of this proposed LEU monolithic fuel plate consists of the U-10Mo plate-type fuel foil with a 25 µm Zr interlayer barrier clad with an aluminum alloy (AA6061). The clad AA6061 is coated with a boehmite layer to prevent corrosion. The boehmite layer has a high pH passivation range, which makes it resistant to oxidation and preferable to protect the Al cladding. Boehmite is usually formed on the AA6061 surface by autoclave processing. Various surface cleaning techniques have been employed such as polishing and etching to clean the surface of the AA6061 prior to boehmite formation. In this study, we examine how pre-treatment of AA6061 using polishing followed by both acid and alkaline etching affects the chemical composition of the boehmite layer using multimodal analysis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron microscopy (XPS), transmission electron microscopy (TEM), and grazing incidence x-ray diffraction (GI-XRD) were used to understand the changes in the boehmite layer as a result pre-treatment. ToF-SIMS provides a surface sensitive technique to understand the surface composition and characteristics. Spectral similarities were verified using principal comment analysis (PCA). XPS is a complimentary technique that provides quantitative information about the oxidation states present on the surface. Both the SIMS and XPS results suggested oxidation at the surface, which was further investigated using TEM-SAED and GI-XRD. While the GI-XRD results suggested the dominant phase present on the coupon surface is boehmite, TEM-SAED found small amounts of α- and γ-Al_2O_3 present as a result of alkaline etching.

11:20am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-11 Study of $Cs_x(CH_3NH_3)_{1-x}PbBr_3$ Perovskite with XPS Imaging and Small Area Spectra***, **Tatyana Bendikov**,* Weizmann Institute of Science, Israel*; Y. Rakita,* Columbia University*; H. Kaslasi, G. Hodes, D. Cahen,* Weizmann Institute of Science, Israel

Interest in halide perovskite (HaPs) is motivated by the combination of superior optoelectronic properties and ease in synthesizing these materials with a surprisingly low density of electrically active defects.[1] HaPs possess high chemical sensitivity, especially those having an organic cation at their *A* position (AMX_3). Although a direct role of the *A* cation in this sensitivity is unclear, and the structural and optoelectronic backbone lie within the *M-X* bond, the type of the *A* cation was shown to impact the chemical stability and, usually indirectly, affect optoelectronic properties of HaPs.[2-3]

X-ray Photoelectron Spectroscopy (XPS), is a surface sensitive technique with a sensitivity that goes down to a single atomic layer, and can provide unique information that relates the elemental composition with the chemical and electronic states of the different elements in the material. Our study focuses on the XPS imaging in combination with selected small area XPS spectra and uses solution-grown, single crystals of mixed *A*-cation $Cs_xMA_{1-x}PbBr_3$($MA = CH_3NH_3^+$) HaPs as a candidate for investigating heterogeneity within the crystals. With XPS we followed the variations in chemical composition of these crystals. By observing the surface, we found significant changes in the N/Cs ratio, which increases towards the interior of the crystal. Similar variations in N/Cs, but also in Pb/(N+Cs) ratios were found when we studied cross-sections of cleaved crystals. This compositional heterogeneity within the HaPs crystal was not previously reported and was discovered and monitored due to exclusive capabilities of the XPS technique.

References:

1. P. K. Nayak, S. Mahesh, H. J. Snaith, D. Cahen, *Nat. Rev. Mater*., **2019**, *4*, 269-285.
2. H. Kaslasi, Y. Feldman, Y. Rakita, D. Cahen, G. Hodes,*Cryst. Growth Des*, **2020**, *20*, 4366-4374.
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11:40am **AS+BI+CA+HC+LS+PS+SE+SS-WeM-12 Surface Characterization of Mineral Associated Organic Matters in Environmental Samples by Using X-Ray Photoelectron Spectroscopy (XPS)***, **Qian Zhao**, M. Engelhard, O. Qafoku, K. Hofmockel,* Pacific Northwest National Laboratory

Surface characterization is an important analytical approach to understanding the most dynamic interface of a material. The understanding of soil organic matter (SOM) persistence is critical to global carbon (C) cycling. Minerals play an important role in persisting SOM by associating with organic matters (OM) through different interactions. Yet mechanisms of the accumulation of OM in soil are still unclear. Chemical characterization of OM that is associated with minerals provides a mechanistic understanding of mineral-OM interactions. X-ray photoelectron spectroscopy (XPS) analysis allows us to probe the chemical states and speciation of OM on the surface of mineral grains or soil particles. This work used both synthetic mineral-OM complexes and natural soil samples to investigate the chemistry of organics that associate with minerals. In the synthetic system, we adsorbed four organic compounds on a calcite crystal. XPS analysis found the relative concentration of C was higher in OM adsorbed calcite than that in pristine calcite. Further, the deconvolution of C 1s spectra reveals that the calcite surface had a relatively lower abundance of carbonate but a higher abundance of alkanes in the OM adsorbed calcite than pristine calcite, indicating the adsorption of OM on the calcite surface. In the soil system, we incubated agricultural soils with ^{13}C-glucose for 12 months to trace the fate of microbial residues. Size and density fractionation was used to separate mineral-associated organic matter (MAOM) from whole soil. XPS analysis determined C chemistry of necromass on soil particle surfaces by scanning C 1s region of MAOM and non-MAOM fractions. We found that the MAOM fraction had a relatively higher abundance of carbonyl and carboxylic C functional groups and a relatively lower abundance of C-C/C=C group than non-MAOM fraction. It suggests that MAOM fraction is enriched in microbial-derived molecules (i.e., proteins) but has fewer plant detritus (i.e., carbohydrates or lignin) on mineral surfaces. XPS technique allows us to understand the surface chemistry of microbial necromass that is associated with minerals in soil. The chemical speciation information provides us with the potential bonding environment at the interface of minerals and OM.

Thin Films Division

Room 317 - Session TF1+SE-WeM

Vapor Deposition and Vapor Infiltration of Organic, Polymeric, and/or Hybrid Materials

Moderator: Siamak Nejati, University of Nebraska-Lincoln

8:00am **TF1+SE-WeM-1 Thermophysical Properties of Organic-Inorganic Hybrid Thin Films Created via Vapor Phase Infiltration (VPI)*, Mark Losego,*** Georgia Institute of Technology

This talk will discuss how thermophysical properties, including the glass transition, thermal expansion, and onset of crystallization, are altered when an organic material is transformed into an organic-inorganic hybrid material via vapor phase infiltration. Vapor phase infiltration (VPI) is a gas-phase technique that exposes organic materials to inorganic vapors (e.g., metalorganics or metal halides) that sorb into the organic, transforming it into an organic-inorganic hybrid. Over the past several years, our lab has examined how the precursor-organic chemistry and VPI process conditions (e.g., temperature) can be used to alter the quantity of inorganic loading and the extent to which the inorganic becomes chemically bound to the organic components. Controlling this physicochemical structure also alters the thermophysical properties of the resultant hybrid material. This talk will describe several examples including altering the glass transition temperature in poly(styrene-co-2-hydroxyethyl methacrylate) (PS-r-PHEMA) random copolymers infiltrated with aluminum oxyhydroxide and in Spiro-OMeTAD hole transport layers infiltrated with titanium oxide. In the PS-r-PHEMA system, random copolymers of varying HEMA composition from 0 to 20 mol% were investigated and the T_g was found to systematically increase with increasing HEMA temperature by as much as 40 °C. Changes in T_{-g} at low HEMA composition, for which the polymer is fully infiltrated, fit the Fox-Flory model for crosslinking phenomena which, in addition to a dissolution study on these materials, suggests that VPI crosslinks the PS-r-PHEMA, raising its glass transition temperature. Interestingly, according to the Fox-Flory model, these cross-links are 5x to 10x stiffer than usually observed for most organic crosslinks, suggesting an interesting phenomenon for inorganic cross-linking. For the Spiro-OMeTAD system, T_g appears to decrease with inorganic infiltration. This result is attributed to a lack of primary bonding between the inorganic and organic phases; the inorganic clusters now serve to disrupt the natural π-π stacking in the Spiro-OMeTAD, lowering T_g. Conversely, though, this disruption of the intermolecular forces leads to an increased resistance to crystallization in these hybrid films. This reduced propensity for crystallization may be useful for improving long-term stability of Spiro-OMeTAD-based organic electronic devices.

8:20am **TF1+SE-WeM-2 Chemical Vapor Deposition of Soft Materials for Garment-Integrated Sensor Systems and Plant Electronics*, Trisha L. Andrew,*** University of Massachusetts Amherst **INVITED**

Chemical vapor deposition is a single-step processing method for forming functional polymer films on unconventional substrates, such as commodity textiles and living plants, and allows fabrication of rugged and sensitive fabric-, fiber- and/or plant-based sensors for wearable electronics and smart farms. I will the detail the materials science and engineering advances made by my team during the process of assembling various garment-integrated sensor systems and plant-based sensors for longitudinal health monitoring in native environments. In particular, I will highlight our recent work in developing garments for portable brain activity monitoring and activity tracking, systems for in-home sleep monitoring, and conductive living plants for detection of selected abiotic stressors in commercial farms.

9:00am **TF1+SE-WeM-4 Effects of Trimethylaluminum Vapor Pressure and Exposure Time on Inorganic Loading in Vapor Phase Infiltrated PIM-1 Polymer Membranes*, Benjamin Jean,*** *Y. Ren, E. McGuinness, R. Lively, M. Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is a process for synthesizing organic-inorganic hybrid materials by infiltrating polymers with inorganic vapor molecules. Recently, our research team has used VPI to synthesize hybrid membranes with consistent nanofiltration performance in a variety of organic solvents that would otherwise swell or dissolve the parent polymer membrane. The properties of these hybrid materials can vary with the amount of VPI generated inorganic loading. However, the relationship between VPI processing conditions and inorganic loading is still not fully understood. This talk will discuss the effects of VPI dose pressure and exposure time on inorganic loading using the technologically relevant membrane material polymer of intrinsic microporosity 1 (PIM-1). At sufficiently low dose pressures and infiltration times (i.e., before saturation), inorganic loading can be controlled with both vapor pressure and exposure time. However, inorganic loading appears to saturate for this system at around 13 wt% inorganic. This apparent saturation point can be reached by infiltrating for 5 hours at TMA dose pressures above 0.4 Torr or after 40 hours at lower vapor pressures of 0.1 Torr. Inorganic loading appears to saturate for this system when the polymer's functional groups become fully populated with bound VPI precursors. These experimental results can be understood with the use of a recently developed reaction-diffusion model for VPI. Critical to applying this model to these post-deposition measurements is re-normalizing the mass loading to the total number of functional groups in the polymer. These findings suggest that the vapor pressure during infiltration affects the kinetics of this infiltration process but does not appear to alter the thermodynamically determined saturation point for inorganic loading.

9:20am **TF1+SE-WeM-5 Elucidating the Sequential Infiltration of Trimethylaluminum and Water Into Polycarbonate Membranes and Thin Films*, Rajesh Pathak,*** *R. Shevate, A. Mane , J. Elam,* Argonne National Laboratory, USA

Sequential infiltration synthesis (SIS) enables the creation of inorganic or polymer-inorganic hybrid nanocomposite materials through the diffusion of metal-organic vapor reagents into polymers and subsequent reactions with the polymer functional groups. Here we report a detailed study of aluminum oxide (Al_2O_3) SIS using trimethyl aluminum (TMA) and H_2O in polycarbonate (PC) thin films and membranes. We employed in situ Fourier transform infrared spectroscopy (FTIR) to elucidate the chemical interactions and in situ spectroscopic ellipsometry (SE) to measure the physical and optical changes that occur during Al_2O_3 SIS in PC. During the first SIS cycle, FTIR measurements revealed a rapid and irreversible reaction between TMA and the PC carbonyl groups to form Al-CH_3 species which then converted to Al_2O_3 upon H_2O exposure during.Virtually no spectral changes were observed by FTIR in subsequent SIS cycles.The SE measurements showed that the PC film thickness increased by ~75% and the refractive index (RI) decreased by ~2% during the initial TMA exposure.These effects were partially reversed during the following H_2O exposure such that the net thickness increase was ~36% and the RI returned to its initial value.During subsequent SIS cycles, the thickness and RI remained essentially constant.Ex situ X-ray photoelectron spectroscopy (XPS) depth profiling measurements showed ~30 at% Al uniformly distributed through the depth of the PC film following a single Al_2O_3 SIS cycle. SIS-derived nano/microstructure materials with tunable structural and optoelectronic properties could be developed for a variety of applications.

Keywords: atomic layer deposition; sequential infiltration synthesis; aluminum oxide, polymer-inorganic nanocomposite.

9:40am **TF1+SE-WeM-6 Kinetics of $TiCl_4$ Vapor Phase Infiltration (VPI) into PMMA and the Resulting Thermophysical and Optical Properties of the TiO_2 -PMMA Hybrids*, Shuaib Balogun,*** Georgia Institute of Technology*; A. Steiner,* Sandia National Lab*; M. Losego,* Georgia Institute of Technology

Vapor phase infiltration (VPI) is a post-polymerization modification technique that imbues inorganic materials into polymers to create organic-inorganic hybrid materials with new properties distinct from the parent polymer. While several VPI precursor-polymer chemistries have been explored, a lack of chemical intuition remains for fully understanding the thermodynamics and kinetics that govern the VPI process. This study seeks to continue to build this knowledge by examining the VPI process kinetics for TiO_2 infiltration into PMMA via the use of $TiCl_4$ and H_2O precursors. In this research, polymethylmethacrylate / TiO_2 hybrid materials are prepared using VPI. The depth of infiltration of the TiO_2species into ~200 nm PMMA thin films is studied using x-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy and spectroscopic ellipsometry. The kinetics for TiCl4 infiltration increases with both VPI process temperature and $TiCl_4$ exposure time. However, the rates of infiltration are considerably slower than those observed in the more commonly studied trimethylaluminum (TMA) / PMMA system. Even at 150 °C, process times of at least 12 hours are required to fully infiltrate a 200 nm PMMA film whereas using TMA similar films are fully infiltrated within 1 hour at the same process temperature. Films that we believe to be fully infiltrated at 150 °C and 24 hours of $TiCl_4$ exposure have a 6 at% Ti in the innermost bulk, as determined by XPS. Interestingly, unlike AlO_x-PMMA hybrids, these TiO_x – PMMA hybrids exhibit significant changes in their optical properties. Increased titanium loading leads to a 4% increase in refractive index and increased UV absorbance in the UV range of 270-350nm. Furthermore, films infiltrated at 150 °C and 24 hours of $TiCl_4$ exposure had a 50 % and 70 % reduction in coefficients of thermal expansion (CTE) below and above T_g respectively. Reduced CTE trends with increased titanium loading. We will discuss possible opportunities to use these new properties for various applications.

