Advanced Surface Engineering Division
Room C123 - Session SE1+TF-MoM

Advanced Multi-Functional Thin Film Materials

Moderator: Suneel Kumar Kodambaka, Virginia Tech

8:20am **SE1+TF-MoM-1 AVS John A. Thornton Memorial Award Talk: Low Temperature Thin Film Growth Using Metal-ion/Surface Interactions*, Lars Hultman*[1]**, *G. Greczynski,* Linköping University, Sweden*; I. Petrov,* University of Illinois, Urbana-Champaign **INVITED**

Ion irradiation is a key tool for controlling epitaxy-to-nanostructure, phase content, and properties of refractory ceramic thin films grown by magnetron sputtering, as described in extended Thornton's structure-zone diagrams. Until recently, film growth relied on enhancing adatom mobility by inert and/or reactive gas ion irradiation to obtain dense layers at low deposition temperatures. The development of high-power pulsed magnetron sputtering (HiPIMS), which provides metal-ion plasmas with tunable degree of ionization, enabled systematic studies of the effects of metal-ion irradiation on refractory ceramic thin films. Metal ions are film constituents, hence they provide the benefits of ion-mixing without causing the high compressive stresses associated with trapping of gas ions.

This presentation reviews our growth experiments of pseudobinary TM nitride model systems including TiAlN, TiSiN, VAlN, TiTaN, TiAlTaN, and TiAlWN [1] carried out in a hybrid configuration with one target powered by HiPIMS, and the other operated in direct current magnetron sputtering (DCMS) mode. [2] A substrate bias potential Vs is synchronized with the metal-ion-rich portion of the HiPIMS pulses to allow for a control of metal-ion energy. Essential input is provided by time-resolved mass spectrometry analyses performed at the substrate position, which reveals the temporal evolution of metal- and gas-ion fluxes. This enables us to suppress the role of gas ion irradiation and study the influence of intense $M_1(^{n+})$ and $M^{(n+)}{}_2$ metal-ion fluxes (*n* = 1, 2) on film growth kinetics over a wide range of M_1M_2N alloy compositions.

The effects of metal-ion irradiation depend on the mass of incident ion with respect to that of film constituents. Irradiation with lower-mass metal-ions (Al^+ or Si^+) results in near-surface trapping with the depth determined by Vs amplitude. This enables growth of NaCl-structure Me1Me2N solid solutions far above the Me1N concentration range achieved with DCMS.[3] At the other extreme, bombardment of the growing film surface with pulsed high-mass metal ion fluxes (W+ or Ta+) during hybrid HiPIMS/DCMS high-rate deposition of dilute $Ti_{1-x}Ta_xN$, $Ti_{1-x-y}Al_xTa_yN$, and $Ti_{1-x-y}Al_xW_yN$ alloys provides fully-dense/low-stress films without intentional substrate heating (temperature ≤130 oC). The high metal-ion mass irradiation leads to low-energy recoil generation that provide sufficient adatom mobility, necessary to obtain high-quality fully-dense films, in the absence of resistive heating. Such energy-efficient PVD contributes to a sustainable development.

For cubic-TiAlWN, we recently discovered that Guinier-Preston (GP) zone hardening- known from soft light-metal alloys - can operate also in refractory ceramics. [4] The present GP hardening at 1000 °C is by the formation of atomic-plane-thick W islands populating {111} planes.

[1] G. Greczynski, I. Petrov, J.E. Greene, L. Hultman, J. Vac. Sci. Technol. A 37 (2019) 060801

[2] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, L. Hultman, Surf. Coat. Technol. 206 (2012) 4202

[3] G. Greczynski, S. Mráz, J.M. Schneider, L. Hultman, J. Appl. Phys. 127 (2020) 180901

[4] O.Pshyk, X.Li, I.Petrov, D.G.Sangiovanni, J.Palisaitis, L.Hultman, G.Greczynski (Submitted 2023)

9:00am **SE1+TF-MoM-3 Multi-Component Materials – Bonding, Disorder and Possibilities*, Erik Lewin,*** Uppsala University, Sweden **INVITED**

Multi-component, often referred to as high-entropy, materials have received a large amount of attention during the past two decades. There are several reasons for this, including applicable properties and the fundamental design aspects connected to the large compositional space available, as well as the so-called core effects. The first research in the field was concerned with bulk alloys, but the concept has been expanded to compounds of metals and p-elements, e.g. nitrides, carbides, oxides, borides. Today, much of the research is on coating materials. In the field of coating research, popular properties and potential applications include hard materials, diffusion barriers, as well as corrosion or radiation resistant coatings.

This presentation will focus on solid solution phases with simple crystal structures where at least five different metallic elements share a crystalline sub-lattice. Recent results on the chemical bonding in multi-component alloy, nitride, and carbide coatings based on the early transition metals Ti, V, Zr, Nb and Hf will be presented. These results are based on the combination of *ab-initio* DFT simulations and electron spectroscopy using, both in-house XPS and synchrotron-based methods, and show that there is a charge transfer between the different metal atoms in a multi-component alloy, and that this effects the size of the atoms. Similar effects are also observed in corresponding nitrides and carbides, despite that all metal atoms have a first coordination of nitrogen or carbon. The results illustrate that chemical bonding matters, and that to fully understand and exploit the possibilities of multi-component materials this need to be considered. The results also show that the variation in local chemical environment effect the local electronic structure, giving rise to a range of chemically different sites.

This leads to a forward looking discussion on the fundamental understanding of the multi-component materials, and the possibilities that may arise from understanding and designing the chemical bonding (charge transfer) in multi-component materials.This will include the both the array of different chemical sites, as well as the intriguing combination of order (the crystalline lattice) and disorder, in the form of unordered occupation of the lattice points by different metals, as well as displacive disorder where the atoms are not on the lattice points (commonly called lattice distortion).

9:40am **SE1+TF-MoM-5 High-k Gate Dielectrics for InAlN and ScAlN Barrier GaN HEMT Structures*, Neeraj Nepal,*** *B. Downey, M. Hardy, D. Meyer, V. Wheeler,* U.S. Naval Research Laboratory

InAlN and ScAlN-barrier GaN high electron mobility transistors (HEMTs) have shown the ability to generate larger two dimensional electron gas (2DEG) densities for a given barrier thickness, leading to improved frequency and power performance in these devices [1-2]. However, HEMT devices utilizing these thin barriers often suffer from higher leakage current [2,3] and premature electric field breakdown, requiring the integration of gate dielectrics in order to realize the full potential of novel InAlN and ScAlN-barrier HEMTs by reducing leakage current, maintaining high electric field breakdown, and mitigating dc-RF dispersion.

In this talk, we report growth optimization and electrical properties of atomic layer deposition (ALD) grown TiO_2 gate dielectric on InAlN and ScAlN HEMTs structures. ALD process windows were initially monitored and optimized on Si substrates using *in-situ* ellipsometry. Films were deposited using tetrakis(dimethylamino)titanium (TDMAT) at 75 ^oC and an Ar/O_2 plasma at 300 W. Optimization of TiO2 films was done by varying the typical growth parameters, such as TDMAT pulse duration and growth temperature, as well as the plasma gas chemistry.Optimum films were then deposited and characterized on HEMT structures to determine electrical performance for device applications.

Atomic force microscopy on HEMT structures measured before and after ALD deposition showed minimal change in roughness as a result of the conformal TiO_2 deposition.Contactless resistivity measurements performed before and after ALD showed negligible change, indicating that no plasma induced damage was occurring during ALD gate deposition. Vertical current-voltage and capacitance-voltage measurements were made on a Schottky-contacted HEMT structure and compared to devices with TiO_2 gate dielectrics deposited at different temperatures to discern the full electrical impact of the ALD process. As an example, an extracted dielectric constant of TiO_2 layer deposited on ScAlN surface at 200°C with O_2 flow of 20 sccm was 50 with no significant change in 2DEG density ($2.6\text{-}2.7\times10^{13}$ cm^{-2}). Using only a 7 nm gate TiO_2 film, the off-state gate leakage in InAlN/GaN HEMTs was reduced by ~10^4 compared to a Schottky gate. Additional electrical HEMT characterization and the band alignment of an optimum ALD TiO_2 on ScAlN structure will be discussed to show the full potential of these films in novel structures.

References:

1. Li et al., *IEEE Electron Device Lett.* 41, 689 (2020).
2. Hardy et al., *Appl. Phys. Lett.***110**, 162104 (2017).
3. Green *et al.*, *IEEE Electron Device Lett.***40**, 1056 (2019).

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[1] **John A. Thornton Memorial Award Winner**

10:00am **SE1+TF-MoM-6 Molecular Layer Deposition for Alumina Gas Separation Membranes***, **Lucie Badouric**, C. Charmette, J. Cartier, M. Drobek, A. Julbe, M. Bechelany,* University of Montpellier, France

Making hydrogen a reliable energy vector in future decades requires the implementation of complex technologies related namely to its production, storage or transport. Intensive research is also underway to optimize its use by increasing its purity and to ensure the safety of hydrogen facilities.

Techniques such as cryogenic distillation, pressure swing adsorption (PSA) or membrane processes can be used to purify hydrogen. Both cryogenic distillation and PSA are used at commercial scale although these techniques are energy intensive. In comparison, membrane processes appear as a promising technology to separate H_2 from gas mixtures, by consuming less energy and operating in a continuous way. They can be either dense or porous, and made of polymers, metals, carbon, ceramics, hybrids or composite materials. Different gas transport and separation mechanisms are involved depending on the type of membrane. In microporous membranes (pore sizes < 2 nm) the separation of gas molecules might occur by molecular sieving, difference in diffusivity and/or competitive adsorption. Molecular sieving is an efficient thermally activated separation mechanism, particularly attractive for gas mixtures with different kinetic diameters. A good compromise between selectivity and permeability values can be reached with pore sizes smaller than the kinetic diameters of the molecules to be retained.

This work is dedicated to the development of a new type of alumina microporous membrane using the Molecular Layer Deposition (MLD) technique. As Atomic Layer Deposition (ALD), MLD allows to synthesize hybrid organic-inorganic materials by conformal coatings on various substrates using both organic and inorganic precursors. We developed a MLD process able to coat uniformly the pores (size~ 5-8 nm) of an alumina tubular support with alucone (aluminum alkoxide). Then, the film was calcined to transform the organic layer into a microporous alumina frame. Maximum pore sizes around 0.3 nm are targeted to obtain a molecular sieve membrane able to extract H_2 from mixtures with larger gas.

The MLD parameters have been optimized to obtain homogenous layers. Then, we investigated the influence of post-synthesis parameters to improve the membrane selectivity and permeability, as well as its stability. Single gas permeance measurements with He (H_2 simulant) and N_2 were used to validate the membrane quality and molecular sieving performance before testing them with gas mixtures under various working conditions (e.g., temperature, transmembrane pressure).

This project was partially supported by the French national research agency (ANR, program ALD4MEM-ANR-20-CE09-0008-01) and the Occitanie Region (React-Eu Défi clé Hydrogène Vert).