This project is supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:20am **TF1+SE-WeM-11 Effect of the Metal-Heteroatom Bond on Film Growth and Properties in Vapor-Deposited, Hybrid Metal Organic Thin Films***, **Jacqueline Lewis**, J. Shi, A. Ravi, S. I-Cheng Hsu, S. Bent,* Stanford University

Growing energy demand and the transition to clean energy set the stage for novel materials to fill gaps in current technologies. Hybrid metal organic thin films allow useful, active materials in the energy field, such as Al2O3 and ZnS, to reach a wider range of functionality by adding organic linkers via molecular layer deposition (MLD). Varying the organic linker and metal center using MLD modifies the film properties significantly, giving an adaptable, layer-by-layer growth scheme for the formation of novel materials. Previous literature reports have mainly focused on metal alkoxide films, where the organic linker is a multifunctional organic alcohol. Typically using a bifunctional linker, these films degrade rapidly in air, limiting their potential applicability for membrane materials, catalysis, and encapsulation. However, different functional groups, including dithiols, change the film properties substantially, with stability in air as one of the most notable effects. In this work, zinc thiolate films were deposited via hybrid MLD with a thiol bonding group, showing increased air stability as the films retain ~60% of the thiolate character after over 6 weeks in air. Films grown using 1,2-ethanedithiol degrade faster than those grown with 1,4-butanedithiol. The degradation mechanism forms at least three separate species, which we study via X-ray photoelectron spectroscopy (XPS) and synchtrotron-based X-ray absorption spectroscopy (XAS). Despite some degradation observed via XPS, the band gap of the material stays consistently close to 5.0 eV assuming direct band gap. This multi-week decay is much slower than the degradation of the known metal alkoxides, which degrade on the timescale of hours or days. The increased functionality exhibited by these metal thiolate films shows that changing the metal-heteroatom bond can create more stable films as well as increase the domain of materials to examine.

11:40am **TF1+SE-WeM-12 Oxidative Molecular Layer Deposition of Electrochemically Active Polymers***, **Matthias Young**[1], Q. Wyatt, M. Vaninger, N. Paranamana, T. Heitmann, H. Kaiser,* University of Missouri

Conjugated polymers such as polyethylenedioxythiophene (pEDOT), polypyrrole (pPy), and polyaniline (pAni) exhibit high electrochemical capacities, making them appealing as electrode materials for energy storage, electrochemical desalination, and chemical sensing. Recent work has established the growth of thin-films of pEDOT using alternating gas-phase exposures of EDOT monomers and a metal-chloride (e.g. $MoCl_5$) oxidant in a process termed oxidative molecular layer deposition (oMLD). Here, we report on recent work establishing oMLD of amine-containing conjugated polymers. We find that pyrrole (Py) and $MoCl_5$ undergo self-limiting surface reactions during oMLD exposures to form conformal pPy thin films, but oMLD using aniline (Ani) and p-phenylenediamine (PDA) monomers yield unexpected azo functionality. The formation of azo groups is attributed to an $MoCl_5$-amine surface adduct that spatially constrains polymerization reactions near the amine group and produces azo groups when coupling two primary amines. pPy grown by oMLD exhibits a record-breaking 282 mAh/g capacity in aqueous electrolyte, and PDA/$MoCl_5$ oMLD yields azo-polymers of interest as anode materials for alkali-ion batteries. Alternating between Py and PDA monomers during oMLD produces molecularly mixed copolymers with qualitatively different electrochemical responses from the isolated monomer structures. This work lays the foundation for the growth of conformal thin films of conjugated amine polymers with molecular-level control of composition and thickness.

12:00pm **TF1+SE-WeM-13 Towards High Throughput Molecular Layer Deposition of Alucone Films***, **Hardik Shantilal Jain**[2],* Holst Centre / TNO and Eindhoven University of Technology, The Netherlands*; M. Creatore,* Eindhoven University of Technology, The Netherlands*; P. Poodt,* Holst Centre / TNO and Eindhoven University of Technology, The Netherlands

The deposition rate and properties of MLD films are for a large part determined by what happens during the precursor exposure step. In some cases, however, the purge step is of equal importance, for example in the MLD of alucone films using trimethylaluminum (TMA) and ethylene glycol (EG). Due to the porosity of alucone films, the reactants during their exposure step not only react at the film surface but also tend to infiltrate into the film. The subsequent outgassing of the infiltrated reactant can take relatively very long thereby becoming the deposition rate-limiting step. If enough purge time is not provided for the reactant to outgas, it will lead to an additional CVD component alongside MLD in the overall growth. To employ/avoid the CVD component in the deposition process, we have developed a kinetic model to correlate parameters like exposure times, partial pressures, purge times and deposition temperature to the amount of CVD component in the growth. We have also investigated the impact of this additional CVD component on the step coverage of the alucone films and evaluated its usage in superconformally filling dielectric gaps.

Additionally, we also looked into solutions to increase the deposition rate of the alucone films and improve their conformality and amongst others found that using a bulkier precursor like DMAI instead of TMA can overcome the problem of precursor infiltration, increase the deposition rate of alucone processes by at least an order of magnitude and provide quite conformal films. We also performed a detailed investigation of MLD of alucone using DMAI as the aluminum precursor wherein the effect of deposition temperature and reactant purge times on deposition kinetics has been investigated and the DMAI alucone films have been compared with those prepared using TMA for their chemical environment and degradation showing striking similarities between both. We believe that the above work could be extended to other MLD systems and can serve as a guide in designing efficient MLD reactors and processes.

Thin Films Division
Room 316 - Session TF2+AP+SE+SS-WeM
ALD and CVD: Surface Reactions, Mechanisms and Kinetics

Moderator: Jessica Kachian, Intel Corporation

8:00am **TF2+AP+SE+SS-WeM-1 Nucleation Enhancement of Ruthenium Atomic Layer Deposition Using Organometallic Molecules***, **Amnon Rothman**, D. Tsousis, S. Bent,* Stanford University

Atomic layer deposition (ALD) is an attractive surface-sensitive thin-film deposition technique used in advanced technologies such as microelectronics, catalysis, and energy applications. The self-limiting surface reactions during the ALD process promote the layer-by-layer growth mechanism, thus providing significant control over the film thickness and conformality. However, due to an island growth mechanism and nanoparticle formation, metal ALD on oxide surfaces can lead to poor-qualify films and display long nucleation delays. One of the main reasons for the nucleation delays can be attributed to the differences in the surface energy between metals and oxide surfaces. In this work, we study the nucleation enhancement of ALD ruthenium layers on Si substrates by using a single monolayer of trimethylaluminum (TMA) or diethylzinc (DEZ) preadsorbed on the substrate prior to deposition. The nucleation enhancement is demonstrated for ruthenium ALD using two different ALD precursors, cyclopentadienylethyl(dicarbonyl)ruthenium(II) (RuCpEt(CO)2) and bis(cyclopentadienyl)ruthenium(II) (RuCp2), with O2 as a counter reactant. The ruthenium ALD nucleation and growth mechanism were studied using scanning electron microscopy (SEM), ellipsometry and X-ray photoelectron spectroscopy (XPS), both on the treated and untreated substrates. The results show that pretreatments using organometallic molecules reduce the nucleation delay of the ruthenium layer. The surface pretreatment strongly influences the ruthenium nucleation, yielding up to a 1.5-fold and a 2.1-fold increase in the surface coverage of the metal while using RuCpEt(CO)2 and RuCp2, respectively. Interestingly, pulsing TMA or

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[1] **2020 TFD Paul Holloway Awardee**

[2] **TFD James Harper Award Finalist**

DEZ, with or without exposure to H2O, is equally effective. We hypothesize that the high coverage in the pretreated samples is attributed to an increase in the substrate's surface energy, enhancing the surface diffusion of nanoparticles and adatoms during growth. We confirm that exposure of organometallic molecules during ruthenium ALD using the precursors above introduces a potential pathway toward achieving high-quality ruthenium thin films.

8:20am **TF2+AP+SE+SS-WeM-2 Ald of Chalcogenide and III-V Materials for Memory Applications***, **Laura Nyns**, A. Delabie, W. Devulder,* IMEC, Belgium*; J. Girard,* Air Liquide, France*; B. McKeown, V. Pallem,* Air Liquide*; T. Peisser, J. Sinha,* IMEC, Belgium*; N. Stafford,* Air Liquide*; J. Swerts,* IMEC, Belgium **INVITED**

To enable fast and powerful storage solutions for next generation mobile applications and other innovative technologies, the memory landscape focuses on various concepts. These concepts include DRAM for high-speed access, NAND flash memory for storage of large amounts of data, and the emerging Storage Class Memories (SCM) for massive data access in short time. Each of these technologies require their own set of materials with specific characteristics. Additionally, material deposition can be challenging because of the high aspect ratios which are typical for these advanced 3D architectures. Atomic Layer Deposition (ALD) has been shown to be a promising technique in that respect, as conformal deposition of a wide range of materials in complex topographies was established over the past decades. In this talk, we will address the ALD of germanium chalcogenides, a class of materials which is being explored as phase change memory and selector elements for SCM applications. GaAs will also be discussed, due to the need for high mobility channel materials to replace poly-Si in NAND flash technologies. We used the dechlorosilylation chemistry for the ALD of chalcogenide and III-V materials, where (nonmetal) alkylsilyl compounds react with metal chlorides to enable the growth of amorphous layers at low deposition temperatures [1]. An ALD GaAs process could be established, resulting in smooth and stoichiometric films that are amorphous as deposited. Crystallization into the preferred cubic phase was obtained at 350-400˚C, despite the presence of a Ga-rich surface oxide due to air exposure. Irrespective of the excellent step coverage in high aspect ratio structures, we found that these films are prone to delamination. We encountered a comparable challenge with ALD GeSe and $Ge_2Sb_2Te_5$ (GST) using this chemistry, and could demonstrate the benefit of proper surface treatments prior to film deposition to engineer the interface structure and improve layer adhesion. For GeSe, the extension of the existing ALD process [2] to ternary and even quaternary compounds is needed to boost the memory cell performance. We will therefore report on the development of an ALD process targeting GeAsSe deposition. Finally, we explored area-selective deposition (ASD) of chalcogenide materials, as this could greatly simplify the fabrication of complex 3D SCM devices. Our results indicate an impressive selectivity of 96% for GST films of ~22nm on TiN compared to SiO_2, by using the dechlorosilylation chemistry in combination with a dimethylamino-trimethylsilane (DMA-TMS) surface treatment.

[1] Pore et al, ***J. Am. Chem. Soc.***, 2009, **131**, 3478-3480

[2] Haider et al, ***Mater. Adv.***, 2021,**2**, 1635-1643

9:00am **TF2+AP+SE+SS-WeM-4 Plasma-enhanced Spatial ALD of SiO_2 investigated by gas-phase Infrared and Optical Emission Spectroscopy***, M. Mione, V. Vandalon,* Eindhoven University of Technology, Netherlands*; A. Mameli,* TNO-Holst Centre & Eindhoven University of Technology, The Netherlands*; F. Roozeboom,* TNO-Holst Centre & Eindhoven University of Technology, Netherlands*; **Erwin Kessels**,* Eindhoven University of Technology, Netherlands

A spatial atomic layer deposition (ALD) process for SiO_2 using bisdiethylaminosilane (BDEAS, $SiH_2[N(C_2H_5)_2]_2$) and an atmospheric O_2 plasma is reported as well as an investigation of its underlying reaction mechanisms [1]. Within the substrate temperature range of 100-250 ^{o}C, the process demonstrates self-limiting growth with a growth-per-cycle between 0.12 and 0.14 nm and SiO_{-2} films exhibiting material properties *on par* with those reported for low-pressure plasma-enhanced ALD (PEALD) [2].

Gas-phase infrared spectroscopy on the reactant exhaust gases and optical emission spectroscopy on the plasma region are used to identify the species that are generated in the ALD process. Based on the identified species and a calibration procedure, we propose a reaction mechanism where BDEAS molecules adsorb on –OH surface sites through the exchange of one of the amine-ligands upon desorption of diethylamine (DEA, $HN(C_2H_5)_2$). The remaining amine ligand is removed through combustion reactions activated by the O_2 plasma species leading to the release of H_2O, CO_2, CO in addition to products such as N_2O, NO_2, and CH-containing species. These volatile species can undergo further gas-phase reactions in the plasma as indicated by the observation of OH*, CN* and NH* excited fragments in emission. Furthermore, the infrared analysis of the precursor exhaust gas indicated the release of CO_2 during precursor adsorption. Moreover, this analysis has allowed the quantification of the precursor depletion yielding values between 10 % and 50 % depending on the processing parameters. On the basis of these results, the overall surface chemistry of the spatial ALD process of SiO_2 will be discussed.

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9:20am **TF2+AP+SE+SS-WeM-5 Role of Al in Enhancing Growth Rate and Crystallinity in Chemical Vapor Deposition of $Hf_{1-x}Al_xB_2$ Coatings Below 300 °C***, **Kinsey Canova**[1], S. Shrivastav, C. Caroff, L. Souqui, G. Girolami, J. Krogstad, J. Abelson,* University of Illinois at Urbana-Champaign

Transition metal diborides are desirable as hard, low-friction, and wear-resistant coatings for applications in extreme environments. To survive high temperatures, the coatings must have a very low rate of microstructural evolution and must resist oxidation, in particular the loss of boron via evaporation of boron oxide. We previously showed that amorphous HfB_2 films can be deposited by chemical vapor deposition (CVD) using a borohydride precursor, $Hf(BH_4)_4$. However, at T > 600 °C, those coatings crystallize and densify, which leads to cracking, and they oxidize readily. Here, we co-flow an aluminum precursor, trimethylamine alane (TMAA), to deposit ternary $Hf_{1-x}Al_xB_2$ alloy films by CVD at temperatures ≤ 300 °C. This affords excellent film deposition and properties: (i) Al incorporation substantially increases the reaction rate of the HfB_2 precursor, yet the growth still gives good conformal coverage over all surfaces in deep features. (ii) The as-deposited films are nanocrystalline, and the lattice parameters are consistent with a random alloy on the metal sublattice, as opposed to a mixture of HfB_2 and AlB_2 grains. (iii) No elemental Al is detected, so there is not a mechanically soft, low-melting phase. (iv) Annealing films to 700 °C in air creates an Al_2O_3 surface layer that protects the underlying film, and negligible grain growth is observed. To determine a cause of the enhanced growth rate, we performed a matrix of growth experiments vs. precursor pressures and temperature; the Al incorporation rate, which is proportional to TMAA flux, has the strongest effect on rates. We hypothesize that Al consumes the excess boron from the HfB_2 precursor – which contains four boron atoms for every Hf atom – and forms AlB_2. This overcomes the probable rate limiting step of HfB_2 deposition, i.e., the associative desorption of excess boron from the growth surface as B_2H_6, and it is consistent with the improved film crystallinity. Finally, this study provides a guide to the parameters controlling growth rate and composition.

9:40am **TF2+AP+SE+SS-WeM-6 Pushing the Limits of ALD Infilling to Produce Macroscopic Nanocomposites***, **Benjamin Greenberg**, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Atomic layer deposition (ALD) infilling is a reliable and popular technique for producing nanocomposite thin films. Typically, ALD precursor dose times on the order of 1 s are sufficient for infiltrating and conformally coating the pores of nanoparticle (NP) networks with thickness on the order of 1 µm or less. In principle, the application space for this nanocomposite production method could be expanded significantly by increasing the NP network thickness to 1 mm or greater. In this work, we investigate the possibility of achieving this scale-up through increasing the ALD precursor dose time by three orders of magnitude. We hydraulically press aluminum oxide nanopowder with particle size on the order of 100 nm to form nanoporous compacts with ~2 mm thickness and ~50% solid volume fraction, and we coat the pores with either Al_2O_3 or ZnO by static-dose ALD, holding precursor vapor in the ALD chamber for >1,000 s per half-cycle. For both coatings, we analyze the ALD chamber pressure traces to understand precursor diffusion and reaction kinetics, and we compare our results to predictions based on a Knudsen diffusion model. For the ZnO coating, we use electrical conductivity measurements, X-ray crystallography, scanning electron microscopy, and energy-dispersive X-ray spectroscopy to evaluate coating composition and uniformity within the nanocomposite, and we compare the ZnO-infilled-Al_2O_3 nanocomposite to a compact of core/shell Al_2O_3/ZnO NPs produced by particle ALD (pALD) in

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[1] **TFD James Harper Award Finalist**

a rotary reactor. Preliminary data suggest that uniform infilling of a macroscopic NP network is possible provided that it can be carried out at a temperature sufficiently low to prevent precursor decomposition.

Plasma Science and Technology Division
Room 315 - Session PS2+SE-WeA

Atmospheric Pressure Plasmas and their Applications

Moderators: Adam Pranda, TEL Technology Center, America, LLC, **François Reniers**, Université Libre de Bruxelles, Belgium

2:20pm **PS2+SE-WeA-1 Organized DBD Streamers for Maskless Chemical and Topographic Patterning of Surfaces***, O. Polonskyi, T. Hartig,* UCSB Chemical Engineering*; J. Uzarski,* U.S. Army Combat Capabilities Development Command Soldier Center*; **Michael Gordon**,* UCSB Chemical Engineering

Current methods for plasma-based modification of material surfaces (e.g., etching; modifying adhesion, surface chemistry, or wettability; and deposition) cannot often deliver precise control over the location of treatment without extensive use of complex lithographic or photoresist masks. Dielectric barrier discharge (DBD) plasmas operating at atmospheric pressure can accomplish such surface treatments through the creation of random plasma filaments or 'streamers' where surface treatment preferentially occurs. Unfortunately, spatially random and intermittent formation of plasma streamers usually precludes precise patterning.

In this work, we demonstrate how DBD streamers can be sufficiently controlled, via self-organization (with voltage and frequency) and more specifically with topographically patterned dielectrics and raster-scanning of a single streamer, to accomplish localized and user-defined spatial treatment of various substrates without the use of lithographic masks. Spatially organized DBD steamers were used to locally modify the wettability (hydrophilic vs. phobic character) and chemistry of various material surfaces (PMMA, nylon, Teflon, glass, metals), as well as modify surface roughness and etch. Contact angle, XPS, AFM, IR and Raman mapping before and after treatment reveal that surface chemical changes occur preferentially where streamers form, and moreover, that streamer exposure can be tailored to achieve different kinds of multifunctional surfaces. Examples to be highlighted include (i) maskless etching of PMMA on Si at specific locations, (ii) creating bio-inspired chemical patterns on glass to mimic insect carapaces with differential wetting, (iii) rendering Teflon hydrophilic at precise locations, and (iv) creating surfaces with orthogonal wetting characteristics (e.g., simultaneously hydrophilic and phobic over different length scales).

3:00pm **PS2+SE-WeA-3 An Atmospheric-Pressure Microwave Plasma Source for "Chemical Waste-Free" Surface Cleaning and Anti-Corrosion Coatings***, D. Ellis,* University of Illinois at Urbana-Champaign*; D. Krogstad,* Applied Research Institute, University of Illinois at Urbana-Champaign*; M. Sankaran, **David Ruzic**,* University of Illinois at Urbana-Champaign

Metals such as steel are widely used in infrastructure, transportation, and manufacturing where they are exposed to corrosive environments. While higher grade metal alloys can have lower corrosivity, they have significantly higher cost. A potentially more cost-effective approach is to protect metals from corrosion by protective coatings. Currently, many of the best protective coatings require application through expensive dip tank processes that result in a high amount of chemical waste that can be potentially hazardous and result in significant waste remediation costs. For this reason, there is a need to develop a low-cost, low-chemical waste process to apply protective coatings to a variety of metals, including mild steel.

We have developed an atmospheric-pressure microwave plasma for the cleaning and coating of metal surfaces. By relying predominantly on gases, such as air or nitrogen, with aerosolized precursors instead of wet chemicals, chemical waste is greatly reduced. Here, we present a study of 1008/1010 mild steel. Cleaning of surfaces was demonstrated by purposefully contaminating with oil or sodium chloride. Following plasma treatment, the surfaces were characterized by Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering spectroscopy (RBS). In the case of salt, a Bresle test was also employed. We find that the plasma is very effective in removing oil, with no hydrocarbons being detected on the treated surface through FTIR measurements. Plasma treatment is also found to be capable of removing thin layers of salt, including residual salt left after rinsing surfaces with water. We have also shown that the atmospheric pressure plasma can be used to deposit nanoscale silica coatings onto the steel substrates to promote corrosion protection and paint adhesion. Films were deposited by introducing tetraethylorthosilicate (TEOS) vapor in the plasma. The film properties, including composition and thickness, were characterized by scanning electron microscopy, FTIR, and RBS. Electrochemical testing was used to determine the corrosion protection properties of the films, while accelerated corrosion testing using salt fog was used to determine the corrosion prevention capability of the film under a compromised paint barrier. Plasma-deposited silicon oxide films were found to substantially decrease corrosion.

3:20pm **PS2+SE-WeA-4 Characteristics of Ionization Wave Propagation on Variable Thickness Dielectric Substrate***, **Joshua Morsell**, S. Shannon,* North Carolina State University

The interaction of atmospheric pressure plasma jets (APPJ's) with various materials and material topologies can greatly influence an array of existing and new plasma based applications.One area of interest is the ionization waves that are generated by these plasma jets. These ionization waves provide consistent and repeatable application of fields and excited species to the target surface. The focus of this work is to study the effect of dielectric thickness on the propagation of ionization waves as they impinge upon the target surface.

The plasma source in question is an APPJ with helium as the working gas as used in [J. Jiang et al., PSST29(2020), 045023]. The work presented utilizes a nanosecond DC pulse of positive polarity. Pulse width is 500 ns with voltage ranging from 3.5-4.5 kV. Voltage and current data is collected via integrated current probe and a high voltage probe at the source head. The dielectric surfaces consist of two experimental configurations. The first is a 3-D printed stage with a metal foil ground plane. Microscope cover glass 150 micron thick is stacked on this stage to provide a dielectric surface from 0.15 – 3.0 mm thick. The cover glass is 24x24 mm. The second configuration is a 3-D printed stage where the ground plane is a 50 mm square glass plate 1.1 mm thick with conductive ITO deposited on one side. 1 mm thick microscope slides are used to make a dielectric surface of 1.1-10.1 mm thick. Both configurations have a constant gap between the source tip and dielectric surface of 10.5-11mm. A PI-MAX 3 ICCD camera is used to image the ionization wave interaction with the target dielectric. The ICCD is gated to 5 ns and a 5 ns delay time step.

For both experiments, the surface wave velocity has a strong dependence with dielectric thickness, increasing by a factor of three from 0.15mm to 1.65mm.For thicknesses greater than 1.65mm the velocity remains relatively constant for measurements out to 10mm thickness. Surface velocity ranges from 1.5-4.5*10^4 m/s. It is noted that the initial conditions for each dataset is kept constant by ensuring that the velocity of the impinging axial ionization wave is constant. Axial velocities for the fine and bulk studies are 1.88*10^5 m/s and 1.81*10^5 m/s, respectively. These results suggest a transition in electric field structure as the axial component of the impinging wave dissipates into the dielectric bulk more readily than the radial field with a maximum penetration depth that eventually saturates the velocity of the surface wave.

This work is supported as part of the Department of Energy Center for Plasma Interactions with Complex Interfaces (PICI).

5:00pm **PS2+SE-WeA-9 Synthesis and Applications of Metal Oxides NPs***, **Davide Mariotti**,* University of Ulster, UK **INVITED**

Metal oxides are an extraordinary class of materials that have found wide applicability for a number of century-defining technologies (e.g. flat-panel display, capacitors and energy storage) mainly due to their dielectric properties and chemical inertness. Doping, defect engineering, quantum confinement and extending to clusters, ternary or high entropy oxides can create disruptive materials with new or improved properties. Atmospheric pressure microplasmas represent a viable synthesis platform to achieve exceptional tuning capability therefore achieving an exquisite control of the size, composition and defects of metal oxide nanoparticles [1-4]. In this contribution we will show how microplasmas can offer a generalized methodology for the synthesis of metal oxide nanoparticles and produce very desirable opto-electronic properties. Therefore we will discuss the formation of metal oxide nanoparticles with gas-phase microplasmas as well as hybrid plasma-liquid systems [5-10]. We will further provide an overview of their application opportunities in energy-related applications as well as other disciplines [8-9]. Examples will include oxides from Ni, Cu, Mn, Sn, Co, Mo and Zn. Finally we will provide future directions at the boundaries between ordered and disordered crystal structures.

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5:40pm **PS2+SE-WeA-11 AVS Graduate Research Awardee Talk: Immobilization of Plasma Filaments in a DBD: Discharge Characterization and Patterned Coating Deposition***, **Annaëlle Demaude**[1,2], A. Remy, D. Petitjean, J. Zveny,* Université libre de Bruxelles, Belgium*; K. Baert, T. Hauffman,* Vrije Universiteit Brussel, Belgium*; E. Goormaghtigh,* Université libre de Bruxelles, Belgium*; M. Gordon,* University of California Santa Barbara*; F. Reniers,* Université libre de Bruxelles, Belgium

Dielectric barrier discharges (DBDs) can be ignited in different discharge modes: glow, homogeneous or filamentary. At atmospheric pressure, in most gases, the latter mode is more often obtained than the others. Filamentary DBDs are characterized by the presence of micro-discharge channels (filaments), which are very short-lived (few ns) and ignite randomly in the interelectrode space.[1] This can be seen as a drawback for surface functionalization/thin film deposition by DBDs, as it can lead to inhomogeneous treatments.[2] Instead of avoiding these filaments, their higher density in current and energetic species was recently exploited to locally modify surfaces. This was achieved using auto-organized filamentary DBDs or directly by immobilization of the filaments.[3,4] Using this latter method, our team has extended the concept further to the deposition of patterned thin films.[5]

In this work, control over the ignition location of the filaments has been achieved in Ar and in N_2 by texturizing one of the dielectric surfaces to locally favor the ignition of the micro-discharges. The distribution of the filaments in the discharge gap and their electrical properties were examined by high-speed camera imaging and by electrical measurements, respectively. By injecting different precursors such as propargyl methacrylate (PMA) or vanadium(V) oxide triisopropoxide in the Ar or N_2 immobilized filaments, hydrophilic/phobic patterned surfaces or crystalline vanadium oxide (VO_x) patterns were obtained, respectively. The spatial differences in chemistry, morphology, wettability (for PMA films) and crystallinity (for VO_x films) of the deposited films were investigated by micro-XPS and micro-IR analysis, by profilometry, water contact angle measurements and XRD, respectively. The properties of the deposited films and of the corresponding discharges could then be correlated.

This opens a new route for the deposition of patterned coatings in a one step-process at atmospheric pressure and could contribute to a better understanding of chemical reactions occurring in filamentary DBDs.

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6:00pm **PS2+SE-WeA-12 Maximizing Photon Flux in a Miniaturized Photoionization Detector***, **Mackenzie Meyer**, X. Huang, A. Sivakumar, X. Fan, M. Kushner,* University of Michigan

Photoionization detectors (PIDs) use wavelength specific UV and VUV radiation to selectively ionize, for example, volatile organic and inorganic compounds (VOCs and VICs). These compounds are then detected by collecting the resulting ion current. Miniature PIDs are of interest for lab-on-a-chip applications. A miniature PID has been developed in which VUV photons are produced by a pulsed He atmospheric pressure plasma generated in a double dielectric barrier discharge (DBD). Maximizing the fluence of photons that reach the analyte inlet will increase performance of the PID, lowering the detection limit or increasing speed of operation. The operation and optimization of a DBD-PID with the goal of increasing photon fluence were computationally investigated using the 2-dimensional model *nonPDPSIM*. Several strategies were identified to increase the photon fluence. For example, making the powered electrode V-shaped instead of flat increased the photon fluence, as the electric field is enhanced at the tip of the powered electrode. Using an array of powered electrodes capable of sustaining multiple streamers also increased the photon fluence, as did positioning the electrodes closer to the analyte inlet. The most substantial increase in photon fluence came from increasing the capacitance of the bounding dielectric by increasing the relative permittivity from 10 (typical of conventional fabrication materials) to 300 (for specialized materials). Increasing the capacitance of the dielectric increased the voltage drop across the plasma and stabilized the plasma filament while increasing current for a given voltage

Work was supported by the Department of Energy Office of Fusion Energy Sciences and the National Science Foundation.

Advanced Surface Engineering Division
Room 317 - Session SE+MN+PS+TF-WeA

Vapor Deposition Technologies and New Trends in Surface Engineering

Moderators: Jianliang Lin, Southwest Research Institute, **Filippo Mangolini**, The University of Texas at Austin

2:20pm **SE+MN+PS+TF-WeA-1 Breaking the Back-Attraction by Bipolar HiPIMS Bursts***, **Rajesh Ganesan**,* University of Illinois at Urbana-Champaign **INVITED**

Limiting the back-attraction of ions is crucial to increase the deposition rate in HiPIMS processing. Back-attraction can be considerably limited by bipolar plasma bursts in which a positive voltage pulse is applied instantaneously after the negative voltage pulse. Energy-resolved mass spectroscopy confirms that, in addition to the increased flux, the energy of the target metal ions travelling from the target to the substrate is also increased, as a function of positive pulse length. Amorphous carbon coatings have been deposited by bipolar HiPIMS (BiPIMS) as a case study. The increased energy of the depositing flux led to a higher density of the carbon coatings and a significant reduction in the incorporation of the sputter gas atom, argon, was observed in the coatings. Langmuir probe measurements suggest the optimum plasma density window to minimize arc generation and reduce the probability of generated arcs moving away from the target racetrack, which results in smoother coatings. BiPIMS voltage pulses of optimized length and magnitude help to coat high quality amorphous carbon coatings with excellent machining functionalities.

3:00pm **SE+MN+PS+TF-WeA-3 Experimental and Theoretical Study of the Thermal Shock Behavior of MAX Phase Thin Films***, **Matej Fekete**, C. Azina, P. Ondračka, L. Löfler, D. Bogdanovski,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; M. Hans, J. Schneider,* RWTH Aachen University, Germany

Components subjected to rapid temperature changes are prone to thermal shock, which may result in damage or catastrophic failure. Thus, thermal shock resistance is one of the performance-defining properties for an application where extreme temperature gradients are required. The thermal shock resistance can be described by the thermal shock parameter (R_T), which depends on the flexural strength, thermal conductivity, Poisson's ratio, linear coefficient of thermal expansion, and elastic modulus. In this study, these thermomechanical properties of Ti_3AlC_2 and Cr_2AlC MAX phase coatings are investigated by both experiment and theory. The R_T of Ti_3AlC_2 obtained through quantum mechanical predictions is in good agreement with the experimentally obtained R_T. However, for Cr_2AlC, the theoretical predictions result in approximately two times larger R_T than experiments. This difference may be caused by omitted spin-polarization in the calculation of the electronic part of the thermal conductivity. Correlating the studied MAX phase thin films, both experiments and theory indicate superior facture behavior of Ti_3AlC_2 in comparison to Cr_2AlC. This is attributed primarily to the higher thermal conductivity of Ti_3AlC_2.