Advanced Surface Engineering Division
Room C123 - Session SE2+TF-MoM

Surface Engineering by Deposition of Protective Coatings

Moderator: Suneel Kumar Kodambaka, Virginia Tech

10:40am **SE2+TF-MoM-8 Advanced Surface Engineering Coating Technologies for Automotive Applications***, **Jianliang Lin**,* Southwest Research Institute, San Antonio Texas **INVITED**

The pursuit of the automotive industry for more efficient engines to reduce fuel consumption and improve fuel economy continues. One means is to reduce the coefficient of friction (COF) of critical moving parts in engines, e.g. piston rings and camshafts using advanced surface engineering coating technologies. The presentation presents an overview of a series of efforts in the development of advanced low friction nanocomposite coatings, diamond like carbon (DLC) based coatings, and their hybrid for automotive applications. The coatings were designed and deposited using different surface engineering coating technologies, including plasma enhanced magnetron sputtering (PEMS), plasma immersion ion deposition (PIID), and high power impulse magnetron sputtering (HiPIMS). The chemistry and structure of the coatings were tailored to achieve a multi-functionality of good adhesion, low friction, low wear rate, and sufficient thickness. The coatings were iteratively optimized for its tribological performance in a series of tests including pin-on-disc test, Plint TE77 test, and block-on-ring test in engine lubricants (e.g. 10W-30) to narrow down the selection of the coatings. The nanocomposite coating showed superior performance in engine lubricants due to its unique structure and surface characteristics. Sets of piston rings were tested in a heavy-duty diesel engine to determine their wear and reliability. Finally, a full set of coated rings was tested robotically in a 4-cylinder gasoline engine on a commercial vehicle using the EPA standard method to determine the fuel economy in city driving and high way driving. This coating technology has been demonstrated to reduce COF and wear between piston rings and cylinder liners, and improve engine fuel economy. Other technical examples of tailoring the nanocomposite coating technology for improving performance of other moving parts in an IC engine (e.g., camshaft and tappets, etc) and applications in auto racing will also be presented.

11:20am **SE2+TF-MoM-10 Thin Film Materials Design & Some Thoughts on Complexity and Sustainability***, **Jochen M. Schneider**,* Materials Chemistry RWTH Aachen University, Germany **INVITED**

Designing the next generation of thermally stable thin films without utilizing trial and error-based methodologies requires truly predictive computational approaches. Important design criteria for protective thin film materials are, besides phase formation, mechanical behavior as well as thermal stability. Examples of predictions thereof showcasing so-called MAB phases [1], transition metal nitrides [2], and transition metal aluminum nitrides [3] which are chemically modified will be presented. Furthermore, the generation of point defects in transition metal aluminum nitrides by ion bombardment is predicted [4,5]. All aforementioned predictions are critically appraised by experimental data. Implications for future design efforts will be discussed also in the context of (chemical and structural) complexity as well as sustainability.

Plasma Science and Technology Division
Room A106 - Session PS+SE-MoA

Plasma Sources, Diagnostics, Sensors and Control

Moderators: Michael Gordon, University of California at Santa Barbara, **Yohei Ishii**, Hitachi High Technologies America Inc.

1:40pm **PS+SE-MoA-1 On the Influence of the Target Material on the Discharge Properties of the High Power Impulse Magnetron Sputtering Discharge***, **Jon Tomas Gudmundsson**, K. Barynova,* University of Iceland*; M. Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany*; J. Fischer,* Linköping University, Sweden*; S. Suresh Babu,* University of Iceland*; M. Raadu, N. Brenning,* KTH Royal Institute of Technology, Sweden*; D. Lundin,* Linköping University, Sweden

High power impulse magnetron sputtering (HiPIMS) operation results in increased ionization of the sputtered species and lower deposition rate than the dc magnetron sputtering discharge, when operated at the same average power. We have applied the ionization region model (IRM) [1] to model HiPIMS discharges in argon with a number of different targets [2,3], to study various processes, such as working gas rarefaction and refill processes, the electron heating mechanisms, ionization probability and back-attraction of the sputtered species, and recycling mechanisms. The HiPIMS discharge can contain a large fraction of ionized sputtered material and often a significant fraction, of the ions involved in the sputter process are ions of the target material. This also implies that a large fraction of the ions of the sputtered species can be attracted back to the target and are not deposited on the substrate to form a film or coating. Self-sputtering and the self-sputter yield are therefore expected to play a significant role in HiPIMS operation, and have a decisive impact on the film deposition rate, at least for metal targets. We explore the relationship between the self-sputter yield and deposition rate as well as the ionization and back attraction probabilities. The back-attraction probability appears to decrease with increased self-sputter yield. The various contributions to working gas rarefaction including electron impact ionization, kick-out by the sputtered species, and diffusion, are evaluated and compared for the different target materials, over a range of discharge current densities. For all cases the working gas rarefaction is found to be significant, and to be caused by several processes, and that their relative importance varies between different target materials. In the case of a graphite target, electron impact ionization is the dominating contributor to the working gas rarefaction, with 55 - 64 % contribution, while the kick-out, or sputter wind, has negligible influence, whereas in the case of tungsten target, the kick-out dominates, with 39 - 48 % contribution. The relative role of kick-out by the sputtered species increases and the relative role of electron impact ionization decreases with increased mass of the target atoms.

[1] Huo et al., Journal of Physics D: Applied Physics 50, 354003 (2017)

[2] Gudmundsson et al., Surface and Coatings Technology 442, 128189 (2022).

[3] Babu et al., Plasma Sources Science and Technology 31, 065009 (2022)

2:00pm **PS+SE-MoA-2 Numerical Analysis of Curling Probe Designing for an Effective Electron Density Measurement in Plasma***, **Daisuke Ogawa**, S. Kato, H. Sugai, K. Nakamura,* Chubu University, Japan

Electrons make a main contribution to generating reactive species in a low-temperature plasma. Optical emission is often utilized to monitor plasma, but it should be noted that the ultimate origin of the emission is due to collisions with the electrons in the plasma. This means that electron monitoring could be the primary information of the plasma. A curling probe is one of the probes that enable an electron density measurement in the plasma. The probe measures the density derived from a shift of the fundamental resonant frequency that the probe holds. Therefore, the probe measures the density even in an environment where the plasma makes a dielectric film deposition. The probe utilizes a slot antenna to make the electromagnetic resonance, which is equipped on the top surface of the probe. This antenna structure gives an advantage in directional electron density measurement. This directionality is useful, particularly when the probe desires to be embedded into a wall and/or an electrode. Recently, we have also developed a technique with the curling probe that enables one to make in-situ measurements of electron density in plasma and the film thickness deposited on the probe surface. The technique requires two different-sized curling probes, so we named it the double curling probe method. This technique is potentially powerful in a plasma-processing reactor with electron density monitoring. However, we noticed that the technique requires further improvement in their measurement resolution; the frequency shift is not always noticeable, especially when the deposited film thickness is small. The frequency resolution depends on the quality factor of an inverted peak in the reflectance spectrum. According to the circuit theory, the factor depends on antenna configuration, such as the antenna's resistance, inductance and capacitance. These parameters depend on the antenna design, so we have researched how curling probe design affects the factor with an electromagnetic wave simulator, CST microwave studio. Our recent result showed that the factor depends on the antenna material, the antenna length, and the antenna thickness. In particular, the long antenna helps stabilize the factor even when increasing electron density in plasma. In this presentation, we will show our recent analysis to suggest what antenna design a curling probe ought to have to improve electron density measurement with a curling probe.

2:20pm **PS+SE-MoA-3 Annular Beam Confocal Laser-Induced Fluorescence Diagnostic for Measurements of Ion Velocity Distribution Function in Industrial Plasmas***, **Ivan Romadanov**, Y. Raitses,* Princeton Plasma Physics Laboratory

Laser-Induced Fluorescence (LIF) is a powerful diagnostic tool for analyzing ion velocity distribution functions (VDFs) in plasma [1]. However, the requirement for two-sided access to plasma for beam injection and fluorescence collection in conventional LIF configuration is not always practical. Confocal LIF configurations, which are widely used in various fields such as biology and medicine, have been developed for several plasma diagnostic applications [2]. The primary advantage of confocal LIF configurations is the coincidence of the laser beam injection and fluorescence collection branches, enabling measurements in systems with limited optical access or complex geometries. This study introduces a novel variation of confocal LIF - Annular Beam Confocal Laser-Induced Fluorescence (ABC-LIF) configuration [3]. The proposed LIF configuration utilizes a structured Laguerre-Gaussian laser beam with an annular intensity profile, generated by diffractive axicons. This approach facilitates LIF signal collection along the main optical axis within the ring region while controlling spatial resolution through laser beam parameters, such as annulus thickness and beam diameter. Consequently, all enclosed fluorescence light is collected, maximizing the signal-to-noise ratio (SNR). This method achieves a spatial resolution of approximately 5 mm at a 300 mm focal distance, with the potential for 1 mm resolution, comparable to conventional LIF. The ABC-LIF configuration benefits from a small depth of field (DOF), typically achieved by Gaussian beams of large diameter, while the Laguerre-Gaussian beam allows for maintaining spatial separation between fluorescence and laser lights at comparable DOF values. Additionally, the configuration circumvents issues with beam back reflection. The ABC-LIF configuration was experimentally verified in industrial DC plasma source measurements of argon ion VDFs. Comparisons between confocal and conventional LIF revealed good agreement in determining plasma parameters, such as ion temperature, flow velocities, and ion density profiles. Applicable to various plasma processing equipment and sources, including hollow cathodes, microplasmas, and electric propulsion, the ABC-LIF configuration presents a promising diagnostic tool for industrial plasmas.

References

[1] Bachet G et al 1998 Phys. Rev. Lett. 80 3260

[2] Thompson D et al 2017 Rev. Sci. Instrum. 88 103506

[3] I. Romadanov, Y. Raitses, arXiv preprint arXiv:2303.12580. (2023)

Funding Acknowledgement: This work was performed under the U.S. Department of Energy through contract DE-AC02-09CH11466.

2:40pm **PS+SE-MoA-4 Control of Electron Energy Distribution Function in Electron Beam Generated ExB Plasma***, **Nirbhav Chopra**, Y. Raitses,* Princeton Plasma Physics Laboratory

Electron beam (e-beam) generated plasmas are promising for low pressure, low damage threshold material processing applications requiring efficient generation of ions and radical species [1,2]. The production of reactive species generated by electron impact is controlled by the electron energy distribution function (EEDF). In this work, we investigate the EEDF and plasma parameters of a partially magnetized plasma generated by e-beam in low pressure (0.1-10 mTorr) argon and nitrogen. The e-beam (energy < 100 eV) is extracted from a negatively biased thermionic filament and injected into a cylindrical vacuum chamber with applied axial magnetic field. The EEDF is measured using electrostatic probes. Results show the presence of e-beam electrons with energies comparable with the applied cathode voltage and a group of warm electrons (10-30 eV). Mechanisms of the formation of this intermediate group of electrons will be discussed. In addition, we will present and discuss the effect of the addition of nitrogen gas to the argon plasma on the EEDF.