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[1] **PSTD Coburn & Winters Student Award Finalist**

[2] **AVS Graduate Research Awardee**

4:20pm **SE+MN+PS+TF-WeA-7 Combinatorial Application of Advanced Characterization Methods to Illuminate the Role of Interfaces in Multilayer Coatings***, **Nina Schalk**, C. Kainz, F. Frank,* Montanuniversität Leoben, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; M. Tkadletz,* Montanuniversität Leoben, Austria **INVITED**

The microstructural characterization of multilayer coatings and their interfaces is challenging, especially if the layer thicknesses are only in the nm range. Within this talk, two model coatings are used to evaluate the suitability of several characterization methods for the investigation of their microstructure and interfaces on different length scales. The fine grained cathodic arc evaporated ZrN/TiAlN and the rather coarse grained chemical vapor deposited TiCN/TiC multilayer model coatings exhibit different bilayer thicknesses and layer thickness ratios and thus allow also insight into the effect of the layer thickness on coherency, grain size and strain state. Starting with methods such as scanning electron microscopy and laboratory X-ray diffraction, an overview of the coating structure and information on the average strain/stress state can be obtained. Depending on the grain size and individual layer thickness, high resolution electron backscatter diffraction allows a more detailed insight into the microstructure and strain state of individual layers. In addition, information about gradients of strain/stress across the coating thickness is accessible by cross-sectional X-ray nanodiffraction. However, for a detailed investigation of the interfaces, the application of high resolution methods such as transmission electron microscopy and atom probe tomography is indispensable, providing information about lattice misfits and related strain evolution in the layers as well as on the sharpness of the interfaces in terms of elemental distribution down to the atomic scale. The present talk highlights that for the characterization of the different multilayer systems the combinatorial application of different characterization methods is possible and reasonable.

5:00pm **SE+MN+PS+TF-WeA-9 Influence of Al-Content on Structure, Mechanical Properties and Thermal Stability of Reactively Sputtered AlTaTiVZr High-Entropy Nitride Coatings***, **Alexander Kirnbauer**[1],* TU Wien, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Austria

In the field of materials research, a novel alloying concept, so-called high-entropy alloys (HEAs), has gained particular attention within the last decade. These alloys contain 5 or more elements in equiatomic or near-equiatomic composition. Properties, like hardness, strength, and toughness can be attributed to the specific elemental distribution and are often superior to those of conventional alloys. In parallel to HEAs also high-entropy ceramics (HECs) moved into in the focus of research. These consist of a solid solution of 5 or more binary nitrides, carbides, oxides, or borides. Within this work, we investigate the structure and, mechanical properties of thin films based on the high-entropy concept, with particular emphasis on the thermal stability, dependent on the Al content in AlTaTiVZr thin films.

Therefore, AlTaTiVZr nitride coatings were reactively sputtered in a lab-scale sputter deposition facility using a single powder-metallurgically produced composite target and Al cubes placed along the racetrack to increase the Al content within the coatings. The coatings in as-deposited state show a fine-columnar growth and crystallise in a single-phase face-centred cubic (fcc) structure. The hardness of our coatings in as-deposited state is ~32.8 GPa and relatively independent on the Al-content. We studied the influence of the Al content on the thermal stability by investigating the structural evolution of our coatings by DSC and powder X-ray diffraction, as well as nanoindentation upon vacuum annealing. The study reveals a distinct influence of the Al-content on the decomposition of the solid solution into an fcc-matrix and Al-rich domains.

5:20pm **SE+MN+PS+TF-WeA-10 Ternary Transition Metal Diborides – Future Defect Engineered Protective Coating Materials?***, A. Hirle, L. Zauner, C. Fuger, A. Bahr, R. Hahn, T. Wojcik, T. Glechner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; **Helmut Riedl**,* TU Wien, Austria

In the progression of novel protective thin film materials, the attention for transition metal diborides (TMB_2) substantially increased during the last years. The unique strength of their hybridized covalent bonds combined with their hexagonal close-packed (hcp) structures is a big advantage and limiting factor at the same time. The related brittleness, variety of crystal structures, and stoichiometries depict significant challenges for a broad usage of these structurally imperfect coating materials. Furthermore, the formation of non-adherent and volatile oxide scales is also a major limiting factor.

Within this study, we want to address these specific challenges on various ternary model systems within group IV to VI transition metal diborides (e.g. $TM_{1-y}X_yB_{2\pm z}$ prototypes). As structural defects play a major role for the phase formation of the two characteristic hexagonal structure types (α–AlB_2 vs. ω-W_2B_{5-x}-prototype), the target composition and ionization degree within the plasma, has been systematically correlated with the deposition parameters for non-reactive DCMS and HiPIMS depositions. In addition, different alloying concepts for enhancing the ductile character – by microstructural design of imperfect grain boundary structures [1, 2] – as well as oxidation resistance – up to 1200 °C through Si alloying [3] – of these superhard ternary diborides will be discussed in detail. To describe all these relations comprehensively, we correlated the synthesis parameters with structural and morphological evolution using XRD, HR-TEM, APT, as well as micro-mechanical testing methods. Furthermore, specific aspects have also been described by atomistic modelling (DFT).

Keywords : Ternary Borides; Protective Coatings; Defect Engineering; High Temperature Oxidation;

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5:40pm **SE+MN+PS+TF-WeA-11 Influence of Interplay of Substrate Template Effects and Bias Voltage on the Microstructure of Cathodic Arc Evaporated Fcc-$Ti_{0.5}Al_{0.5}N$ Coatings***, **Michael Tkadletz**, N. Schalk, H. Waldl,* Montanuniversität Leoben, Austria*; B. Sartory, J. Wosik,* Materials Center Leoben Forschung GmbH, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria

Ever since the implementation of hard coatings as wear protection for cutting tools, their microstructural design has been of major interest. While the effect of the deposition parameters, such as the applied bias voltage or the substrate temperature, on the microstructure are frequently investigated and rather well understood, commonly less attention is paid to the used cemented carbide substrates. Yet properties like their phase composition and carbide grain size significantly influence the resulting coating microstructure. Thus, within this work substrate template effects are studied on fcc-$Ti_{0.5}Al_{0.5}N$ coatings grown by cathodic arc evaporation onto cemented carbide substrates with different WC grain sizes. A systematic variation of the bias voltage resulted in coarse, intermediate and fine grained coating microstructures, which revealed substrate template-based coating growth at low bias voltages and bias dominated coating growth at high bias voltages. In addition, a strong influence of the applied bias voltage on the resulting preferred orientation of the deposited coatings was observed, providing the basis to tailor the texture to 100, 110 or 111. Elaborate X-ray diffraction and electron microscopy studies contributed to gain further understanding of the substrate template effects and revealed that implementation of a suitable baselayer offers the possibility to effectively prevent any influence of the used substrate on the microstructural evolution of the coating. Supplementary micromechanical experiments illuminated the impact of microstructure, template and non-template based coating growth on the obtained mechanical properties. The obtained results set the fundament to implement tailored microstructures with designed gradients of crystallite size, preferred orientation and consequently mechanical properties, which, as required, either utilize substrate template effects or avoid them.

6:00pm **SE+MN+PS+TF-WeA-12 Super Hard High Temperature TaC-Based Superlattice Protective Coatings Prepared by Magnetron Sputtering***, **Barbara Schmid**,* TU Wien, Austria*; S. Kolozsvari,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Austria

Transition metal carbides belong to ultra-high temperature ceramics (UHTC) and are particularly valued for their high thermal and mechanical stability as well as melting points of even above 4000 °C. Therefore, those materials are especially interesting for the application as protective coatings. However, a considerable limitation of these materials is their high inherent brittleness. Inspired by the success of nanolayered superlattice architecture—shown to enhance both hardness and toughness of transition metal nitrides like TiN/CrN or TiN/WN—we developed superlattice films based on TaC. These combinations are motivated by ab

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[1] **2021 ASED Young Investigator Awardee**

initio density functional theory calculations exhibiting large and small shear modulus and lattice parameter misfits. Our coatings are prepared via non-reactive DC and pulsed DC magnetron sputtering using binary carbide compound targets. In our study, we want to compare TaC-based superlattice systems and investigate the influence of the superlattice architecture on material characteristics like mechanical, thermal and electrical properties. Apart from nanoindentation and micromechanical cantilever testing for hardness and fracture toughness, material stability at elevated temperatures as well as thermoelectrical properties are being characterized.

Advanced Surface Engineering Division
Room 317 - Session SE+AS+BI+SS+TF-ThM

Nanostructured and Multifunctional Thin Films and Coatings I

Moderators: Suneel Kodambaka, University of California Los Angeles, **Jianliang Lin**, Southwest Research Institute

8:00am **SE+AS+BI+SS+TF-ThM-1 Nanostructured Optical Thin Films for Energy Applications and More***, **Bill Baloukas,*** Polytechnique Montréal, Canada **INVITED**

The range of applications of optical coatings is ever expanding, and the list of requirements they must fulfil, be it in terms of performance and in terms of functionality, is also increasing. This has stimulated the need for thin film materials with novel nanostructures often based on unconventional materials. The present talk will focus on various coating systems for applications ranging from antireflective (AR) coatings to plasmonic nanocomposites to passive and active materials for anticounterfeiting, smart windows and micro/nanosatellites.

AR coatings are the most widely implemented optical coating solution as they can be found on ophthalmic and camera lenses, displays, solar cells, etc. Most often based on dielectric materials, their mechanical performance can often be problematic when implemented onto polymer substrates, the latter possessing much higher thermal expansion coefficients. As a means of improving their elastoplastic properties, hybrid films consisting of a combination of organic and inorganic materials were explored. We will also show how this concept was pushed further by producing ultralow refractive index hybrid films by glancing angle deposition (GLAD).

GLAD films have also found application in angular selective coatings, which display anisotropic optical properties. Typically based on metals, we show how the angular selectivity (AS) can be tuned independently from the thickness of the film by conformally overcoating dielectric GLAD films with an absorbing film (e.g.: TiN) deposited by atomic layer deposition (ALD).

While the previous examples are based on passive materials, we have also extensively studied active materials, mainly electrochromic (EC) WO_3 and thermochromic (TC) VO_2. We will discuss how by tuning the deposition conditions, one can deposit, for instance, electrochromic interference filters and highly durable EC films when in the presence of significant ion bombardment. In the case of TC VO_2 films, we will show how, by incorporating them into judiciously designed optical filters, one can enhance their overall optical performance (e.g.: luminous transmittance, solar transmission variation, emissivity change, etc.).

Finally, we will conclude this talk by discussing our most recent implementation of a gas aggregation cluster source to produce various nanoparticles of interest for the above-mentioned optical applications.

8:40am **SE+AS+BI+SS+TF-ThM-3 Constitution, Microstructure and Mechanical Properties of Magnetron Sputtered RuAl Thin Films***, **Vincent Ott,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; T. Wojcik,* TU Wien, Austria*; S. Ulrich,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany*; S. Kolozsvári,* Plansee Composite Materials GmbH , Germany*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer, H. Riedl,* TU Wien, Austria*; M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Considering high temperature applications, aluminide intermetallics arrived increasing importance over the last decades. They are well known for their mechanical properties, such as high melting point, strength and good oxidation resistance. In Ni-superalloys, for example, aluminide precipitations are widely used as toughening phase, increasing the high temperature strength and durability of the construction material. Although they are commonly used as an additive in composite materials, their usage as a bulk material is hindered by their poor manufacturing due to its brittle behavior at room temperature.

A relatively new candidate material of B2 structured aluminides is the RuAl intermetallic phase. Compared to other candidates of its class, such as NiAl or TiAl, RuAl exhibits a ductile-brittle-transition below room temperature, which may considerably expand the range of its potential applications.

Thin film synthesis can enable the exploitation of their full potential for example as a protective coating in aircraft and aerospace applications. To elucidate this potential, RuAl single layer thin films were synthesized by magnetron sputtering, utilizing a powder manufactured sputtering target with a composition of 50 at. % Ru and 50 at. % Al. Thin film deposition was done for a variation of the process parameters such as the mode of the power supply, gas pressure and substrate bias voltage to investigate their impact on the thin films constitution and microstructure. Major structural thin film characterization was done by X-ray diffraction and transmission electron microscopy methods. These data are subsequently used to discuss the mechanical properties of the thin films, determined by microindentation.

9:00am **SE+AS+BI+SS+TF-ThM-4 Microstructure, Thermal Stability and Oxidation Resistance of an arc-evaporated $Cr_{0.74}Ta_{0.26}N$ Coating***, **Christina Kainz,*** Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz, M. Burtscher,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Institute of Materials Physics, Helmholtz-Zentrum Hereon, Germany*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; D. Kiener,* Department of Materials Science, Montanuniversität Leoben, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria

CrTaN coatings have recently received increasing industrial interest due to their combination of high hardness, beneficial fracture toughness and promising performance in cutting tests. However, up to now, no thorough investigation on the thermal stability and oxidation resistance of this coating system is available. Thus, this work aims to elucidate the evolution of the microstructure and phase composition of an arc evaporated $Cr_{0.74}Ta_{0.26}N$ coating in protective atmosphere and air up to 1400 °C. The as–deposited coating crystallizes in an fcc–$Cr_{0.74}Ta_{0.26}N$ solid solution with a preferred <311> orientation. Alternating Cr–enriched and Ta–enriched nano–layers are identified in the cross–section, which arise from the three–fold rotation during deposition. $Cr_{0.74}Ta_{0.26}N$ powder is stable in protective atmosphere up to temperatures of ~1200 °C, where a transformation into fcc-$Cr_{0.74}Ta_{0.26}N$ to t–$Cr_{1.2}Ta_{0.8}N$ sets in. Vacuum annealing of $Cr_{0.74}Ta_{0.26}N$ on sapphire substrate results in the loss of the nano-layers at 1000 °C, a texture change to <200> at 1270 °C and the transformation to t-$Cr_{1.2}Ta_{0.8}N$ at 1300 °C. When exposed to ambient atmosphere, powdered CrTaN starts to oxidize to t–$CrTaO_4$ and r–Cr_2O_3 at 1050 °C. A partly oxidized CrTaN coating on sapphire was found to consist of intact fcc-$Cr_{0.74}Ta_{0.26}N$ grains close to the substrate interface, a porous transition layer of r-Cr_2O_3 and t-$CrTaO_4$ and a dense r-Cr_2O_3 layer at the surface. The present study confirms the exceptional thermal stability and oxidation resistance of CrTaN coatings, making them promising candidates for use in demanding machining applications.

9:20am **SE+AS+BI+SS+TF-ThM-5 Microstructural Characterization and Tribological Evaluation of TiN, CrN, TiSiCN, and CrSiCN Coatings for Applications in Cold Regions***, **Nicholas D'Attilio,** F. Thompson, G. Crawford,* South Dakota School of Mines and Technology*; E. Asenath-Smith,* US Army Corps of Engineers Cold Regions Research and Engineering Laboratory

Transition metal nitride and nanocomposite coatings have the potential to improve the efficiency, service lifetime, and durability of equipment operating in the extremely cold and dry environments found in Earth's polar regions. Ceramic coatings are sensitive to their operating conditions, and development efforts have been focused on ambient and high temperature environments. Thus, there is a need to understand the influence of arctic conditions on the performance of these materials. To investigate the influence of coating phase content on cold environment performance, TiN, CrN, TiSiCN, and CrSiCN coatings were deposited by plasma enhanced reactive magnetron sputtering. The structure and composition of the coatings was characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, atomic force microscopy, and X-ray diffraction. Tilting base contact angle goniometry was used to determine the surface energy using the Owens-Wendt-Rabel-Kaelble method. Coating hardness and apparent elastic modulus were measured by nanoindentation. Sliding wear tests were conducted under simulated arctic conditions with a ball-on-flat tribometer equipped with an active cooling stage. Coating microstructure, surface properties, and their relationships to the wear mechanisms identified at low temperatures are discussed.

9:40am **SE+AS+BI+SS+TF-ThM-6 Development and Evaluation of TiAlNb/YSZ Protective Coatings for Titanium Alloys***, **Jianliang Lin,*** Southwest Research Institute, San Antonio Texas*; T. Stinnett,* Lockheed Martin Missiles and Fire Control

There are increasing demands in the development of advanced thermal protection coatings for aerospace components made by titanium alloys for hypersonic applications. A conventional thermal barrier coating based on MCrAlY/YSZ produced by thermal spray or EB-PVD (Electron Beam Physical Vapor Deposition) provided thermal protection, but was found insufficient in thermal stain tolerance and mechanical strength match for titanium alloys. In this study, TiAlNb alloy with specific chemistry was selected as the bond coat for Ti-6Al-4V alloys. The TiAlNb bond coats were prepared by different magnetron sputtering techniques, including plasma enhanced magnetron sputtering (PEMS), high power impulse magnetron sputtering (HiPIMS), and a combination of PEMS and HiPIMS. The structure, adhesion, oxidation resistance, and thermal fatigue resistance of the TiAlNb coatings was studied by different means. Then an yttrium stabilized zirconium oxide (YSZ) top coat was applied on the top of the optimized TiAlNb by thermal spray. The thermal strain resistance and phase stability of the overall coating system were evaluated using high energy laser irradiation and compared to a thermal spray MCrAlY/YSZ coating in ambient air. It is found that TiAlNb/YSZ outperform MCrAlY/YSZ in high energy laser irradiation, and exhibited no structure and integrity degradation.

11:00am **SE+AS+BI+SS+TF-ThM-10 Imperfections in Metal Diborides – from Ab-Inito Calculations to Transmission Electron Microscopy***, **Martin Dahlqvist,*** IFM, Linköping University, Sweden*; M. Dahlqvist,* Linköping University, Sweden **INVITED**

Transition metal diborides (*M*B$_2$) are considered as an extremely hard ceramics owing to their outstanding chemical, mechanical, corrosion, thermal and electrical properties. This makes *M*B$_2$ coatings attractive for applications in erosive, abrasive, corrosive, and high-temperature environments [1]. Typical coatings are overstoichiometric in boron (B/*M*>2) [2] but the recent addition of understoichometic *M*B$_2$ coatings (B/*M*<2) have widened their compositional range [3-8]. However, when comparing calculated and measured lattice parameters of *M*B$_2$, perfect match is found for *M* from Group 3 (Sc, Y) and 4 (Ti, Zr, Hf) while deviations are found for *M* from Group 5 (V, Nb, Ta) and 6 (Cr, Mo, W). Reason for this have been discussed to be attributed to non-stoichiometric *M*B$_2$. In our quest for improving the properties of *M*B$_2$ we must thus not only master their composition but also related defects. Reliable theoretical studies thus require detailed information about type of defects and their distribution in *M*B$_2$. It will be shown how theory can be used to identify possible defects in MB$_2$ and explain the discrepancy between theory and experiment. It will be demonstrated that vacancies in *M*B$_2$ have a significant impact for *M* from Group 5 (Nb, Ta) and 6 (Mo, W) with improved thermodynamical and dynamical stability as well as mechanical properties. Moreover, extended planar defects have also been identified for multiple *M*B$_2$ where atomically resolved aberration-corrected scanning transmission electron microscopy imaging, electron energy loss spectroscopy elemental mapping and first principles calculations have been applied to decode the atomic arrangements of the observed planar defects in non-stoichiometric *M*B$_2$ coatings.

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11:40am **SE+AS+BI+SS+TF-ThM-12 Mechanical Property and Corrosion Resistance Evaluation of Ti$_x$ZrNbTaFeB$_y$ High Entropy Alloy Thin Films***, B. Lou,* Chang Gung University, Taiwan*; F. Kan,* Ming Chi University of Technology, Taiwan*; **Jyh-Wei Lee,*** Ming Chi University of Technology, Taiwan

High entropy alloy (HEA) thin films have been widely explored due to their unique properties as compared with conventional alloy coatings. In this work, an equimolar TiZrNbTaFe HEA target and a TiB2 target were used to fabricate five TixZrNbTaFeBy HEA thin films with different Ti and B contents using a hybrid high power impulse magnetron sputtering and radio frequency power deposition system. The Ti and B contents were increased by decreasing the input power of TiZrNbTaFe HEA target. The (Ti+B)/(Zr+Ta+Nb+Fe) ratio of the thin films increased from 2.70 to 19.44 as the ZrTiNbTaFe HEA target input power decreased from 200 to 50 W. The TixZrNbTaFeBy thin film kept its amorphous structure while the (Ti+B)/(Zr+Ta+Nb+Fe) ratio was less than 19.44. A nanocomposite microstructure consisting of TiB$_2$ nanocrystallites embedded in an amorphous TiZrNbTaFe matrix was obtained for the $Ti_{26.4}Zr_{1.1}Nb_{1.0}Ta_{1.3}Fe_{1.1}B_{61.1}$ thin film. The hardness of TixZrNbTaFeBy thin films increased with increasing Ti and B contents. Good adhesion properties were found for five thin films. Each amorphous TixZrNbTaFeBy thin film enhanced the corrosion resistance of bare 304 stainless steel substrate because of the dense microstructures to block the attack of corrosive electrolytes. The amorphous structured $Ti_{26.9}Zr_{3.5}Nb_{3.4}Ta_{3.8}Fe_{3.7}B_{54.6}$ thin film coating exhibited a potential application as a protective coating in harsh environments due to its high hardness of 18.8 GPa, excellent adhesion, good wear resistance, and adequate anticorrosion property.

12:00pm **SE+AS+BI+SS+TF-ThM-13 Tuning the Properties of Thin Films via Disorder***, **Alessandro Troglia,** M. van de Poll,* Advanced Research Center for Nanolithography (ARCNL), Netherlands*; J. van de Groep, A. de Visser,* Van der Waals-Zeeman Institute, University of Amsterdam, Netherlands*; R. Bliem,* Advanced Research Center for Nanolithography (ARCNL), Netherlands

Structural disorder in thin films is often considered detrimental compared to the well-defined nature of epitaxial layers. However, some examples of amorphous thin films show superior properties such as better corrosion resistance, mechanical strength and catalytic performance. Structural disorder can thus serve as an ideal parameter to tune the properties of thin films to specific applications. In this work, we investigate how structural disorder affects the properties of metallic thin films for two selected alloys: CuZr and HfMoNbTiZr. Due to its excellent glass-forming ability, CuZr is an ideal model system for metallic glasses, while the refractory high-entropy alloy (HEA) HfMoNbTiZr has shown a strong preference towards crystallinity. For both materials, amorphous and crystalline alloy thin films of identical composition were achieved by varying the substrate temperature during deposition onto sapphire substrates via pulsed laser deposition (PLD). Grazing-incidence x-ray diffraction (GI-XRD) demonstrate that CuZr thin films grown at room temperature are fully amorphous, while signs of polycrystallinity are observed at 500°C. The effect of disorder is clearly visible in the optical, transport and corrosion properties. The amorphous films are optically transparent in the visible, while polycrystalline films are dark and reflective. The temperature-dependent electronic transport changes its mode from a bad metal to a charge-hopping conductor with an increase in structural disorder. Moreover, the surface chemical properties measured with x-ray photoelectron spectroscopy (XPS) show a clear preference in the surface oxidation of the Cu species. Cu is fully metallic in the disordered film after air-exposure, whereas both oxide and hydroxide species are detected in the polycrystalline film. On the other hand, HfMoNbTiZr thin films grown with PLD are amorphous according to GI-XRD and display a remarkable thermal stability. In contrast with literature, no sign of crystallinity is detected with GI-XRD from room temperature up to 700°C. A further increase of the growth temperature reveals the onset of directed crystallization at 900°C. These results pave the way to the synthesis of metallic thin films with superior and tunable properties via disorder for a wide variety of technological applications.

Thin Films Division
Room 316 - Session TF1+SE+SS-ThM

Nucleation, and Interface Phenomena in Thin Films

Moderators: Adrie Mackus, Eindhoven University, Netherlands, **Qing Peng**, University of Alabama

8:00am **TF1+SE+SS-ThM-1 Opportunities of Complex Oxides Prepared by Atomic Layer Depositions***, P. Sallés, P. Machado, **Mariona Coll,*** ICMAB-CSIC, Spain **INVITED**

The rapid development of electronic devices, telecommunication systems, and sensors pushes new functional demands with increasingly stringent requirements like flexibility, light weight, and miniaturization. Transition metal oxides present the richest variety of functional properties due to the large diversity of chemical compositions and structures that they can offer. However, the preparation and manipulation of crystalline yet bendable functional complex oxide membranes has been a long-standing issue as they require specific crystalline substrates and high temperature treatments. We have developed a facile chemical route based on the use of

$Sr_3Al_2O_6$(SAO) sacrificial layer to detach oxide thin films of various compositions from the growing substrate and enable their transfer to flexible substrates.[1] Meticulous chemical and structural study of the SAO film have allowed us to identify the formation of an amorphous SAO capping layer and carbonates upon air exposure, which dictate the crystalline quality of the subsequent oxide film growth.[2] Judicious cation substitution in SAO enabled both decreasing reactivity with ambient moisture and modulating the strain state of the subsequent heterostructures grown on it. Upon detailed investigation of oxide adhesion on polymeric substrates and sacrificial etching (figure 1), crystallinity, surface morphology, interface cation diffusion, mechanical and electrical properties of transfer printed heteroepitaxial $BiFeO_3/La_{0.7}Sr_{0.3}MnO_3$ membranes have been studied and compared with rigid substrates. From this work it is envisaged many new opportunities to prepare artificial oxide heterostructures and devices offering a whole new dimension for electronics and beyond.

[1] P. Salles, M. Coll et al. Adv. Funct. Interfaces, 2001643 (2021)

[2] P. Salles, M. Coll et al. ACS Appl. Mater. Interfaces , 14, 10, 12845–12854 (2022)

8:40am **TF1+SE+SS-ThM-3 An Atomic-Scale Study of Si Epitaxial Growth on Cl-Si(100)***, **Azadeh Farzaneh**,* University of Maryland, College Park*; R. Butera,* Laboratory for Physical Sciences

Atomically-precise fabrication techniques utilize a scanning tunneling microscope to lithographically define electronic devices and components, where a monatomic layer of H or Cl adsorbed on Si(100) acts as a resist. Unlike traditional resists, these monatomic resists either desorb or remain at the growth front during subsequent growth of Si capping layers.While the body of literature extensively explores Si deposition and subsequent diffusion on H-Si(100), Cl-Si(100) has remained relatively unexplored.A detailed understanding of the thin film growth mechanism enables atomic level control of the interface, which starts with diffusion of adatoms in dilute regimes on the surface. Here we explored the initial stages of Si growth on Cl-Si(100) and characterized thin Si films (~25 nm) grown on this surface. The activation energy for Si adatom diffusion on Cl-Si(100) was extracted from STM observations combined with simulations of a simple random walk model rooted in the mechanism of Si chain formation at different temperatures. Ex-situ characterization of thin Si films grown on Cl-Si confirmed the formation of crystalline layers and the near complete removal of Cl from the Si matrix. The epitaxial film obtained on Cl-Si(100) and absence of Cl from the interface confirm Cl as a viable resist for current atomically precise fabrication schemes. This opens up new pathways for introducing new chemistries and materials into the picture.

9:00am **TF1+SE+SS-ThM-4 The Effect of Oxygen Plasma on the ZnO Growth on Polymer Substrates During Plasma-Enhanced Atomic Layer Deposition***, **Lisanne Demelius**,* Graz University of Technology, Austria*; M. Blatnik,* CEITEC – Central European Institute of Technology, Brno University of Technology, Czechia*; K. Unger,* Graz University of Technology, Austria*; P. Parlanti, M. Gemmi,* Istituto Italiano di Tecnologia, Center for Materials Interfaces, Italy*; A. Coclite,* Graz University of Technology, Austria

Atomic layer deposition (ALD) is a powerful technique to deposit highly conformal thin films the thickness of which can be precisely controlled. However, the use of polymeric substrates often leads to non-ideal ALD processes that result in precursor diffusion and subsurface growth of the deposited material.
Plasma-enhanced ALD (PE-ALD) is known to enhance nucleation due to the surface-activating effect of plasma and can be expected to significantly reduce subsurface diffusion, enabling the surface-limited deposition of thin conformal coatings. However, plasma can also have detrimental effects on polymeric substrates.

Our work contributes to a deeper understanding of how oxygen plasma applied during PE-ALD affects film formation, nucleation, and interface formation of ZnO on polymer substrates. In-situ spectroscopic ellipsometry was used as the main technique to monitor the PE-ALD growth of ZnO on selected polymer thin films. To better understand how the chemical structure of the polymer influences plasma-substrate interactions and ZnO thin film formation, both crosslinked and linear polymers exhibiting varying degrees of reactivity with the ALD precursor were studied.

Our results show that while the plasma efficiently activates the polymer surface to enable rapid ZnO nucleation, it can also cause significant substrate etching that dominates the initial stage of growth until, at a certain point, ZnO growth takes over and the regime of normal ALD growth behavior is entered. The strength and extent of etching strongly depends on the type of polymer. Despite the initial etching, the resulting thin films exhibit sharp interfaces and a quality, in terms of surface roughness, crystallinity and ZnO density, comparable to those of ZnO deposited on silicon.

A closer examination of the first 25 PE-ALD cycles showed that, on the nanometer scale, the simultaneous etching of the polymer and ZnO nucleation leads to a certain degree of intermixing at the interfaces, the extent of which depends on the type of polymer. It was also revealed that, during the first few cycles, no stochiometric ZnO is yet formed but instead Zinc is found to be bonded to hydroxyl groups and presumably oxygen-carbon species from the polymer, forming hybrid bonds. This points to a strong interaction between the polymer substrate and the forming ZnO, which can be expected to result in good film adhesion, a property that is critical in all applications involving mechanical stress and strain.