[1] Zhao F et al C G 2021 *Carbon* **177** 244–51

[2] Walton S G et al 2015 *ECS J. Solid State Sci. Technol.* **4** N5033–40

3:00pm **PS+SE-MoA-5 Expanding the Capabilities of Microwave Hairpin Resonator Probes***, **Steven Shannon**,* North Carolina State University **INVITED**

Microwave hairpin resonator probes are a common diagnostic for measuring electron density in plasmas. They are particularly effective in low temperature plasmas, RF driven plasmas, reactive (particularly depositing) plasma chemistries, and other plasma environments that can challenge the effective use of comparable probe diagnostics such as Langmuir probes or emissive probes. Efforts to increase the utility of these probes through both innovative probe design (such as biasing and curling probe design) and combination of the hairpin probe with other diagnostic techniques (such as laser photodetachment studies in electronegative discharges) have increased the utility of hairpin probes in the field of experimental plasma science. This work presents efforts to expand on the measurement capabilities of these probes in two ways. First, the analysis of resonance data is expanded to account for plasma contributions to the Q-factor of the loaded resonance circuit. From this, additional plasma parameters such as electron neutral collision frequency can be estimated. Second, the time resolution of these probes are expanded to provide insight into the time modulation of plasma discharges including pulsed RF discharges, and can be extended to time resolved measurements within the period of an RF driven system, complimenting the growing area of phase resolved plasma characterization. The methods for expanding the capabilities of these probes are presented in this talk as well as examples of where this extension of probe capability has provided insight into basic plasma phenomena including moderate pressure operation of RF discharges, sheath heating, probe perturbation effects on density measurement, electronegative plasma instabilities, and the role of plasma edge uniformity on power coupling in inductively coupled plasma reactors. This work has been supported by the National Science Foundation, U.S. Department of Energy, Samsung Electronics, Applied Materials Inc. MKS Instruments and the state of North Carolina.

4:00pm **PS+SE-MoA-8 Time-Resolved Electron Energy Distribution in a Multi-Frequency Capacitively Coupled Plasma Reactor***, C. Kelly, **Md. Amzad Hossain**, D. Kapelyan, D. Ruzic,* University of Illinois at Urbana-Champaign

This work uses a time-resolved Langmuir probe to measure the electron energy distribution function (EEDF) in a capacitively-coupled parallel-plate (CCP) plasma reactor. The EEDF completely determines the plasma chemistry in a low-temperature plasma, and that is why it is so important to obtain. By seeing how the EEDF changes throughout an RF cycle, both as a function of time and position, one then knows the extent by which altering the RF waveform can affect the energy of the electrons. Often industry mixes RF frequencies to alter the plasma -- particularly the ion energy distribution at the substrate. Here we add a second frequency in a systematic manner and examine the changes in the instantaneous EEDF. We also examine the turn on and turn off times of the RF generator itself.

Specialized circuits were designed for this work to ensure high frequency fidelity so digitization at 1.5 GHz is possible and accurate. A set of experiments were conducted to show how only altering circuit parameters affect the results, and steps were taken to eliminate those effects. Spatial variations of the resulting EEDFs were investigated, especially near the edge of the CCP reactor, to see which aspects change the most with radius.

4:20pm **PS+SE-MoA-9 Mass Spectral Characterization and Control of Plasma Etch Processes***, L. Shoer, P. Heil, S. Pursel,* Intel Corporation*; N. Salovich,* Edwards Vacuum*; **David Shykind**,* Intel Corporation

As semiconductor critical dimensions have reached the single-digit nanometer scale, reproducible control of etch processes has become critically dependent on consistent wafer-to-wafer processing. Nanometer feature sizes and atomically thin layers have led to a regime where traditional bulk plasma characterization techniques no longer give insight into the chemical processes occurring on the wafer. Furthermore, the number of moles of reactants on the walls of an etch chamber are greater than or equal to the quantity of reactants intended to be etched on a wafer itself. Uncontrolled, this situation complicates etch processes, introducing hysteretic behavior even assuming an ideal input stream of identical wafers, and exacerbates actual wafer-to-wafer variation effects. We show how high-speed (subsecond time resolution), non-invasive mass spectrometry of plasma cleaning, seasoning and actual etch steps themselves leads to improved performance and enhanced mechanistic understanding of plasma etch processes.

4:40pm **PS+SE-MoA-10 Development of a Catalytic Probe for the Detection of Fluorine Radicals with Applications to Semiconductor Manufacturing***, **Nicholas Connolly**, J. Mettler, R. Garza, R. Sankaran, D. Ruzic,* University of Illinois Urbana-Champaign

Plasma processing is an essential part of integrated circuit manufacturing, with plasma etching, plasma strip, and chamber cleaning being three critical steps. All of these steps rely on radicals, highly reactive neutral species created in the plasma, to drive the desired etching reactions. Because of the importance of radical species in etching reactions and rates, quantification of the densities of these species is important for understanding plasma etching dynamics. Additionally, spatial resolution of radical densities allows specific knowledge of etch dynamics at a substrate or a chamber component of interest.

One technique that has been developed to detect and quantify radical species is a catalytic probe, which consists of two thermocouples each coated with a different metal. The different metals catalyze the recombination of radical species at different rates, leading to a temperature difference between the thermocouples. This temperature difference is proportional to the density of radical species, and so a radical density can be determined. The catalytic probe technique provides in-situ, spatially resolved radical densities. This has advantages over techniques which gather a line-averaged signal, such as optical emission spectroscopy (OES), and measurement methods that require ex-situ analysis, such as coupon etch rates.

Previous studies have applied catalytic probes to the detection of hydrogen (H), oxygen (O), and nitrogen (N) radicals.[1] To our knowledge, a catalytic probe for fluorine (F) has yet to be reported. Here, we present a thermocouple-based catalytic probe to determine spatially resolved fluorine radical densities in SF_6/Ar plasmas. The catalytic activity of zinc, copper, and gold is reported. The radical densities determined from the radical probes are compared to those determined via actinometry and coupon etch rates. These methods also provide verification of the recombination coefficient of the probe material and thereby confirm the quantitative results of the radical probe.

[1] D. Qerimi, I. Shchelkanov, G. Panici, A. Jain, J. Wagner, and D.N. Ruzic. J. Vac. Sci. Technol. A 39, 023003 (2021).

5:00pm **PS+SE-MoA-11 Multi-Diagnostic Investigation of Etching Plasma Species in an Industry-Grade Inductively-Coupled Plasma Etcher***, **Jeremy Mettler**[1], N. Connolly, S. Dubowsky, D. Ruzic,* University of Illinois at Urbana-Champaign

Plasma etching kinetics and reaction mechanisms often involve complex interactions between radical, neutral, and charged species. Optimization of etch rate and selectivity for a given process can be tedious without a detailed mechanistic understanding of the etching mechanisms, which in turn can be difficult to determine without accurate measurements of all relevant plasma species. Many diagnostics exist which are able to measure some of these species, but each has their own tradeoffs, and none are able to measure all species under all conditions.

In this work we discuss the development of a suite of plasma diagnostics for measuring the environment in an etching system, including neutral, charged, and radical species. To accurately measure each component of the etch process, results from appearance energy mass spectroscopy, optical emission spectroscopy, fluorine radical probe analysis, and Langmuir probe analysis are combined, with overlap in the sensing capabilities of each diagnostic used for cross-validation. The use of multiple independent diagnostics with different spatial resolutions and species sensitivities provides flexibility and increased confidence in quantitative results. This work will present a comparison of results obtained by the individual diagnostics across several CF_4 based etching conditions in an industry-grade inductively-coupled plasma etching tool. Further comparison will be made between experimental etching results and 0-D plasma modeling of the etching system.

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

Advanced Surface Engineering Division
Room C123 - Session SE+TF-MoA

Mechanics and Tribology of Thin Films and Coatings

Moderators: Rebecca Cai, Virginia Tech, **Suneel Kumar Kodambaka**, Virginia Tech

1:40pm **SE+TF-MoA-1 Mini-Module Stress Testing to Assess 'Fatigue-Like' Failure Mode of Gridlines on Silicon Solar Cells***, A. Chavez, **Sang Han**,* University of New Mexico*; S. Huneycutt, A. Ebong,* University of North Carolina at Charlotte*; D. Harwood, N. Azpiroz,* D2Solar

Microcracks in solar cells can eventually propagate through metal gridlines and busbars, leading to PV module power loss over time. With the latest glass/glass PV module construction – in which the glass is only heat-treated (not tempered) and its thickness is reduced from 3.2 mm to 2.0 mm – along with ever-increasing module size, the stress-induced cell cracks are rapidly becoming one of the main degradation modes. In this study, we compare how metal matrix composite gridlines fare in comparison to standard silver gridlines against three-point-bending stress test. We have fabricated two-cell, mini-modules with full-size Passivated Emitter and Rear Contact (PERC) cells. The backside of each cell is laser-scribed prior to encapsulation to initiate cell cracks. The completed mini-modules are then placed on a three-point-bending setup and flexed until the cells crack, and the cracks propagate through the gridlines to cause electrical discontinuity. The mini-modules are then subjected to cyclic mechanical stress on the three-point-bending setup up to the sub-critical fracture stress level to simulate the field operation and to characterize the long-term 'fatigue-like' wear-out failure. The results show that enhanced ductility and compliance of composite gridlines lead to their increased durability compared to standard silver gridlines, strongly suggesting increased lifetime of PV modules against cell cracks.

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office Award Number DE-EE0009013.

2:00pm **SE+TF-MoA-2 Relating Stress in Thin Films to the Underlying Kinetic Processes: Experiments and Modeling***, E. Chason, **Tong Su**,* Brown University

Stress in thin films can have a significant impact on their performance and reliability.Since stress is affected by many parameters (growth rate, temperature, microstructural evolution, composition, particle energy for sputter deposition, etc.), a fundamental understanding of its origins stress would allow it to be predicted and optimized.We describe a model for we have developed to explain stress evolution during deposition in terms of the underlying kinetic processes. The model includes mechanisms related to non-energetic growth kinetics, microstructural evolution and energetic particle bombardment.Examples are discussed that use the model to explain the dependence of stress on the growth rate, grain growth kinetics and sputter pressure.A user-friendly computer program based on the model is described that is available to interested users to analyze wafer curvature measurements.