9:20am **TF1+SE+SS-ThM-5 Measuring Local Atomic Structure Variations Through the Depth of Ultrathin ALD Aluminum Oxide***, **Nikhila Paranamana**, M. Young, R. Gettler, H. Koenig, S. Montgomery-Smith, X. He,* University of Missouri, Columbia

Understanding the atomic structure of ultrathin (<20 nm) atomic layer deposition (ALD) coatings is critical to establish structure property relationships and accelerate the application of ALD films to address technological needs. Previous studies have measured the atomic structure of nanoscale ALD films using cryogenic electron diffraction with a large (~200 nm) beam diameter. However, for ultrathin ALD coatings, these measurements provide only ensemble average structural information and cannot be used to directly measure differences in atomic structure through the depth of the ALD film. In this study, we localize the electron beam to a small (~ 5 nm) spot size using cryogenic scanning transmission electron microscope (STEM) and we collect electron diffraction data at multiple points along the depth of a 12 nm thick ALD AlO_x film deposited onto a CNT substrate without a contribution from the substrate. We couple these diffraction measurements with pair distribution function (PDF) analysis and iterative reverse Monte Carlo-molecular statics (RMC-MS) modeling to compare atomic structure metrics at different positions in the film depth. We interpret the modeling results considering the 3D concentric cylindrical sample geometry of a CNT with uniform AlO_x coating. These measurements confirm a two-phase bulk/interface structural model proposed previously for ALD AlO_x, and indicate that the interfacial layer at the CNT-AlO_x interface is 2.5 nm thick – five times larger than previously reported. This report demonstrates direct measurement of atomic structural variations across ultrathin films that is of broad interest for understanding local differences in atomic structure across material interfaces.

9:40am **TF1+SE+SS-ThM-6 Interfacial Reactions and Energy Transfer in Sputter Deposited Thermite Reactive Nanolaminates***, **Chloe Skidmore**, J. Maria,* Pennsylvania State University

Cost effective energetic materials with highly tunable ignition and actuation have important applications in both military and commercial sectors. Recently, interest has grown in nanoenergetic composites due to their potential as stand-alone explosives with greater reliability, heat release, and combustion efficiency. Thermite is a versatile inorganic energetic of specific significance due to the highly exothermic reduction-oxidation reaction that occurs between metal and oxide constituents, resulting in self-sustaining heat production. However, if the high energy release and improved tunability provided by the diverse chemistries of inorganic energetics is to be utilized, a fundamental understanding of the initiation and propagation processes in new nanoenergetic materials such as thermite is necessary. Thin film deposition of multilayered stacks of alternating metallic and oxide layers with well defined interfaces offers a streamlined process to observe energy transduction and the chemical reactions that mitigate interface reactions. These multilayered stacks, termed reactive nanolaminates (RNLs), facilitate control over reactant thickness, diffusion distance, interface quality and the total material involved, while also reducing premature intermixing of metal and oxide layers. This presentation explores energy release in sputter deposited CuO-Mg RNLs as a function of bilayer thickness, plasma energetics, and metal-oxide layering sequence. These samples are analyzed via in-situ high temperature x-ray diffraction (XRD) and differential scanning calorimetry (DSC), as both probe the oxygen exchange process by structure evolution and energy production, respectively. The bulk properties associated with the Mg-CuO thermite system suggests extensive oxygen dissolution in the starting metal and the possibility of transient eutectic liquid formation during reaction. XRD results indicate that CuO/Mg RNLs exhibit eutectic liquid formation during reaction, with Cu_xMg_yintermetallics temporarily appearing around 565°C. DSC analysis reveals exotherm maxima at temperatures associated with critical points in the Mg-Cu phase diagram. More precisely, as interfacial area is increased the max exothermic peak shifts from ~650°C (T_m Mg) to ~565°C (T_m Mg_2Cu) before finally occurring at ~483°C (T_m eutectic Mg/Mg_2Cu). Preliminary DSC analysis also suggests that, relatively speaking, sputtering energetics resulting in smoother, more crystalline Mg interlayers, shifts the maximum exothermic peak to higher temperatures. These findings provide insight into the mechanisms of energy transfer in thermite RNLs, allowing for highly tunable, reliable energetic materials.

Advanced Surface Engineering Division
Room 317 - Session SE+AS+MN+SS-ThA

Mechanical and Tribological Properties of Thin Films and Coatings

Moderators: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan , **Filippo Mangolini**, The University of Texas at Austin

3:00pm **SE+AS+MN+SS-ThA-3 Differential Impact of Scale Dependent Roughness on Lubricant Infused Surfaces***, **Robert Chrostowski**, B. Fang, J. Smith, F. Mangolini,* University of Texas at Austin

Lubricant Infused Surfaces (LIS), which consist of an engineered surface texture with an absorbed lubricant, have recently emerged as an innovative approach for achieving pressure-stable omniphobicity and for improving tribological performance in the presence of external contaminants. The design of successful LIS heavily relies on the effect of surface texture, which is quantified using a single dimensionless parameter, namely the ratio of the true surface area to the nominal surface area. Previous published studies have thus focused on the evaluation and optimization of microscale pattered morphologies with simple geometries (for which the ratio of the true surface area to the nominal surface area can be determined analytically), such as ordered arrays of pillars. Texture, however, is defined both by these larger-scale structures, and by smaller sub-micron scale asperities called roughness. Roughness can exhibit scale-dependent fractal self-similarity, and the absolute finest scales of roughness can have outsize impact on the quantitative value of the area ratio. Despite the scientific relevance of previous studies on fractal surfaces and the effect of roughness on contact mechanics, our understanding of the effect of surface roughness on the retention of a lubricant is elusive.

Here, we evaluate the lubricant infusion behavior of two different fluorinated polymer lubricants of substantially different molecular size, but similar surface chemistry, on fractal nano-rough boehmitized aluminum surfaces. Power spectral density (PSD) analysis of atomic force microscopy (AFM) topography maps is used to estimate the area ratio for each surface at the length scale of the radius of gyration of the different lubricants. The area ratio values computed from the PSD are then related to true area value that matches predicted spin-coating curves to observed gravimetric ones. The experimental results demonstrate, for the first time, the impact of fractal roughness on the shear-retention of LIS.

The outcomes of this work, providing evidence that different molecular length fluids could experience different quantitative magnitudes of roughness on the same, significantly contribute to our understanding of the impact of scale-dependent roughness on the retention of liquids on engineered surface textures, while enhancing the scalability of LIS systems and their cost-effective implementation in several technological applications.

3:20pm **SE+AS+MN+SS-ThA-4 Imperfectly Perfect Coatings for Rolling Bearing Applications***, **Esteban Broitman**,* SKF B.V. - Research and Technology Development, Netherlands **INVITED**

Machines with rotating components usually rely on bearings to reduce friction in moving its parts around a fixed axis. The increasing demand for more precise bearings to lower power consumption and heat generation, while simultaneously support increasing applied loads and/or higher speeds, has given place to the use of surface engineering processes.

In the case of bearings, it is widely accepted the advantages of using coatings as the surface process to improve its performance. During the last three decades, advanced coatings have enjoyed a growing interest in several industrial applications because they can be engineered to provide different properties like electrical insulation, low friction, and resistance to corrosion, plastic deformation, etc.

In this talk I will compare the structural, mechanical and tribological properties of two coatings that are used nowadays to improve the performance of rolling bearings made of standard bearing steel: they provide lower friction, resistance to surface initiated rolling contact fatigue, and decreased wear: NoWear® (a carbon-based nanostructured coating made by plasma-assisted chemical vapor deposition PACVD) of about 3 µm-thick, and Black Oxide (an iron oxide film made by a chemical conversion method) of about 1 µm-thick. Being coatings produced by different techniques, both have a common feature: they are *"imperfectly perfect coatings."* Scanning electron microscopy, X-ray photoelectron spectroscopy, and nanoindentation measurements show that, from the microstructural point of view, these coatings are full of *"imperfect"* features, like cracks, voids, porous, columns, and other naughty irregularities. The different mechanisms contributing to the positive tribological behavior of each coating under lubricated conditions will be discussed. I will demonstrate that these coatings, taking advantage of their own different *"imperfect"* features, behave *"perfectly"* from the tribological point of view, and therefore can successfully be used to extend maintenance and life expectancy of specialized rolling bearings.

4:00pm **SE+AS+MN+SS-ThA-6 Tribological Behavior of WC/WCN/CNx Thin Films Deposited by HIPIMS***, **Luis Flores-Cova**, O. Jimenez, M. Flores,* Universidad de Guadalajara, Mexico

Coatings and thin films are used to protect against wear in many applications. If that coating also shows a low coefficient of friction, it brings better benefits, therefore, the research on coatings with these properties is of great interest. In this respect, carbon containing, or carbon-based coatings are the most popular. 52100 alloy used in wear environments has its own disadvantages. Consequently, many coating systems have been deposited on this alloy to improve its wear resistance. In this study, a multilayer coating with carbon content (WC/WCN/CNx) was deposited by High Power Impulse Magnetron Sputtering (HiPIMS) on AISI 52100 alloy. No external heating was applied during the deposition, energetic tungsten ions increase adatoms mobility that enhance adhesion. The thickness and the growth morphology of the films were studied from FE-SEM cross-sectional images. The chemical composition was analyzed by XPS. The structure of the coatings was analyzed by XRD technique. The mechanical properties (hardness and Elastic Modulus) were studied through nanoindentation techniques. The adhesion of coatings to the substrate was measured by means of scratch tests. Wear tests were performed using a tribometer with a pin on disc configuration, using a 10 mm diameter 52100 ball. The wear tracks were analyzed by SEM and the wear volume was obtained by optical profilometry. The coating showed a coefficient of friction lower than 0.3 and the wear rate was reduced 100 times relative to the substrate.

Surface Science Division
Room 319 - Session SS+AS+SE-ThA

ALD and CVD Surface Chemistry

Moderators: Melissa Hines, Cornell University, **Dario Stacchiola**, Brookhaven National Laboratory

2:20pm **SS+AS+SE-ThA-1 ALD Surface Chemistry on Lithium-Ion Battery Cathodes***, **Jeffrey Elam**,* Argonne National Laboratory **INVITED**

Next-generation energy storage devices demand superb control over interfaces. Atomic layer deposition (ALD) is a powerful strategy for controlling interfacial properties. ALD coatings can suppress undesirable electrochemical reactions between lithium-ion battery (LIB) cathode surfaces and the organic liquid electrolyte and improve LIB cycling stability. While numerous reports have evaluated the electrochemical performance of ALD treated cathode materials, the chemical changes induced on the surface of the cathode materials by the ALD coatings and the individual ALD precursors are not fully studied. This presentation highlights our recent work investigating the surface chemistry of ALD on LIB cathode surfaces. We find that the nucleation and growth of Al_2O_3 ALD on$LiMn_2O_4$ (LMO) is much different compared to conventional surfaces such as hydroxylated SiO_2. For instance, LMO does not have surface hydroxyls under typical ALD conditions. During initial Al_2O_3 ALD cycles, trimethyl aluminum reacts with Mn-O bonds and reduces surface Mn ions generating C_2H_6. Al_2O_3 ALD on LMO is highly precursor-dependent and the degree of surface Mn reduction is strongly influenced by the Lewis acidity of the precursor ligands. In addition, the Al_2O_3 ALD growth per cycle (GPC) on LMO varies by 30x among 5 Al_2O_3 ALD precursors that exhibit essentially the same GPC on SiO_2. We next examined the surface chemistry for Al_2O_3 and AlF_3 ALD on 12 different cathode surfaces ranging from simple transition metal oxides (e.g., NiO and MnO) to complex multi-element cathode materials (e.g., $LiNi_xMn_{1-x-y}Co_yO_2$, NMC). We found that the Ni, Mn, and Co transition metals in the cathode undergo selective oxidation/reduction depending upon the nature of the precursor, the coating, and the cathode material. Furthermore, our measurements revealed the conversion of surface carbonate species to the corresponding metal fluorides upon HF exposure. This conversion reaction is self-limiting but extends hundreds of nanometers below the surface in the case of Li_2CO_3. ALD and chemical vapor treatment provide new avenues to systematically control the interface of the cathode materials in LIBs that are not possible by conventional coating methods.

3:00pm **SS+AS+SE-ThA-3 Role of Temperature, Pressure and Surface Oxygen Migration in the Initial Atomic Layer Deposition of HfO_2 on Anatase TiO_2(101)***, G. D'Acunto, R. Jones,* Lund University, Sweden*; L. Pérez Ramírez,* Synchrotron Soleil, France*; P. Shayesteh, E. Kokkonen, F. Rehman,* Lund University, Sweden*; F. Lim, F. Bournel, J. Gallet,* Sorbonne Université, France*; R. Timm,* ***Joachim Schnadt***, Lund University, Sweden

Atomic layer deposition (ALD) has become one of the prime methods for deposition of ultrathin films with atomic-scale precision [1,2]. Yet, for many ALD processes the underlying surface chemistry or aspects of it remain unclarified [3,4]. Experimental methods that allow the real-time monitoring of the ALD surface chemistry, i.e. time-resolved methods that can be applied during an ongoing ALD process, can provide much deepened insight into the ALD surface chemistry. One such method is time-resolved ambient pressure x-ray photoelectron spectroscopy (APXPS), which is an excellent match to ALD since it easily can be used in standard ALD pressure conditions of up to around 1 mbar. Here, we have applied APXPS to the study of the surface chemistry of the initial full cycle of HfO_2 ALD on TiO_2(101) from tetrakis(dimethylamido) hafnium (TDAMHf) and water precursors at both high (500 K) and low (300 K) surface temperature as well as high (~10^{-1} mbar) and low (~10^{-6} mbar) pressure.

Generally, we find that the initial ALD process on TiO_2(101) is characterised by an absence of surface hydroxyls, which implies that the reaction cannot proceed via the ligand-exchange mechanism standardly proposed for oxide ALD from amido complexes and water. Instead, dissociative adsorption and subsequent hydrogen insertion reactions take place during the first metal half-cycle, which lead to the formation of a number of different surface species, including a dimethyl ammonium ion and an imine. Their formation requires either a bimolecular reaction pathway or an active role of the TiO_2(101) surface as an oxygen supplier. Both pathways are viable and may compete with each other. Oxygen transport is evident from the formation of HfO_2 during the very first half-cycle and a concomitant reduction of the TiO_2 support already. The water half-cycle then allows hydroxyl formation, but only at sufficiently higher water pressure. In this case, a transition towards a ligand exchange reaction mechanism is possible, which, however, is hindered if the water pressure is too low.

Our study highlights how chemical models for transition metal oxide ALD from amido complexes and water need to be extended, by consideration of hydroxyl-free surfaces, oxygen transport and bimolecular reactions paths, and how time-resolved *in situ* studies can help understand how deposition parameters affect the growth of HfO_2.

[1] Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R. L. *J. Appl. Phys.* 2013, **113**, 021301

[2] Johnson, R. W.; Hultqvist, A.; Bent, S. F. *Materials Today* 2014, **17**, 236

[3] Zaera, F. *Coord. Chem. Rev.* 2013, **257**, 3177

[4] Richey, N. E.; De Paula, C.; Bent, S. F. *J. Chem. Phys.* 2020, **152**, 1

3:20pm **SS+AS+SE-ThA-4 ALD of Well-Defined Mixed-Oxide and Metal-Oxide Catalytic Interfaces***,* ***Francisco Zaera,*** University of California - Riverside

As the chemistry of solids is in most instances determined by the nature of their surfaces, control over the nature of surface sites during preparation is critical to the design of materials for specific applications. This is a difficult task, especially when complex multicomponent atomic ensembles are required. In this presentation we illustrate how atomic layer deposition (ALD) may be used to prepare such sites. We will describe the development of prototypical surface sites comprised of mixtures of silica supports (mainly well-structured mesoporous materials such as SBA-15), titania thin films, and gold nanoparticles, as that combination has proven to offer some unique and useful surface chemistry for low-temperature catalysis. The materials resulting from the use of ALD approach have been characterized using a surface-science approach, relying on the use of adsorption-desorption isotherms and well-defined mesoporous structures together with electron microscopy and a variety of spectroscopic techniques, including IR, NMR, XPS, EPR, and Visible-UV absorption. They showed some unique redox properties, and were tested for the promotion of low-temperature oxidation and selective hydrogenation reactions. Time permitted, other mixed-oxide interfaces, in particular silica-alumina, will be introduced as well.

3:40pm **SS+AS+SE-ThA-5 Mechanistic studies on Catalytically Activated ALD of Fe_2O_3 on Pt***,* ***Andreas Werbrouck,*** Stanford University, Belgium*; J. Schneider, S. Nathan, A. Rothman, S. Bent,* Stanford University

Atomic layer deposition (ALD) of Fe2O3 is well-studied process. Fe2O3 has numerous applications, for example in catalysis or as a ferroelectric material. While many Fe2O3 ALD processes have been reported, almost all of those use an iron precursor in combination with strong oxidizers such as H2O2, O3, or O2 plasma. Recently, ALD of Fe2O3 on Pt substrates has been demonstrated using just O2 gas as the co-reactant, with tert-butyl ferrocene (TBF) as the metal precursor [1]. The process was area selective, with no growth occurring on other substrate materials (SiO2, Al2O3, Au); hence, it is hypothesized that the Pt substrate creates reactive oxygen species in situ, effectively catalyzing the reaction to grow Fe2O3. Intriguingly, the activation continues after the Pt substrate has been completely covered by Fe2O3. The continued growth is attributed to the formation of a sub-surface oxygen reservoir.

In this work, we further investigate this process, with a focus on the underlying oxygen activation and transport mechanisms. In situ ellipsometry was used to study the growth characteristics and x-ray diffraction confirmed the Fe2O3 crystal structure. X-ray photoelectron spectroscopy results show a clear correlation between the amount of deposited Fe2O3 and the Pt surface coverage. To study the kinetics and mechanistic steps of the process, quadrupole mass spectrometry (QMS) was employed. H2O (m/z 18) CO (m/z 28, which is also N2) and CO2 (m/z 44) are observed as reaction products when Pt is present, indicating a combustion-like mechanism. Furthermore, as expected, the kinetics of the reservoir change as the film grows thicker; this behavior is confirmed by the QMS measurements.

Finally, a simple 1D diffusion model was developed to describe the sub-surface oxygen reservoir process (fig. 1). Given the partial pressure of O2, the model captures adsorption, transport and desorption of the oxygen in the layer before (O2) and after (O*) activation. The Pt surface coverage is parametrized too. The model yields observable outputs such as the amount of desorbing species and reaction products, but also parameters which are harder to access experimentally, such as the activation energies and kinetic constants and concentrations of the different species in the layer. Comparison of the model results with experimental data should help provide deeper insight into the mechanism of catalytically activated ALD.

[1] Singh, Joseph A., et al. "Area-selective atomic layer deposition of metal oxides on noble metals through catalytic oxygen activation." Chemistry of Materials 30.3 (2018): 663-670.

Advanced Surface Engineering Division
Room Ballroom A - Session SE-ThP

Advanced Surface Engineering Poster Session

SE-ThP-1 Can a Nanoindenter be Used as a Hardness Spectrometer?*, **Esteban Broitman**,* SKF B.V. - Research & Technology Development, Netherlands

The precise knowledge of material microstructures is of vital importance to understand their mechanical and tribological performance. Standard microstructural characterization, carried out by optical and electron microscopy together with X-ray diffraction, is usually correlated to the hardness determined by Rockwell or Vickers indentation at macro- and microscale, and nanoindentation at nanoscale.

In the first part of the presentation, the background of a novel statistical nanoindentation technique to measure hardness and Young's modulus of materials is described [1]. We indicate how experiments are designed, and how the distribution of the hardness and modulus of elasticity determined from the nanoindentation observations are deconvoluted to generate hardness histograms that reflect unique characteristics (fingerprints) of each coating or bulk material. We show how the statistical deconvolution analyses gives an estimate of the microstructural constituents, their volume fraction and corresponding plastic and elastic properties at nanoscale. In the second part, numerous examples on different kind of coatings and bulk materials are presented to illustrate the usefulness of the novel technique.

We demonstrate that, by using nanoindentation as a novel tool for static nanomechanical spectrometric analysis of coatings and bulk materials, a fundamental understanding of the relation between local microstructure (phases and their size) and local material response during elastic and plastic deformation can be obtained.

[1] *"Microstructural Analysis of Bearing Steels by a Statistical Nanoindentation Technique,"* E. Broitman, M. Y. Sherif, B. Minov, U. Sachadel, Bearing World Journal 5 (2020) 47-54.

SE-ThP-2 Diagnosing Stress in Thin Films with High-Throughput Experimentation and Simulation-Based Methods*, **Matias Kalaswad**, A. Shrivastava, S. Desai, J. Custer, S. Addamane, M. Rodriguez, P. Kotula, M. D'Elia, H. Najm, R. Dingreville, B. Boyce, D. Adams,* Sandia National Laboratories

Stress in metal thin films is a critical aspect of fabrication processes, as excess residual stress can have a detrimental effect on the reliability, performance, and durability of devices. Although there are well-established methods to determine the amount of residual stresses in thin films, unraveling all sources of stress remains challenging due to the numerous factors involved in thin film deposition. Similarly, efforts to quantify relationships between film microstructure and stress remain challenging because of the multimodal nature of microstructural data. Here we seek to identify material "fingerprints" utilizing high-throughput characterization together with simulations to identify process-structure-property correlations related to the development of stress in metal thin films. Mo thin films were deposited onto oxidized Si wafers by magnetron sputtering over various Ar pressures and sputter powers. Traditional wafer curvature measurements were first performed to obtain average residual stress results consistent with those reported in the literature. An automated, high-throughput XRD process was then used to determine out-of-plane lattice spacings in agreement with the in-plane stress according to the Poisson effect. In-plane images of the film were collected through scanning electron microscopy (SEM) and atomic force microscopy (AFM) complemented by measurements of film resistivity. To supplement the experimental results and add to the multi-fidelity of information, simulations of metal transport were completed to estimate the deposition profile and rate as well as properties of the metallic flux during sputtering.The Monte Carlo code SIMTRA, simulating the transport of atoms from the source to the substrate during PVD, provides estimates of ion energy distributions and angular distributions of arriving species, and these characteristics were then applied to a phase-field model to produce the growth dynamics of microstructures resembling those acquired experimentally (verified by transmission electron microscopy). The synthetic and experimental information was ingested by machine learning models with architectures adept at identifying patterns in multimodal data streams. Initial attempts are made to identify meaningful process-structure-property relationships from the experimental and simulated data using a multimodal-based deep learning model. The deep learning model will be further analyzed to explore the dominant mechanisms that underlie the stress developed in metal thin films.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

SE-ThP-3 Significant Texture and Wear Resistance Improvement of TiN Coatings Using Pulsed DC Magnetron Sputtering*, **Nicholas Richter**, B. Yang, J. Barnard, T. Niu,* Purdue University*; Y. Zhang,* Los Alamos National Laboratory*; D. Shaw,* Advanced Energy Industries, Inc.*; H. Wang, X. Zhang,* Purdue University

Titanium nitride (TiN) coatings fabricated through reactive sputtering feature a suite of parameters capable of altering the microstructure and properties. Here, we explore the influence of using a bipolar pulsed direct current (DC) power supply in place of conventional DC when depositing TiN coatings, focusing on the influence of pulse frequency. The implementation of a pulsed DC voltage profile promotes a drastic texture change from randomly oriented to strongly TiN(111) across the full range of pulse frequencies. Additionally, higher pulse frequencies promote significant grain size reduction, which directly influences the resulting mechanical properties. Nanoindentation and nanoscratch testing were conducted and revealed a corresponding increase in hardness and wear resistance, respectively. The mechanism for this microstructural and texture change is also explored.

SE-ThP-4 Investigation of Laser Ablation Coating Removal (LACR) for Steel Surface Cleaning and Coating Adhesion*, **William Moffat**,* University of Virginia*; J. Provines, S. Sharp,* Virginia Transportation Research Council (VTRC)*; S. Agnew, J. Fitz-Gerald,* University of Virginia

Laser cleaning has recently received much attention for its ability to clean and prepare metallic surfaces for recoating and bonding operations such as welding, mold cleaning, surface texturing, paint removal, and for adhesive bonding. Laser ablation coating removal (LACR) is gaining acknowledgment as a potential replacement for the current method of grit blasting for surface cleaning and preparation in niche applications. In this work, the feasibility of using LACR to remove old coatings and corrosion products from carbon steel substrates to prepare surfaces for recoating is investigated. Carbon steel is common structural material used in infrastructure due to its reliable mechanical properties and low cost, but due to its tendency to corrode easily, it must be heavily coated and frequently inspected. Because of the harsh service conditions that low carbon steel components are often exposed to, coatings deteriorate and require removal followed by stringent surface preparation for recoating. Surface preparation is a key step in order to ensure that the newly reapplied coating will adhere and perform as expected over the entire service time of the coatings and meet industry standards. In order to test the effectiveness of laser cleaning for surface preparation, extensive adhesion testing of laser cleaned surfaces is needed to determine the feasibility of laser cleaning for steel surface preparation. To investigate the use of LACR to prepare surfaces, steel plates were subjected to laser ablation coating removal (LACR), induction coating removal (ICR), a combination of ICR and LACR, in addition to the incumbent cleaning method of grit blasting. The surfaces were then recoated using a typical three-layer coating system consisting of both organic (epoxy) and inorganic (silica based) zinc rich primers. Pull-off adhesion testing in addition to detailed surface analysis using scanning electron microscopy (SEM) and profilometry show that despite a lower average roughness on the LACR surfaces (avg. Ra 4 µm), the adhesion is equivalent to that of the grit blasted steel (avg. Ra 12.3 µm). In addition, complementary chemical analysis was performed using both energy dispersive spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS) on the cleaned surfaces. These results show that LACR is a valid candidate that rivals the incumbent method of grit blasting in terms of safety, cleanliness, and environmental sustainability, for both surface cleaning and preparation.

SE-ThP-5 Study of the Corrosion Resistance and Adhesion of DLC with a CrC/CrCN/Cr Bonding Multilayer Deposited by HIPIMS on AISI 4317 Steel*, **Martin Flores**, L. Flores,* Universidad de Guadalajara, Mexico*; J. Aguilar, A. Gonzalez,* Universidad Autonoma de Tamaulipas, Mexico

Diamond-like carbon (DLC) coatings are utilized in a wide range of applications to reduce the sliding friction, wear and corrosion resistance of components. AISI 4317 steel is used in machinery bearings for the transport of minerals with sulfur content in port facilities. These bearings suffer from wear and corrosion promoted by sulfide and chloride ions. On many substrates, DLC has limited adhesion, so it is necessary to develop interfaces and bonding layers to overcome this limitation. One way to increase adhesion and reduce corrosion is by metal ion etching using the HIPIMS technique and gradual bond layers.The metal ion etching was performed with a delay in the synchronized polarization pulse of the substrate with respect to the applied to the Cr target. This work reports the results of the potentiodynamic polarization and Daimler-Benz Rockwell C test methods used to evaluate corrosion and adhesion respectively. Synthetic seawater and seawater plus dilute sulfuric acid were used as electrolytes. Raman spectroscopy was used to study the sp2 and sp3 content of the DLC layer. SEM was used to observe the cross section and corroded surface of coated and uncoated samples of AISI 4317 steel. The structure of the bonding multilayer was studied by XRD. The results show an improvement in the corrosion resistance of the samples coated with the multilayer, the correlation between the adhesion and corrosion tests is analyzed.

Plasma Science and Technology Division
Room 315 - Session PS2+SE-FrM

Plasma Sources, Diagnostics, Sensors and Control

Moderator: Nathan Marchack, IBM T.J. Watson Research Center

8:20am **PS2+SE-FrM-1 Optical and Electrical Diagnostics of Industrial Plasma Reactors: Measuring the Relevant Physical Quantities to Assist Process Development***, **Gilles Cunge**,* LTM/CNRS-UJF, France*; S. Younesni,* STMicroelectronics/CNRS-LTM France*; N. Loubet, M. Kogelschatz, E. Pargon, C. Petit-Etienne, O. Joubert, E. Despiau-Pujo, N. Sadeghi,* CNRS-LTM, Université Grenoble Alpes, France **INVITED**

As new devices with 3D architectures and new materials are introduced in the microelectronic industry, plasma etching processes are more and more challenged. The necessity to pattern nanometer size features (with high aspect ratio) with an ultrahigh selectivity towards underlayers has pushed the development of new plasma processes with advanced RF power and/or gas injection pulsing schemes. The goal is either to achieve atomic layer etching processes or simply to overcome typical plasma limitations (charging effects, ARDE…etc). However, since the number of different processes possible in a reactor increases rapidly with each new control knob, the development of innovative processes is becoming extremely difficult with empirical approaches (i.e. DOE). It is thus mandatory to get a deep understanding of the impact of knew control knobs on the plasma properties to develop such new processes efficiently, which can only be achieved by using plasma and surface diagnostics. In this paper, we will review plasma diagnostics that are the best adapted to get a clear picture of the impact of the reactor control knobs on the process performances. Plasma diagnostics are separated in two categories: 1) those used to detect radicals (etchants or etch products) with a time resolution of about 1 ms, i.e. modulated beam mass spectrometry as well as spectroscopic techniques such as optical emission spectroscopy, absorption spectroscopy (from the VUV to near IR range) and Laser induced fluorescence. 2) techniques used to measure the charged species with a µs time resolution: specific Langmuir probe for the ion flux measurements in aggressive environment, RFEA for ion energy distribution function and mass spectrometry/RFEA to analyses the ion nature. We will show that it is important to couple plasma diagnostics with surface analysis (e.g. XPS, Raman…etc) to get a clear picture of the mechanisms involved in new processes and illustrate this point with several concrete processes developments in industrial reactors (ranging from pulsed ICP plasmas to downstream processes).

9:00am **PS2+SE-FrM-3 Hole Transport Properties of Nickel Oxide Films Grown via Hollow-Cathode Plasma-Assisted Atomic Layer Deposition***, S. Ilhom, A. Mohammad, M. Niemiec, D. Zacharzewski, P. Chardavoyne, S. Abdari, **Necmi Biyikli**,* University of Connecticut

In contrast to the relative abundance of as-grown unintentionally doped n-type semiconductor materials, there are only a few alternative alloys showing p-type conduction without needing extra high-temperature doping processes. NiO is of particular interest mainly due to its stability and promising performance as hole-transport layers in emerging solar cell device structures. However, to broaden the NiO application domain towards potential back-end-of-the-line (BEOL) transistor devices as potential p-type channel layers, the transport properties of NiO needs to be improved significantly. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in p-type NiO films with atomic-level precision and large-area uniformity, the hole mobility is far from being sufficient, typically lower than 1 cm^2/Vs.