2:20pm **SE+TF-MoA-3 Tailoring the Tribocorrosion Resistance of Al-based Metallic Thin Films via Alloying and Nanolayering***, **Wenjun (Rebecca) Cai**,* Virginia Tech **INVITED**

The increasing complexity and severity of service conditions in areas such as aerospace and marine industries, nuclear systems, microelectronics, batteries, and biomedical devices etc., imposes great challenge on the reliable performance of metallic thin films subjected to simultaneous surface stress and corrosion. However, the design of strong and corrosion-resistant coatings, especially those containing passivating elements such as Al are challenged by the tradeoff between strength and corrosion resistance. Towards this end, this talk will focus on the development of novel microstructure design strategies for metallic thin films to mitigate the combined attack of wear and corrosion (i.e. tribocorrosion) under harsh conditions. Two design strategies will be discussed to overcome this long-standing dilemma: by forming solid solution alloys and nanostructured multilayers. These studies provide insights for general design guidelines to engineer more robust, high-performance metals for use under harsh conditions.

3:00pm **SE+TF-MoA-5 Tribological Properties of Conversion Layers and Carbon-based PVD Coatings for Rolling Bearing Applications***, **Esteban Broitman**, A. Ruellan, R. Meeuwenoord, D. Nijboer,* SKF B.V. - Research and Technology Development, Netherlands

In this study, different coatings and conversion layers have been compared in terms of friction performance based on a single-contact oil-lubricated tribometer and on a grease-lubricated double row bearing friction test rig ran under relevant operating conditions for a railway application. Conversion layers like zinc-calcium-phosphate, manganese-phosphate and black-oxide have been compared on friction performance to that of an un-coated steel surface and to a proprietary diamond-like-carbon base coating.

Results demonstrate that the optimum conversion layer can reduce friction by more than 25% on rolling/sliding raceway contacts (ball-on-disk) and up to 80% on the sliding flange contacts (roller-on-disk), which share a significant portion of power losses in roller bearing units. Results at the bearing level demonstrate that the same optimum conversion layer can reduce the running torque by approximately 30% compared to the current products both at low and intermediate speeds relevant to intercity trains.

3:20pm **SE+TF-MoA-6 The Tribological Behaviour of TiAlN Coating Under High-Temperature Conditions***, **Aljaž Drnovšek**,* Jozef Stefan Institute, Slovenia*; P. Šumandl,* Faculty of Natural Sciences and Engineering, University of Ljubljana, Slovenia*; Ž. Gostenčnik,* Jozef Stefan Institute, Slovenia*; M. Čekada,* jozef Stefan Institute, Slovenia

TiAlN coating is a popular hard coating for high-temperature applications such as high-speed cutting and cutting of new, hard-to-cut materials. However, the most commonly used method for depositing this coating on cutting tools, cathodic arc evaporation, can result in a relatively rough surface due to the emission of micro-droplets. This roughness and the presence of embedded droplets in the coating matrix can significantly affect the coating's wear and friction properties

Our objective was to assess the wear and friction properties of the TiAlN coating during both the running-in and steady-state periods under varying temperature conditions. To evaluate the performance of the TiAlN hard coating, we conducted tribological tests using a high-temperature pin-on-disc tribometer. The tests were carried out with an Al_2O_3 ball as a counter body at different temperatures: room temperature, 250 °C, 500 °C, and 700 °C. We varied the test duration at specific temperatures, ranging from 50 up to 140,000 cycles, to examine the effect of test length on the coating's wear and friction properties. After each tribological test, we analysed the coatings.

The results indicated that the coating experienced the highest wear during the room temperature test. Conversely, the wear during the running-in phase and steady-state friction was the lowest at 250°C. As the temperature increased, the wear rate rose, which we attributed to tribo-oxidation and fatigue caused by the high test lengths. Ultimately, the coating delaminated from the WC-C substrate at the highest temperature. The asperities on the surface of the coating due to micro-droplets played a significant role in friction and wear behaviour, as they were a primary source of wear particles and the first spots of oxidation on the coating.

We conducted detailed 3D profilometry, SEM and FIB analyses on numerous samples to determine the wear mechanisms at different stages of high-temperature wear. In addition to tribological evaluation, we performed high-temperature mechanical tests at the same temperatures as the tribological tests.

The combination of these analyses allowed us to gain a comprehensive understanding of the wear mechanisms and behaviour of the TiAlN coating at high temperatures. By analysing the samples at different stages of wear, we were able to identify the dominant wear mechanisms and how they evolved over time.

4:00pm **SE+TF-MoA-8 Atomic Layer Deposition Coatings on Micron-Sized Iron Powders for Increased Oxidation Resistance***, **Chris Gump**, J. Burger, T. Porcelli, J. Travis, B. Boeyink, T. Champ,* Forge Nano

The physical, electrical, and magnetic properties of micron-sized and smaller metal powders make them useful for a variety of applications, including additive manufacturing, electronic components, metal injection molding, microwave absorption, and powder metallurgy. As the particle size of these metals becomes smaller, oxidation of the particle surface becomes a larger issue. In the case of flammable metal powders like iron and titanium, this can have severe safety implications, as the rapid oxidation of the powder can result in a metal fire or dust explosion. However, even the slower oxidation reactions that occur in salty, foggy, or typical ambient conditions can reduce shelf life and have other negative effects on the properties of products made from these feedstocks. The desirable properties of these materials can be preserved by encapsulating the powders with a barrier film. To minimize the effects on the properties of the composite particles, the barrier film should be as thin as possible.

Atomic Layer Deposition (ALD), long used in the semiconductor industry for coating wafers, has in recent years been applied to a wider range of application spaces, including the surface modification of powders with nanometer-scale films. We studied the deposition of thin, nanoscale alumina ALD barrier films onto metal powders, using carbonyl iron powder (CIP) as a model substrate that has a range of applications.Coatings were performed on 30 g batches of powder in a highly scalable fluidized bed reactor. The barrier properties of the films were studied as a function of deposition temperature (80 – 230°C) and film thickness (1 – 8 nm), using thermogravimetric analysis in oxygen as the performance metric. Optimal barrier performance, in terms of the shift in onset temperature for oxidation, occurred for the middle range of deposition temperatures. The thickest films were able to shift the onset temperature for oxidation by as much as 300°C (from 250°C to 550°C). The barrier performance as a function of temperature was found to correlate with previously published studies of the film density and growth per cycle (GPC) of Al_2O_3 ALD deposited as a function of temperature.Although not characterized in this case, the barrier films are also expected to decrease electrical conductivity while maintaining magnetic susceptibility. The deposition process has been successfully demonstrated at the 1-5 kg scale, and the 100 kg scale for similar metal powders, with the potential for even higher throughputs on established coating tools.

4:20pm **SE+TF-MoA-9 Characterizing the Composition, Structure, and Mechanical Properties of Titanium Silicon Nitride Erosion Resistant Coatings***, **Gilad Zorn**, P. Shower, S. Weaver, R. Rose, J. Her, J. Salisbury,* GE Research Center

Titanium nitride (TiN) coatings have a wide range of applications due to their practical properties such as high hardness, good corrosion resistance, heat resistance and excellent wear resistance. They have been widely used in various industries including decorative coatings, diffusion barriers and hard coatings. The properties of TiN can be greatly enhanced by addition other elements, such as Si [1-2]. Incorporation of Si in the TiN cubic structure leads to formation of TiSiN coatings characterized by high hardness and high oxidation resistance up to 800 °C. This enables synthesizing coatings and designing materials with a broad range of applications, especially as materials that should perform under harsh environments. The ternary TiSiN system is formed due to the total miscibility of Si, which creates a solid solution while preserving the crystalline structure B1 of TiN. Si is also believed to create nanocomposite structure of TiSiN coatings consisting of nanocrystalline TiN grains encapsulated by an amorphous silicon nitride (Si_3N_4) matrix.To achieve high hardness TiN films, significant bonding strength between Ti and N must be achieved.If the bonding is too weak, the surface of the coating can oxidize, forming titanium oxynitride and eventually TiO_2 even at room temperature conditions [3]. The oxynitride and oxide forms are known to exhibit a lower hardness than TiN and experience oxidation propagation.

This study is focused on the characterization of TiSiN hard coatings. For example, X-ray Photoelectron Spectroscopy (XPS) was used to study the compositions and high resolution XPS was used to determine the surface oxide to nitride ratios. Mechanical tests were performed with nano indenter to determine the hardness of these coatings. Figure 1 shows the correlation between the hardness of the films and the percentage of the XPS titanium oxide component.X-ray diffraction confirmed the formation of titanium nitride cubic phase and different crystallographic orientations were observed depending on the composition of each film. The results of this study show that adding Si and reducing the oxygen level improved the performance of the nitride films as erosion resistant coatings.

1. Akhte, Rumana; Zhou, Zhifeg; Xie, Zonghan, Munroe, Paul *Surface and coating technology* 425 (2021) 127687.
2. Greczynski, G.; Bakhit, B.; Hultman, L.; Odén, M. *Surface and coating technology* 398 (2020) 126087.
3. Logothetidis, S.; Meletis, E.I.; Stergioudis, G.; Adjaottor, A.A. *Thin Solid films* 338 (1999) 304.

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Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA+AS+LS+LX+MN+SE+SS-TuM

Novel Developments and Applications of Interfacial Analysis

Moderators: Andrei Kolmakov, National Institute of Standards and Technology (NIST), **Slavomir Nemsak**, Advanced Light Source, Lawrence Berkeley National Laboratory

8:00am **CA+AS+LS+LX+MN+SE+SS-TuM-1 Hypervelocity Nanoprojectile Impacts on Graphene, Graphene-Solid/Liquid Interphases: From Mechanisms of Interaction/Ejection to Practical Applications*, Dmitriy Verkhoturov,*** Texas A&M University*; S. Lee,* Mayo Clinic*; M. Eller,* California State University Northridge*; M. Gołuński, S. Hrabar,* Jagiellonian University, Poland*; S. Verkhoturov,* Texas A&M University*; Z. Postawa,* Jagiellonian University, Poland*; A. Kolmakov,* National Institute for Science and Technology (NIST)*; A. Revzin,* Mayo Clinic*; E. Schweikert,* Texas A&M University **INVITED**

Presented here are the experiment and theory on processes accompanying the impacts of C_{60} and Au_{400} projectiles (~1 keV/atom) on graphene/matter interphases. A variety of targets were used: a) free standing graphene, b) molecules and extracellular vesicles (EVs) deposited on free standing graphene, c) interphases graphene-solids/liquids, d) EVs deposited on functionalized monocrystals.

Two custom-built Cluster ToF secondary ion mass spectrometry (SIMS) devices with similar parameters were used. The experiments were run in the event-by-event bombardment/detection mode where the regime of bombardment is super-static[1]. The analyzed surfaces were bombarded at the rate of ~1000 impacts/sec with 1-6×10^6 impacts collected on a surface area of 50-500 µm in diameter. This regime allows acquisition of individual mass spectra for each impact, thus allowing the comparison of experimental data with MD simulations at the level of single projectile impacts. The method allows detection of ejecta in reflection (3D case) and transmission (2D case) directions.

The mechanisms of ejection from 2D and 3D materials (including graphene-solid/liquid interphase) are different. For example, in the case of C_{60} impacts on a molecular layer deposited on graphene (2D case) the mechanism of ejection is described with the “trampoline” model[2]. For the 3D case of graphene-solid/liquid interphase, graphene suppresses the ejection of molecules. The compression of matter in the excitation volume around the impact is not sufficient to destroy the graphene[3].