In this study we have carried out a systematic study on plasma-enhanced ALD (PEALD) of NiO films on Si and glass substrates using nickelocene ($NiCp_2$) and O_2/Ar plasma mixture using hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD). Detailed saturation studies using in-situ ellipsometer monitoring were carried out in the HCP-ALD reactor, scanning for $NiCp_2$ pulse time, O_2 plasma exposure time, purge time, and plasma power. Optimal growth conditions were identified as 90 ms $NiCp_2$ pulse / 5 s purge / 10 s O_2-plasma at 100 W plasma exposure / 5 s purge. 800 cycle runs were conducted to evaluate the substrate temperature impact (100 - 250 °C) on growth-per-cycle (GPC) and film properties.

The resulting p-type NiO films are characterized for their structural, optical, and electrical properties. Films grown at optimal conditions (200 °C) exhibit refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on both Si and glass substrates exhibit polycrystalline single-phase cubic structure (*c*-NiO). In order to determine the carrier type and extract field-effect mobility values, we have fabricated vertical NiO/n-Si p-n junction diodes as well as NiO/Al_2O_3/Si thin-film-transistor (TFT) device prototypes to characterize diode I-V behavior and confirm p-type layer structure for NiO, and extract the field-effect carrier mobility, respectively. Our I-V measurement results confirmed p-n junction diode characteristics with decent ON/OFF ratios for forward and reverse diode current values. TFT characterization results as well as detailed temperature-dependent Hall measurements will be used to identify critical hole transport parameters.

9:20am **PS2+SE-FrM-4 In-Situ Measurement of Electron Emission Yield at Silicon Surfaces in Ar/CF4 Plasmas***, **Mark Sobolewski**,* NIST

Plasma simulations require accurate data for the ion-induced electron emission yield at plasma-exposed surfaces. For industrially relevant plasmas, however, direct measurement of yields using ion beams is impractical. In contrast, measurements made in situ, during plasma exposure, provide useful values for the total or effective yield produced by all incident ions. Here, in-situ measurements were performed in an icp system in Ar/CF4 mixtures at 1.3 Pa. The current and voltage across the sheath adjacent to the rf-biased substrate electrode were measured, along with Langmuir probe measurements of ion current density and electron temperature. The measurements are input into a numerical sheath model, which allows the emitted electron current to be distinguished from other currents. The effective yield was determined for thermally oxidized, in-situ etched, and sputter-cleaned silicon surfaces. For thermal oxides in pure Ar, yields agreed with previous measurements [1] on sputtered oxides. By combining measurements made for several mixtures with mass spectrometer data for the relative flux of each ionic species, estimates or bounds were obtained for the individual electron emission yields of the most prevalent ions. [1] M. A. Sobolewski, Plasma Sources Sci. Technol. 30 025004 (2021).

9:40am **PS2+SE-FrM-5 Plasma Characterization: Radical Recombination Sensor Based on Dual Probe Thermopile Heat Flux Sensors***, **Johannes Velthuis**,* TNO Science and Industry, the Netherlands

Hydrogen radicals play an important role in e.g. the cleaning of EUV reflective mirrors. Therefore there is the need to quantify the surface radical flux in the various (plasma) setups where these effects are studied. In this paper a catalytic radical sensor is presented, based on the measurement of the recombination heat of radicals on a surface, using dual probe thermopile Heat Flux Sensors (HFS). The first HFS1 has a high recombination (probability) coefficient coating, e.g. Pt. The second HFS2 has a low recombination coefficient coating, e.g. Al2O3. Signal subtraction largely eliminates common mode heat losses/gains such as conduction/convection and IR-radiation, the net result representing the radical recombination heat. The signal can be improved by switching the radical source on/off at regular intervals. Radical recombination rates where measured in a remote microwave (MW) plasma chamber (38 Pa H2) over the range 1E18−1E21 atH/(m2s), with nearly linear response as function of plasma power setting. The sensor full scale limit is ~1E23 atH/(m2s) and is dictated by the maximum allowable sensor surface temperature (<250oC).

10:00am **PS2+SE-FrM-6 Dielectric Toroidal Plasma Sources for Improved Plasma Resistance***, **Ilya Pokidov**,* MKS Instruments

A new sintered alumina toroidal plasma source has been developed that overcomes the limitations that a quartz or hard anodized coated aluminum alloy applicator have. This alumina ceramic applicator is implemented in R*evolution® toroidal remote plasma source (RPS) chassis replacing the quartz, which predominantly is used in photoresist strip by oxygen plasma. The toroidal body is made of 99.5% pure alumina, more resistant than quartz to harsh plasma chemistries, such as H, F and Cl. It can withstand higher ignition and operating voltages, allowing to ignite plasma directly in process gas. Ceramic alumina is a very pure material. Impurities are below 0.5% versus the hard anodized coating typically grown from the base 6061 alloy with impurity content of up to 4.2%. The ceramic extends the principal limitation of quartz in handling halogen and hydrogen plasmas.

The torus is fabricated by first machining two identical halves in green state and then co-firing them together to form a high strength hermetic bond. Afterwards, the alumina torus' exterior surface is surrounded by a potting compound with high thermal conductivity and low elastic modulus and encapsulated inside a copper cooling jacket to minimize thermo-mechanical stress on the ceramic.

Tests of the alumina ceramic applicator indicate that it can safely operate up to 6kW, full range of R*evolution RPS power without fracturing. Plasma successfully ignited in process gases such as O_2/N_2, H_2, and N_2/H_2 with healthy operating windows. The alumina applicator underwent a 1000-hour life test in forming gas plasma without significant signs of surface erosion. Similar construction methodology is applicable to sapphire. However, a prototype sapphire torus has shown a lower operating power range than the alumina torus.

The paper will present the design methodology to address key technical challenges in the development of a dielectric toroidal applicator for a transformer coupled remote plasma source. Test data will also be presented to demonstrate operating windows and radical output capabilities of the ceramic toroidal remote plasma source in different gas chemistries.

10:20am **PS2+SE-FrM-7 What We Still Won't Know About Plasmas in Simple Diatomic Gases- or Using a DC Glow Discharge in Pure O_2 as an Ideal Test-Bed for Experimental Validation of Models***, **Jean-Paul Booth***[1]*,* LPP-CNRS, France **INVITED**

Despite many decades of study, models of discharges in molecular gases still lack accurate data on many key collisional processes, even for such “simple” and ubiquitous gases as O_2. Good data is lacking for near-threshold electron-impact dissociation with neutral products, the role of metastables; of gas heating, vibrational excitation and energy transfer processes; as well as surface recombination and thermal accommodation. Direct measurement of the rate constants of individual processes is a fastidious process, where it is even possible. As an alternative approach, we compare comprehensive measurements of internal plasma parameters to simulations for a plasma with relatively simple chemistry, namely a DC positive column discharge in pure O_2. This well-characterized, stable and uniform discharge is optimal for experiment-model comparison. Although this system has been studied for a many decades, new experimental methods, including synchrotron Vacuum ultraviolet absorption spectroscopy and laser cavity ringdown absorption spectroscopy (CRDS), allow the densities of all the major species (atomic, molecular, in ground and excited states) to be measured, with much-improved absolute accuracy, and with time resolution. The gas translational temperature, and vibrational energy distribution, were also probed. Applied to (partially- and fully-) modulated discharges, these measurements provide unprecedented insight into the kinetic processes occurring, and a profound test of the models. Whereas models can be quite easily adjusted to fit steady state measurements at one given set of operating conditions, trends with pressure and discharge current, and especially the temporal response to current modulation, are much harder to reconcile. In practice, model failures can often be attributed to simple omission of key processes, or to the neglect of their temperature-dependence. If the chemistry studied is simple enough, and the measurements cover all of the principal species (stable molecules in their ground and metastable states, atoms and negative ions) as well as the gas temperature, it becomes possible to identify the missing reactions, and even estimate their rates and activation energies, by adjusting their values in the model to fit the observations. As examples, we have demonstrated that the kinetics of metastable O_2 b molecules cannot be modelled without the inclusion of quenching by oxygen atoms with a significant activation energy. We have also demonstrated the production of ozone by the reaction of O_2 molecules with oxygen atoms chemisorbed on the glass discharge tube walls.

11:00am **PS2+SE-FrM-9 Voltage and Sheath Dynamics in Electropositive Capacitively Coupled Plasmas with Focus Ring and External Circuit***, **Yuhua Xiao**, J. Brandon, J. Morsell,* NCSU*; S. Nam, J. Lee,* Samsung Electronics Co., Inc., Republic of Korea*; S. Shannon,* NCSU

Capacitively coupled plasmas (CCPs) are widely used in semiconductor processes. The control of plasma to obtain uniform deposition and etching over a large process space is still an open problem, particularly within a few millimeters of the substrate edge. Complex material stacks commonly referred to as focus rings (FR) or process kits are placed at the wafer edge to balance process non-uniformities and provide uniform process to the edge of the substrate. This solution has limitations with regard to process window and eventual material erosion.One promising approach is to combine a focus ring assembly with a tunable external circuit (EC) ground path termination to extend the plasma uniformity to the wafer edge over a wider process space. The effect of FR combined with EC for fine adjustment and minimization of edge process area are presented here. In this work, a simplified FR with EC structure consisting of a variable capacitor and an inductor is adopted to change the impedance between electrodes and the ground, and the sheath voltage distributions and width are modified. Experimental results are measured using hairpin probe, high-voltage RF and DC probes, in-line RF metrology at the powered electrode, and intensified CCD camera imaging of the electrode edge and FR region. The results are further compared to simulations, which use an equivalent circuit model to simulate the effect of this structure on sheath properties. Results show that the FR with EC structure can partially control the DC self-bias and distribute the voltage and the energy loss among different sheaths associated with different electrodes. The EC can affect the sheath dynamics and equipotential lines of the center and near the wafer edge prominently. These results point to possible source design based pathways for engineering the distribution of power dissipation across these sheaths in industrial plasma reactors to improve process performance at the electrode edge.

11:20am **PS2+SE-FrM-10 Time Resolved Diagnostics of a Silver HiPIMS Discharge***, **Zachary Jeckell**, D. Barlaz, R. Ganesan, D. Kapelyan, K. Martin,* University of Illinois at Urbana Champaign*; W. Huber, B. Jurczyk,* Starfire Industries LLC*; D. Ruzic,* University of Illinois at Urbana Champaign

This work aims to investigate the temporal evolution of a high-power impulse magnetron sputtering (HiPIMS), with a positive cathode reversal, discharge by using the Hiden ANALYTICAL PSM probe, that can measure the ion energies as well as perform charge to mass (q/m) measurements. This allows for time resolved differentiation between the working gas and the sputtered material, which in this case is silver, and enables the quantification of the population of ions at higher charge states. Q/m differentiation allows for the construction of Ag^+/Ar^+, which when combined with previous IEDF measurements can help tailor future depositions to maximize the flux of silver ions. Our previous work studying the time evolution of the IEDF showed the peak energy of the distribution shifts to the set positive pulse voltage within 3 us regardless of conditions, and that there is a clear difference in the distribution during the first 20 us of the cathode reversal and the end of the cathode reversal, which we attributed to a higher presence of metal ions that are ionized in flight. This work would aim to verify this claim as well as quantify the population of silver in higher charge states. Investigating the population of Ag^{2+}, and other higher level charge states, is of interest because it is believed to lead to film damage for cases of large positive pulse biases, as the energy of the ions will likely be in the etching regime on the HiPIMS structural zone diagram. Multi-ionization results will be compared with fast camera measurements to see if the population of higher order charged states are correlated to the presence of hot spots. The fast camera measurements are taken using the PI-MAX 4 camera with a selected gate width of 100 ns. Additionally, the ionization fraction of silver can be found and the correlation between measured ionization fraction and the deposition rate measured with a quartz crystal microbalance (QCM) can help to determine the fraction of ions that return to the target and self-sputter as well as the fraction of ions that are transported to the substrate.

11:40am **PS2+SE-FrM-11 Title: Curling Probe Analysis for Practical Measurement of Electron Density***, **Daisuke Ogawa**, K. Nakamura, H. Sugai,* Chubu University, Japan

Optical monitoring is a powerful diagnostic tool for plasma processing, but it should be reminded that optical emission from plasma is still secondary information.As learned from a plasma textbook, photon emission results from many electron relaxations of excited species.Behind the relaxation processes, electrons play a role in transferring their energy to create the excited species. The reaction rate of such reactive species strongly depends on electron density and temperature.Therefore, electron monitoring can be a powerful processing diagnostic even in a practical plasma because electron information can be utilized to know radiative and non-radiative species.Aiming for practical use of electron diagnostic, we have developed a curling probe, one of the diagnostics for finding electron density in plasma with a microwave-range electrical resonance.Plasma has a smaller dielectric constant than vacuum, making resonant frequency smaller. The degree of the frequency shift indicates electron density in plasma. The curling probe utilizes the measurement principle, and in particular, the probe utilizes a slot antenna to obtain the resonance.Due to the regulation of the probe space, the antenna is spiral-shaped and configured in a plane.So, the antenna configuration has some unique characteristics, which are not found in other microwave resonating probes, such as a hairpin probe. One of the unique characteristics of the probe is that the probe has a directionality of electron density measurement.We currently consider that the probe enables us to include the probe into an electrode.This

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[1] **2019 PSTD Plasma Prize Winner**

configuration is possibly applied to a narrow-gaped capacitively coupled plasma. Our former work showed that the probe is getting ready for practical use because the probe operates under film depositing situations (Ogawa et al., PSST 30 (2021) 085009) with high pressure (<1000Pa). However, the probe still needs to be improved because we have noticed that the probe temperature affects the degree of the resonant frequency shift.We recently measured and analyzed the probe temperature and degree of resonant frequency shift, and found that the resonant frequency shift has a regularity in temperature. The regularity successfully enabled us to calibrate the probe measurement and showed that the probe is ready to utilize temperature-varying situations.This presentation will show our recent progress in electron density measurement with a curing probe under the temperature-varying situation.This presentation will provide an opportunity to discuss how to apply the probe to an industry reactor.

Advanced Surface Engineering Division
Room 317 - Session SE+MN+PS-FrM

Nanostructured and Multifunctional Thin Films and Coatings II

Moderators: Jyh-Wei Lee, Ming Chi University of Technology, Taiwan , **Filippo Mangolini**, The University of Texas at Austin

8:20am **SE+MN+PS-FrM-1 New Challenges and Opportunities for Hard and Superhard Coatings*, Aharon Inspektor,*** Carnegie Mellon University**INVITED**

Many hard, superhard and lubricious coatings with superior mechanical properties, thermal stability and chemical resistance are being developed and applied for surface protection in harsh and demanding applications. In this paper we will discuss the status and foreseen trends in PVD hard, superhard and lubricious films.

First, we will review the design of current multifunctional hard coatings and their applications in metal cutting, in automotive and in aerospace industries. Next, we will examine how the Forth Industrial Revolution, a multi-level connectivity of sensors and systems, with “Smart Manufacturing”, computer controlled automated facility system, will affect future usage of multifunctional coatings. The talk will conclude with a critical discussion of the resultant challenges and opportunities for next generation of hard, superhard and lubricious coatings.

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