Our method allows to test individual nano-objects. A biological example is EVs. There were anchored on functionalized Si and graphene substrates, with the EVs labeled with antibodies carrying lanthanide tags (Ab@Ln) for normal hepatic and liver cancer markers. Up to four Ab@Ln tags could be detected simultaneously, enabling analysis of population heterogeneity with single EV resolution and to distinguish between normal and cancer EVs based on surface marker expression. Using co-localization of cancer biomarkers, it is possible to find small subpopulation of EVs originating from cancerous cells potentially allowing for early cancer detection. The sensitivity of the method can be increased several folds via transmission configuration where ejecta are emitted and detected in the forward direction. In this case nano-objects, such as EVs, are anchored on graphene oxide, a 2D material.

[1] S.V. Verkhoturov et al. J. Chem. Phys. 150 (2019)

[2] R.D. Rickman et al. Phys. Rev. Lett. 92, 047601 (2004)

[3] D.S. Verkhoturov et al. Biointerphases 11, 02A324 (2016)

Acknowledgements: NSF Grant CHE-1308312, NIH Grant R01 GM123757-01,

Polish National Science Center 2019/33/B/ST4/01778, PLGrid Infrastructure Grant

8:40am **CA+AS+LS+LX+MN+SE+SS-TuM-3 Applying *in Situ* Bias During TOF-SIMS Analysis to Investigate Ion Migration in Perovskite Devices*, Steven Harvey,*** National Renewable Energy Laboratory*; I. Gould,* University of Colorado, Boulder*; D. Morales, M. McGehee,* University of Colorado Boulder*; A. Palmstrom,* National Renewable Energy Laboratory

Metal Halide Perovskite Photovoltaics have the potential to be a game-changing technology in photovoltaics, with low cost solution processing inherent to the technology and a rapid progress in device efficiency and stability. Understanding ion migration in these materials has lead to improvements in both efficiency and reliability, and further understanding of these phenomena is of great importance.

Time of flight secondary ion mass spectrometry is well suited to provide unique insight for this class of materials, as it can reveal the distribution of both the organic and inorganic components of a device stack (both through the depth as well as laterally with 2-D and 3-D imaging). We will briefly cover our past work on technique development for this class of materials, before presenting new work where an *in situ* electrical bias was placed on a perovskite device while under investigation with TOF-SIMS. This was completed with simple commercial off the shelf components in an ION-TOF TOF-SIMS V instrument and could be easily implemented on other instruments. A device stack of glass / ITO / Me-4PACz / DMA0.1FA0.6Cs0.3Pb(I0.8Br0.2)3 / LiF (1 nm) / C60 (30 nm) / SnOx (15 nm)/Au (20 nm) was used for this study. An electrical bias was applied between the top gold contact and the bottom ITO contact during TOF-SIMS measurements. By applying a +0.75V and -0.75V forward and reverse bias to the device, a driving force for negatively charged halide ions is created to migrate towards the back or front of the device, respectively. The *in-situ* data shows the halide ion migration towards the back ITO contact after the forward bias is applied. The negative bias was then applied and the halide ions migrate back towards the front of the device and return to the original unbiased state. In both cases the formamidinium and lead traces do not show similar migration, showing only the charged species in the device are affected by the bias. The results show a framework that can be used for further study. Potential complications with the analysis of this type of data will be discussed.

9:00am **CA+AS+LS+LX+MN+SE+SS-TuM-4 Oxidation of a Single Fe Nanoparticle at the Nanoscale and Real-Time by Operando Atom Probe*, Sten V. Lambeets,*** Pacific Northwest National Laboratory*; N. Cardwell, I. Onyango,* Washington State University*; T. Visart de Bocarmé,* Université libre de Bruxelles, Belgium*; J. McEwen,* Washington State University*; D. Perea,* Pacific Northwest National Laboratory

Physics governing surface chemical reactions and interfaces involved in heterogeneous catalysts fundamentally depends on the synergistic interactions between reactive gases and specific surface structures. Surface science techniques are continuously evolving to help bridge knowledge gaps between fundamental research and real-world applications. In the past decade, an increasing number of analytical techniques successfully achieved their evolution towards an in situ and operando version of themselves, and recently such approaches are being developed for atom probe microscopy (APM) techniques. In this work, we will present the recent advances in the conversion of Atom Probe Tomography (APT) to study surface dynamics of O_2/Fe using two different APM techniques and modifications: Field Ion Microscopy (FIM), and Operando Atom Probe (OAP).

APM techniques are capable of imaging the apex of sharp needles with nanometric lateral resolution, which can be seen as model nanoparticles. FIM is used to image such needles with atomic resolution and to identify the crystal orientation along with the local surface reaction dynamics during oxygen interaction with Fe. The resulting FIM image corresponds to a stereographical projection of the apex and allows the identification of the crystal orientations with atomic resolution. Regular APT, from which the OAP derives, relies on the thermally assisted field evaporation of positively charged ions from a needle shaped specimen. In regular use, the APT is performed in an Ultra High Vacuum (<10^{-11} mbar) while the sample is cooled at 50K. The OAP modification consists of performing the atom probe analysis in the presence of reactive gas at 300 K.

Once the FIM characterization is complete the sample is maintained at 300K before starting APT analysis and introducing 1.1×10^{-7}mbar of pure O_2. As soon as the O_2 is introduced, we can measure the surface formation of Fe oxides by monitoring the local concentration of Fe_2O^{n+} ion species extracted from the surface over time. We can track the local concentration over the different surface regions in real time. We observe the progressive surface oxidation starting from open facets structures, such as Fe{222} and Fe{112}, towards the central Fe(011) and the Fe{024} which show significantly higher resistance toward oxidation. The combination of the different concentrations allows us to reconstruct the full movie of the surface oxidation in real-time. However, since the measurements are performed in the presence of very strong electric fields (>10 V/nm), it is necessary to discuss the potential influences of it on the system as well.

9:20am **CA+AS+LS+LX+MN+SE+SS-TuM-5 Reporting Interfaces: Unconventional Excitation of Interfaces Enables Exquisite Gas Sensing Toward Our Sustainable Future*, Radislav Potyrailo,*** GE Research **INVITED**

As our society is developing solutions for more sustainable types of energy, the need for reliable, yet affordable tools for monitoring of emissions of greenhouse and other gases in urban and industrial environments is a substantial undertaking for two main reasons. First, to achieve a desired accuracy, existing gas monitoring solutions in complex backgrounds utilize traditional analytical instruments. While their mathematical design principles provide needed independent response outputs, their hardware design principles do not allow cost-effective ubiquitous implementations. Second, all gas sensors based on interface-driven interactions between gases of interest and sensing materials are single-output devices. By their original design principles from early last century, these sensors operate well only when levels of interfering gases are low. Once levels of interfering gases increase, existing sensors lose their accuracy because of competing interactions between the sensor interface and numerous interfering gases versus a gas of interest.

In this talk, we will present gas sensors that we built following mathematics of traditional analytical instruments but with our own different types of independent variables for detection of multiple gases with enhanced accuracy and stability. These sensors are multivariable gas sensors where independent response outputs are provided by our unconventional methodologies of excitation of interfaces between a sensing material and different ambient gases. We will show that our approach results in a reliable differentiation of one or more analyte gases in complex backgrounds of interfering gases with an individual multivariable gas sensor. This exquisite (i.e., accurate and reliable) gas sensing provides an affordable technical solution for monitoring of emissions of greenhouse and other gases in urban and industrial environments. Such technical solution is mathematically not feasible using conventional single-output sensor designs. We will also show that such multivariable gas sensors have the ability for self-correction for sensor drift. Our approach for the multi-gas detection and drift self-correction should allow implementations of gas sensors in diverse applications that cannot afford weekly, monthly, or quarterly periodic maintenance, typical of traditional analytical instruments.

11:00am **CA+AS+LS+LX+MN+SE+SS-TuM-10 A "Simple" Approach to Combine Electrochemistry and Operando Near Ambient Pressure XPS Studies***, F. Mirabella,* ***Paul Dietrich,*** *A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany **INVITED**

Electrochemical water splitting is an environmentally friendly technology to store renewable energy in the form of chemical fuels. Among the Earth-abundant, first-row transition metal-based catalysts, Ni and Fe oxides have shown promising performances as effective and low-cost catalysts of the oxygen evolution reaction (OER) in alkaline media. Notably, their structure evolves under oxygen evolution operating conditions with respect to the as-prepared catalysts but these changes and consequently the active sites have not been identified yet due to the difficulties associated with surface analysis measurement under working conditions (*operando*).

In this presentation, we will demonstrate the enormous potential of laboratory NAP-XPS for investigations of solid-liquid interfaces in electrochemical systems at elevated pressures (≤ 25 mbar), also illustrating the ease of use of this specific setup. We will show a versatile three-electrodes electrochemical setup that allows for operando studies of solid-electrolyte interfaces, i.e., of nickel oxide foils as cathode for OER in alkaline environment as a simple laboratory NAP XPS experiment.

11:40am **CA+AS+LS+LX+MN+SE+SS-TuM-12 Recent Developments in Probing Buried Interfaces Using Standing-Wave Photoelectron Spectroscopy*, Slavomir Nemsak,*** Lawrence Berkeley Lab

Standing-wave photoelectron spectroscopy of multi-layer structures proved to be a very powerful technique for probing solid/solid, but also solid/liquid and solid/gas interfaces. Its superior depth selectivity and non-destructive nature were crucial to answer key questions in problems spread over several scientific fields, such as emergent phenomena at complex oxide interfaces [1], artificial multiferroics [2], adsorption mechanisms in liquids [3], corrosion [4], and electrocatalysis [5].These achievements were only possible thanks to innovative approaches both in experiments and analyses, including development of X-ray optical simulations package [6] and its coupling with the black-box optimizer [7]. In this talk I will introduce novel tools and approaches for standing-wave experiments and I will highlight some of the recent applications [8,9,10].

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[2] H. P. Martins et al., *arXiv preprint arXiv:2012.07993.*

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[5] C. Baeumer et al., *Nature Materials* **20**, 674 (2021).

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[7] O. Karslioglu et al., *Journal of Electron Spectroscopy and Related Phenomena* **230**, 10 (2019).

[8] M Scardamaglia, et al., *Journal of Electron Spectroscopy and Related Phenomena* **262**, 147281 (2023).

[9] G. Conti et al., *Journal of Micro/Nanopatterning, Materials, and Metrology* **20**, 034603 (2021).

[10] H.P. Martins et al., *Journal of Physics D: Applied Physics* **56**, 464002 (2021).

12:00pm **CA+AS+LS+LX+MN+SE+SS-TuM-13 The Influence of Surface Structure and Electrostatics on Measuring Unoccupied Electronic States via Low Energy Inverse Photoemission Spectroscopy (LEIPS)*, James Johns,*** Physical Electronics USA

A material's energetic distribution of electronic states near the fermi level is a key physical property for determining how it behaves in electronic, chemical, and optical applications.Photoemission has long been the gold standard for measuring the occupied electronic states below the Fermi level and is one of the most common surface science techniques worldwide.Inverse photoemission (IPES), the related process whereby an electron is absorbed at the surface and a photon is emitted, is similarly a very powerful tool for measuring the unoccupied electronic states. Unfortunately, the intrinsically lower rate for IPES and technical hurdles related to relevant photodetectors has historically necessitated the use of electron sources with sufficient energy to damage all but the most chemically robust surfaces.

The availability of narrow bandpass optical filters at UV photon energies between 3.5 and 6 eV over the past decade have enabled the development and commercialization of Low Energy Inverse Photoemission Spectroscopy (LEIPS)[1,2].Efficient detection of low energy UV photons (lower than traditional IPES at 9-10 eV) enables the use of low energy electrons (below 5 eV) which avoid damaging sensitive materials including organics.This key innovation has revitalized interest in IPES because the technique can now be applied to molecular materials and interfaces relevant to wide range of applications *e.g.* batteries, photovoltaics, organic semiconductors and OLEDs, chemical sensors.Furthermore, optical UV filters also improve the energy resolution, further enhancing the appeal of LEIPS over traditional IPES.

Like any surface science technique, the quality of LEIPS data depends on both the instrumentation and sample preparation. Here, I will discuss the material requirements and limitations for successful LEIPS measurements, several of which differ from more common techniques such as XPS, SPM, or electron microscopy.I will also present LEIPS data from taken at the interface between two metals and explain those results using calculated trajectories of the electron beam.Finally, I will illustrate a key difference between LEIPS, which probes the true unoccupied electronic density of states, and optical methods, such as optical spectroscopy or EELS which measure the joint density of states, by presenting LEIPS spectra of an excitonic 2D material.

[1] Yoshida, H; "Near-ultraviolet inverse photoemission spectroscopy using ultra-low energy electrons" *Chem. Phys. Lett.* **539-540**, 180-185, (2012)

[2] Lida, S.; Terashima, M; Mamiya, K; Chang, H. Y.; Sasaki, S; Ono, A; Kimoto, T; Miyayama, T; "Characterization of cathode-electrolyte interface in all-solid-state batteries using TOF-SIMS, XPS, and UPS/LEIPS" *J. Vac. Sci. & Tech. B*, **39**, 044001, (2021)

Biomaterial Interfaces Division
Room B117-119 - Session BI+AS+EM+NS+SE+TF-TuA

Functional Biomaterials II: Sensing and Diagnostics

Moderators: Joe Baio, Oregon State University, **Caitlin Howell**, University of Maine

2:20pm **BI+AS+EM+NS+SE+TF-TuA-1 AVS Nellie Yeoh Whetten Awardee Talk: Detection of SARS-CoV-2 using Surface-enhanced Raman Spectroscopy and Deep Learning Algorithms***, **Yanjun Yang**[1],* University of Georgia*; H. Li,* Chongqing University, China*; L. Jones, J. Murray, D. Luo, X. Chen, H. Naikare, Y. Mosley, R. Tripp,* University of Georgia*; B. Ai,* Chongqing University, China*; Y. Zhao,* University of Georgia

A rapid and cost-effective method to detect the infection of SARS-CoV-2 is crucial in the fight against *COVID-19* pandemic*.* This study presents three strategies to detect SARS-CoV-2 from human nasopharyngeal swab (HNS) specimens using a surface-enhanced Raman spectroscopy (SERS) sensor with deep learning algorithms. The first strategy is to use DNA probes modified silver nanorod array (AgNR) substrate to capture SARS-CoV-2 RNA. SERS spectra of HNS specimens have been collected after RNA hybridization, and a recurrent neural network (RNN)-based deep learning (DL) model is developed to classify positive and negative specimens. The overall classification accuracy was determined to be 98.9%. For the blind test of 72 specimens, the RNN model gave 97.2% accuracy in the prediction of the positive specimens, and 100% accuracy for the negative specimens. The second strategy is to use a human angiotensin-converting enzyme 2 protein (ACE2) functionalized SERS sensor to capture the intact viruses. Such a method can differentiate different virus variants, including SARS-CoV-2, SARS-CoV-2 B1, and CoV-NL63. A convolutional neural network (CNN) deep learning model for classification and regression has been developed to simultaneously classify and quantify the coronavirus variants based on SERS spectra, achieving a differentiation accuracy of > 99%. Finally, a direct SARS-CoV-2 detection on SiO_2 coated AgNR substrate is tested. SERS spectra of HNS specimens from 120 positive and 120 negative specimens are collected. The HNS specimens can be accurately distinguished as positive or negative with an overall 98.5% accuracy using an RNN-based deep learning model, and the corresponding Ct value can be predicted accurately by a subsequent RNN regression model. In addition, 99.04% accuracy is achieved for blind SARS-CoV-2 diagnosis for 104 clinical specimens. All the detections are accomplished in 25 min. These results indicate that the SERS sensors combined with appropriate DL algorithms could serve as a potential rapid and reliable point-of-care virus infection diagnostic platform.

2:40pm **BI+AS+EM+NS+SE+TF-TuA-2 Wafer-Scale Metallic Nanotube Arrays: Fabrication and Application***, **Jinn P. Chu,*** National Taiwan University of Science and Technology, Taiwan

This presentation reports on the wafer-scale fabrication of 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 the photoresist. We have used ferrous (stainless steel) and nonferrous (Cu-, Ni-, Al-, and Ti-based) alloys, as well as elemental metals (Cu, Ag, and Au), to form MeNTAs. The proposed nanotubes can be fabricated over a wide range of heights and diameters (from a few hundred nm to 20 µm) in various shapes, including tall cylinders and dishes. In addition, after combining with other nanomaterials (e.g., ZnO nanowires, graphene oxide, or Au nanoparticles), MeNTAs become nanohybrids suitable for many applications. These applications include thermal emitters, triboelectric nanogenerators, SERS-active biosensors, microfluidics, and anti-icing devices.

3:00pm **BI+AS+EM+NS+SE+TF-TuA-3 Low-Cost, Continuous Spectroscopic Monitoring of Chemical and Biological Contamination in Liquids***, **Liza White**, C. Howell,* University of Maine

Traditional UV-visible spectroscopic testing of liquids to assess contamination typically involves manual collection and measurement in a dedicated instrument at discreet time intervals. Here, we describe how low-cost, mass-produced diffraction gratings can be used to approach the functionality of traditional UV-visible spectroscopic readouts under continuous flow conditions. We designed and built a flow chamber setup that permitted uninterrupted monitoring of the diffraction pattern as water with different contaminants was passed over it. Various chemical dyes as well as biological contaminants such as bacteria and algae at varying concentrations in water were tested using standard LEDs as a light source. Information was extracted from the diffraction patterns by analyzing changes in the transmitted wavelengths as well as changes in scattering. Our results showed that the system permitted reasonable detection of each of the contaminants tested within a subset of the concentration range of a standard UV-vis instrument. Tests using the toxic dye methylene blue showed accurate detection well below the toxic limit (5 µg/mL), although the limit of detection for *E. coli* was higher at ~10^7 cells/mL. Our results demonstrate how mass-produced diffraction gratings can be used as low-cost detection systems for the continuous detection of contamination in liquids, opening the door for autonomous monitoring for a range of different applications.

3:20pm **BI+AS+EM+NS+SE+TF-TuA-4 Clickable Cerium Oxide Nanoparticles with Gadolinium Integration for Multimodal Micro- and Macroscopic Targeted Biomedical Imaging***, **Anna du Rietz**, C. Brommesson, K. Roberg, Z. Hu, K. Uvdal,* Linköping University, Sweden

Multimodal and easily modified nanoparticles enable targeted biomedical imaging at both the macro- and micro level. Computed tomography and magnetic resonance imaging are biomedical imaging techniques used daily in clinical practice all over the world. These non-invasive techniques can identify more medical conditions if contrast and sensitivity are increased. Commonly, targeted imaging is realized by conjugating biomolecular recognition elements such as antibodies to the contrast agent.

Herein, we present a clickable nanoparticle of our own design, consisting of a Cerium oxide nanoparticle core with integrated Gadolinium, coated with polyacrylic acid and functionalized with both a clickable moiety and a fluorophore. Click chemistry is a versatile toolbox of conjugation reactions that can be performed under gentle conditions enabling facile tailoring of the nanoparticles. Results from XRD and TEM studies clearly show that the cores are mono-crystalline and approximately 2 nm in diameter, the hydrodynamic radius of <5 nm is measured by DLS. The soft coat of the nanoparticles is characterized by IR spectroscopy as well as zeta potential measurements. We have verified the presence of azide-groups on the finished particles and the carboxylic groups of polyacrylic acid are firmly bound to the nanoparticle core. The nanoparticles have high colloidal stability even in physiological ionic strength environments with a zeta potential of -48 mV. We have proven direct anchoring of monoclonal antibody cetuximab to the nanoparticles enabling targeting of epidermal growth factor receptor, a common target in many cancer types. Fluorescence spectroscopy and relaxivity measurements were used to evaluate and optimize the properties for future imaging applications of tumors. The nanoparticles provide high MRI contrast with a T_1 relaxivity of 42 $s^{-1}mM^{-1}$ Gd, more than two times higher than currently used contrast agents. The finished antibody functionalized nanoparticles are efficiently purified using size exclusion chromatography, separating them from unbound nanoparticles and antibodies. Finally, the cellular uptake of the nanoparticles was evaluated using fluorescence microscopy as well as live/dead assays. We show that the nanoparticles are taken up by cell lines of head- and neck squamous cell carcinoma, in a lysosomal pattern. The nanoparticles are visualized at the nm scale inside the lysosomes using TEM. In conclusion, we have designed and synthesized a versatile nanoparticle with functionalized capping that enables facile fabrication of tailored nanoprobes for biomedical imaging.

4:20pm **BI+AS+EM+NS+SE+TF-TuA-7 Molecularly Imprinted Polymers (MIPs): Rising and Versatile Key Elements in Bioanalytics***, J. Völkle, A. Feldner,* Center for Electrochemical Surface Technology, Wiener Neustadt, Austria*; P. Lieberzeit,* University of Vienna, Faculty for Chemistry, Department of Physical Chemistry, Vienna, Austria*; **Philipp Fruhmann**,* Center for Electrochemical Surface Technology, Wiener Neustadt, Austria **INVITED**

Molecularly imprinted polymers (MIPs) are specific materials with tailored binding cavities complementary to a specific target molecule. Although the first example of artificial materials with molecular recognition were already described 80 years ago, they experienced a surge of popularity since the late 1990s due to improved synthetic methods and their great potential as recognition element in (biomimetic) sensors. MIPs can achieve similar selectivity and sensitivity as antibodies[1], while their robustness and stability is superior compared to biomolecules. They can also be used under non-physiological conditions, are suitable for long-term storage and accessed by scalable synthetic methods. These properties make them highly promising

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[1] **AVS Nellie Yeoh Whetten Awardee**

candidates for a wide range of applications, from biomimetic receptor layers to nanomaterials or artificial antibodies.

Despite this versatility, their design and optimization towards a specific analyte is probably the most challenging task in the development of a sensor. In general, MIP based sensors either rely on electrochemical, mass sensitive or optical transducers and are commonly used as thin film or nanoparticle (nanoMIP). While there is a considerable amount of literature on electrochemical sensors with MIPs available, new developments such as the improvement of conductive MIPs[2], optimized epitope imprinting[3], or the development of novel synthetic techniques such as the solid-phase synthesis of nanoMIPs[4] are highly important for the further development of MIPs in sensing.

For this reason, this presentation will provide an overview about different MIP types, their synthesis, application, and challenges. Furthermore, their potential in future applications with be addressed to give a wholistic impression of the numerous possibilities of this versatile compound class.

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#equal contribution

5:00pm **BI+AS+EM+NS+SE+TF-TuA-9 X-ray Fluorescence Analysis of Metal Containing Cytostatics in HeLa Cells using the Ultra-compact Cryo-vacuum Chamber µ-HORST***, **Lejla Jusufagic**, C. Rumancev, A. Rosenhahn, A. Steinbrück, N. Metzler-Nolte,* Ruhr-University Bochum, Germany

Synchrotron-based X-ray fluorescence spectroscopy (XRF) is an excellent method for investigating elemental distributions and metal concentrations in biological systems.[1-4] The method provides a high sensitivity down to the detection of trace elements with high spatial resolution and penetration depth.[3,4] We introduced an ultra-compact cryogenic vacuum chamber called "µ-HORST" at the P06 nanoprobe beamline at PETRA III, DESY to measure 2D-XRF elemental distribution maps and concentrations in cryogenically fixated cells treated with cytostatic metal complexes with varying ligand sphere.[1,2] The cells are grown on silicon nitride membranes and treated with a 10 µM solution of the metal complexes for different durations and all physiological processes were stopped by rapid cryo-fixation. Cryogenic fixation is a non-destructive method that keeps the cells as close as possible to their biologically hydrated state. The frozen cell samples can be transferred into the µ-HORST setup and maintained in a frozen state throughout the nano-XRF measurements. The acquired data show that the concentration of the metal complexes and their intracellular location can be correlated to the one of physiologically relevant ions such as potassium and zinc as well as associated changes in the metal homeostasis. The developed chamber can not only be used for the analysis of intracellular cytostatic metal complexes, but also to the accumulation of antimicrobial metal complexes or of anthropogenic metals in environmental samples.

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5:20pm **BI+AS+EM+NS+SE+TF-TuA-10 Hemocompatibility Analysis of Novel Bioinspired Coating***, **AnneMarie Hasbrook**, R. Faase, M. Hummel, J. Baio,* Oregon State University

Surface-induced thrombosis is a critical concern in medical device development. To minimize thrombosis, current extracorporeal circulation units require systemic anticoagulation. However, systemic anticoagulants can cause adverse effects such as thrombocytopenia, hypertriglyceridemia, and hyperkalemia. To address this issue, we combine the technology of polydopamine (PDA) functionalization with slippery liquid infused porous surfaces (SLIPS) to potentially enhance the biocompatibility of medical devices. PDA readily coats a wide variety of surfaces and can be functionalized with a thiolated fluoropolymer, via Michael Addition, to form a pseudo self-assembled monolayer (pSAM) which serves as the porous surface component of SLIPS. Liquid perfluorodecalin can then be added to complete the SLIPS coating. We hypothesized that the PDA SLIPS coating provides enhanced hemocompatibility due to its omniphobic properties and composition of compounds currently used in medical applications. Surface modifications were confirmed using contact angle and X-ray photoelectron spectroscopy (XPS) which revealed significant changes to the surface chemistry after the addition of each subsequent layer of PDA SLIPS. The coatings were evaluated for thrombogenicity via quantification of Factor XII (FXII) activation under static and dynamic settings, fibrin formation, platelet adhesion, and clot morphology. The PDA SLIPS coating activated 50% less FXII than glass and 100% more FXII than bovine serum albumin (BSA) coated substrates. PDA SLIPS had similar plasma clotting time to BSA and plasma clotted two times slower on PDA SLIPS than on glass. Platelet adhesion was increased two-fold on SLIPS compared to BSA and decreased two-fold on SLIPS compared to glass. PDA SLIPS had approximately 20% higher fiber diameter and 25% lower clot density than glass and was significantly different in fiber diameter and density than BSA.

5:40pm **BI+AS+EM+NS+SE+TF-TuA-11 Signal Enhancement for Gravimetric Biomimetic Detection – Conjugation of Molecularly Imprinted Polymer Nanoparticles to Metal Nanoparticles***, **Julia Völkle**,* CEST GmbH, University of Vienna, Austria*; A. Weiß, P. Lieberzeit,* University of Vienna, Austria*; P. Fruhmann,* CEST GmbH, Austria

Over the past decades, the field of biosensors and -diagnostics has been increasingly dominated by a growing demand for non-centralized point-of-care devices that do not rely on extensive laboratory infrastructure and trained personnel. Recently, the COVID-19 pandemic has emphasized the crucial role of such fast, reliable, and affordable diagnostic tools. Novel, tailor-made nanomaterials are considered a key component for tackling the upcoming challenges of miniaturization and cost-efficiency in the field of biosensing.

One emerging class of such biomimetic nanomaterials are molecularly imprinted polymer nanoparticles (nanoMIPs). nanoMIPs are artificial receptors that can mimic the highly selective binding capabilities of biological recognition units, such as antibodies and enzymes. Unlike their natural counterparts however, they are stable under a wide range of non-physiological conditions, suitable for long-term storage, and can be derived from a straightforward, rapid synthesis procedure without the need for cell culturing or animal experimentation. Thus, they are ideal candidates for the development of sensitive, robust and inexpensive bioanalogous sensors.

While impressive results regarding their high selectivity and low non-specific binding have been reported [1], nanoMIP-based gravimetric (quartz crystal microbalance, QCM) assays are restricted with regards to the achievable limit of detection by their comparatively low overall mass. This project therefore is focused on the synthesis of well-defined nanoMIP-metal nanoparticle (NP) conjugates, which would result in a larger change in mass upon binding of the recognition units to the QCM transducer. Moreover, conjugation to gold-NPs would allow the incorporation of nanoMIPs into other analytical techniques such as lateral flow devices (LFDs). Experiments therefore are focused on the incorporation of suitable functional groups for further conjugation into the nanoMIP polymer network, the surface functionalization of metal NPs with complementary linker moieties and a suitable coupling procedure. In the poster, nanoMIPs selective for various biologically relevant species are coupled to metal NPs and the performance of the conjugates in QCM-based detection is presented in detail and discussed.

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Advanced Surface Engineering Division
Room Oregon Ballroom 203-204 - Session SE-TuP
Advanced Surface Engineering Poster Session

SE-TuP-1 Characterizations and Drill Performance of AlCrCn Coatings Deposited by High-Power Impulse Magnetron Sputtering, *F. Yang,* National Taiwan University of Science and Technology, Taiwan*; B. Lu, J. Tsao,* Ming Chi University of Technology, Taiwan*; Y. Kuo,* National Taiwan University of Science and Technology, Taiwan*;* ***Chi-Lung Chang,*** Ming Chi University of Technology, Taiwan

In recent years, the production capacity of printed circuit boards (PCBs) has increased significantly resulting in an increase in the demand for micro drills, especially in the requirements of wear-resistant properties. Therefore, various PVD technologies are applied, especially the high power pulsed magnetron sputtering (HiPIMS) technology has the most potential for application, which due to the high ionization rate leads to high density and high mechanical properties of the thin film.

In this study, AlCrCN coatings were prepared via HiPIMS with four Al70Cr30 targets and two Cr targets, with a focus on the effects of carbon content and substrate bias on the microstructure, mechanical properties, and drill performance of the coatings. FE-SEM revealed the interlayers designed to improve adhesion strength from 10 N up to 58N. The highest hardness (3045 Hv) and highest adhesion force (58 N) were obtained by increasing the bias voltage (－75 V) with a carbon content of 9.4 at%. The drill test results showed better wear resistance and useful lifetime than CrAlN coating for PCBs application.

SE-TuP-2 Fabrication of FeCrAlY-Al_2O_3 Composite for Additive Manufacturing, ***Hsin-Mei Kao***, *K. Son, S. Yang, N. Ghanadi, S. Pasebani, B. Paul, C. Chang,* Oregon State University

FeCrAlY is commonly utilized because of its exceptional oxidation resistance, whereas alumina ceramics are valued for their high fracture toughness, resistance to wear, and corrosion[1]. Therefore, developing Al_2O_3-FeCrAlY composites is a promising approach for engineering applications requiring high temperature and strength, such as engines, solid oxide fuel cells, thermal barrier coatings, and catalytic supports[1-2]. The production of these composite powders involves using multiple materials or phases subjected to physical or chemical treatments such as ball milling and fluidized bed chemical vapor deposition to synthesize homogeneous powders. These fabrication processes have produced many functional materials, such as ceramics, metals, and composites, which possess improved mechanical, thermal, or electrical properties[1]. However, these methods are very time-consuming and expensive.

In this study, we investigated a new method to synthesize spherical composite powders consisting of FeCrAlY powders with Al_2O_3 coatings, which are used as feedstock materials for metal additive manufacturing. Chitosan is used as a binder to hold FeCrAlY and Al_2O_3 together, and then the mixture is spray-dried into spherical composite powders. We tailored the sizes and microstructures of the FeCrAlY-Al_2O_3 composite by controlling various parameters such as material content, mixing, flow rates, and reaction temperature. By engineering these composite powders, we can improve the uniformity of material distribution and reduce powder denudation while printing complex structures using metal additive manufacturing technologies. This approach creates a bi-continuous FeCrAlY and Al_2O_3 structure after laser melting and annealing. Furthermore, Al_2O_3 acts as a templating material, which can be selectively etched away, resulting in a highly porous FeCrAlY structure with a large surface area. The composite powders' and printed structures' structure and surface properties were characterized using X-ray diffraction, X-ray 3D tomography, Brunauer-Emmett-Teller analysis, Scanning Electron Microscopy, and Energy Dispersive X-ray Spectroscopy techniques.

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SE-TuP-3 Avoiding Mistakes During the Nanoindentation of Coatings, ***Esteban Broitman,*** SKF B.V. - Research and Technology Development, Netherlands

Nowadays, nanoindentation has become a routinely technique for the mechanical characterization of thin films and small-scale volumes. Thanks to the development of friendly analysis software and advances in high sensitive instrumentation, it feels like the measurement and calculation of hardness and elastic modulus can be easily done by just *"the pushing of one button."* However, the consequences of easy procedures have led many researchers to multiple publications with erroneous data.

Recently, we have reviewed the nanoindentation hardness of materials at macro, micro, and nanoscale (E. Broitman, Tribology Letters, vol. 65, 2017, p. 23). Some misconceptions in the nanoindentation technique were highlighted, and solutions to errors were proposed. In this presentation, five typical mistakes in the measurement and data analysis during the nanoindentation of thin films will be critically reviewed, and the possible ways to avoid them will be discussed: 1) the wrong area selection to calculate instrumented indentation hardness; 2) the wrong data conversion from Vickers microindentation to Berkovich nanoindentation; 3) the confusion of thermal drift with creep and viscoelastic effects; 4) the wrong correlation of hardness with tip penetration; 5) the preconceptions about a direct relationship between elastic modulus and hardness.

The origins of the aforementioned mistakes will be elucidated from the lack of understanding on contacts mechanics theory, the limits and validation of the Oliver and Pharr's method, and preconceptions transmitted from generation to generation of nanoindenter users. At the whole, it will be stressed that it is not enough to know *"how to push the start button of the nanoindeter"* in order to measure the nanoscale mechanical properties of coatings.

SE-TuP-4 Plasma Deposited Si-Rich Silicon Nitride: Deposition, Characterization, thickness scaling limitation and applications in Cap/Passivation of Advanced nano Devices, ***Son Nguyen,*** *V. Pai,* IBM Research Division, Albany, NY*; Y. Yao,* IBM Corporation, East Fishkill Facility*; M. Rizzolo, A. Dutta, D. Canaperi,* IBM Research Division, Albany, NY*; U. Sharma,* IBM Research Division, Albany, NY (IBM Intern**)

Most current nano-electronic devices are using final composited SiNx-SiOy layer to prevent moisture penetration in final devices prior to chip packaging (1). Silicon nitride (SiNx) as a dielectric plays an important role in the semiconductor industry for many years. Si-Rich SiN have been evaluated over the years in electronic device application (2,3). With device scaling to sub-5nm dimension, both passivation and capping layers also needs to scale down to the sub-5nm thickness without compromising the following properties: 1) Excellent Oxidation and diffusion Barrier. 2) High Electrical Breakdown and Low Leakage Current. 3) High stability under thermal stress with low Hydrogen content. 4) Positive performance impacts to the passivating electronic devices including electrical and mechanical properties. 5) Conformal step coverage over high topological structure at low deposition temperature.

This work is focusing on the Si-rich SiNx as an encapsulation film and its ultrathin thickness limitation as oxidation barrier and encapsulation layers. Low-temperature (200^o C -300^{o}C) plasma enhanced chemical vapor deposition (PECVD) process was used to deposit Si-rich SiNx for encapsulation/capping of temperature sensitive nano-electronic devices. Deposition temperature impact on the Si-Rich SiNx capping film's electrical, conformality, oxidation and barrier properties of the films are evaluated with completed material compositional analysis vs film's performance. To obtain a good process at low temperature for encapsulation/capping of temperature sensitive nano-device, novel cyclic multilayers deposition/plasma treatment approach was developed. Ultrathin (3-4 nm) Si-Rich Silicon Nitride film with excellent conformality, oxidation barrier and passivation performance are achieved for passivation/capping with novel cyclic multilayer deposition/plasma treatment approach at low deposition temperature of 200 C and with > 80% conformality over high aspect ratio nanodevice structures. Carbon doped ultrathin (4 nm) SiN (SiCN) was also evaluated and achieved similar robust cap performance for nanodevice fabrication. These high-performance Si-Rich SiN and SiCN films have excellent potential for logic and memory nanodevice as passivation and capping layers.

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SE-TuP-5 Multifunctional Optical Surfaces Using Scalable Nanostructuring

Iliyan Karadzhov, *J. Rombaut, C. Graham, A. Mezzadrelli, J. Arres Chillon,* Institute of Photonic Sciences (ICFO), Spain*; W. Senaratne, R. Bellman, D. Thelen, P. Mazumder,* Corning Research and Development Corporation*; V. Pruneri,* Institute of Photonic Sciences (ICFO), Spain

Current optoelectronic applications such as touchscreen displays, photovoltaic cells or lenses require surfaces that can possess multiple functions, for example, easy optical and/or electrical tunability, high transparency, self-cleaning properties, and antimicrobial properties, to name a few. Borrowing from designs found in nature such as the eyes of nocturnal insects or the lotus leaf, much progress has been made towards bio-inspired surfaces. Yet developing mass-scalable, and cost-efficient methods for fabricating multifunctional optical surfaces is still a major challenge due to the limitation of the existing nanofabrication methods that rely on traditional optical and e-beam lithography. In this talk, we review recent efforts from our group in developing optical surfaces based on the use of ultrathin metal films (UTMF) and solid-state dewetted nanoparticles (DNPs) as a scalable and lithography-free approach to confer functionalities such as high transparency, broadband and omnidirectional antireflection effect, self-cleaning properties, and antimicrobial properties.

Solid-state thermal dewetting of ultrathin metal films (Ag, Cu, Ni) has emerged as a viable strategy to obtain features down to few nanometers, therefore, it has great potential to be implemented as a fast and low-cost method in industrial scale nanofabrication. The dewetted nanoparticles on glass surfaces serve as a mask in creating nanopillars or nanoholes using dry etch process. Initial metal films thickness, temperature, and duration of the dewetting, and dry etching times are the parameters that give us morphological and optical control on the nanostructures. The structured surfaces present omnidirectional broadband antireflection effect with low scattering and have self-cleaning properties. Importantly, structures maintain their optical and wetting properties after repeated abrasion making them attractive to be used in consumer display devices. Moreover, when high aspect ratio nanopillars in fused silica are fabricated, we observe increase of the optical emissivity in the infrared range, which can be exploited for passive radiative cooling. The versatility of dewetted nanoparticles is also shown by using Cu DNPs to make transparent, antimicrobial surface.

SE-TuP-9 Investigating the Microstructure and Mechanical Behavior of the Particle-Particle and Substrate-Particle Interfaces in Cold Sprayed Coatings

Tanvi Ajantiwalay, *S. Niverty, R. Kalsar, V. Joshi, A. Devaraj,* Pacific Northwest National Laboratory

During cold spray, powder particles undergo severe plastic deformation upon impact with the substrate. This results in particle flattening, oxide breakage, and metallurgical bond formation at particle-particle and substrate-particle interfaces. At smaller length scales, heterogeneity of the bond coating can create property differences, which are yet to be explored. Thus, a comprehensive understanding of local interfacial bond strength at this heavily deformed interface would assist in designing optimal cold spray processes. In this study, we investigated the microstructure and mechanical properties of zinc (Zn) cold sprayed on AZ91 magnesium (Mg) substrates via correlative microscopy and in situ micro-tensile testing.Micro-tensile dogbones fabricated using Plasma Focused Ion Beam (PFIB) were tested in a displacement-controlled mode to estimate the interfacial strength and live deformation behavior.

SE-TuP-10 Icephobic Coating Using Polymers/Silica Nanoparticles Composite via Self-Formation of Superhydrophobic Surface

Aravind H. Patil, Incheon National University/ Korea Polar Research Institute, Korea (Democratic People's Republic of)*; N. Trinh,* Incheon National University, Korea (Democratic People's Republic of)*; H. Do,* Korea Polar Research Institute, Korea (Democratic People's Republic of)*; G. Seo, J. Wook Choi,* Seoul National University, Korea (Democratic People's Republic of)*; Y. Kang,* Incheon National University, Korea (Democratic People's Republic of)*; J. Lee, C. Chung,* Korea Polar Research Institute, Korea (Democratic People's Republic of)*; H. Lee,* Incheon National University, Korea (Democratic People's Republic of)

The accretion of ice has resulted in adverse impact on a variety of household, industrial, and polar research station activities. Despite significant efforts being made to prevent ice adhesion with different surfaces by developing various passive anti-icing coatings, it is still essential to enhance overall performance and durability. Herein, we report the designing of icephobic coatings through self-formation of 3D porous micro-nanostructure utilizing siloxane/fluoropolymer/silica nanoparticles (NPs). The spin coating method was used for coating PDMS/PTFE composite on aluminium (Al 6061) substrate. The excellent miscibility and adhesion in PDMS and PTFE were observed due to the secondary electrostatic interactions between H and F atoms. These interactions were supported by the density functional theory (DFT) calculations and structural studies. Moreover, the controlled addition of PTFE powder to PDMS improved the water-repellency properties, mechanical strength, and adhesion strength of the coating. The self-formation of superhydrophobic Cassie Baxter state of PDMS/PTFE composite was achieved by sprinkling SiO_2 NPs on it. The PDMS/PTFE/SiO_2 NPs composites, surface morphology images showed the formation of porous 3D micro-nanostructure that produces a highly textured surface with several trapped air pockets. These air pockets minimise the surface contact area with water droplets or ice, which enhanced the water contact angle (WCA) and reduced the ice adhesion strength (IAS). Additionally, we experimentally demonstrated that the freezing at low temperatures can be delayed by controlling the heat flow rate, interfacial contact area, and surface texture.These results suggest the feasibility of the method for a wide range of promising anti-icing applications.

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Keywords: Superhydrophobicity, Icephobicity, PDMS/PTFE composite, SiO_2NPs, freezing delay time

Applied Surface Science Division
Room B117-119 - Session AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM

Multi-Modal & Multi-Dimensional Analysis

Moderators: Gustavo Trindade, National Physical Laboratory, UK, **Paul Mack**, Thermo Fisher Scientific, UK, **Tim Nunney**, Thermo Fisher Scientific, UK

8:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-1 Growth and Characterization of Large-Area 2D Materials***, Glenn Jernigan,* US Naval Research Laboratory **INVITED**

Nothing could be more coupled than Growth and Characterization. When two dimensional (2D) materials appeared on the radar of the scientific community (with the amazing properties of graphene), it was immediately obvious that large area samples would be needed. Exfoliating flakes was insufficient for the demands of scientific studies, in addition to not being viable should a commercial application be developed. Thus, the search began for growth methods to produce large-area 2D materials for large scale testing and development.

The Naval Research Laboratory has, over the past 15 years, pursued research programs in producing large areas of graphene, transition metal dichalcogenides (TMDs), boron nitride (BN), and other 2D materials. In every one of those programs, they began with surface analysis of composition, chemistry, and morphology of the grown films. The uniquely sensitive nature of x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and scanning tunneling and atomic force microscopy (STM and AFM) to 2D materials was necessary to measure the electrical, chemical, and physical properties obtained in the large area films and to understand what was observed in the exfoliated flakes. The production of large areas allowed “mass-scale” optical and electrical characterization, which then became a feedback loop in the search for new and interesting properties and relevant applications. In this presentation, I will show how we developed large-area graphene, by both epitaxial growth and chemical vapor deposition methods, TMDs, and other 2D materials for characterization and device utilization.

8:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-3 Using a Correlative Approach with XPS & SEM to Measure Functionalized Fabrics for Antimicrobial Applications***, **Tim Nunney**, H. Tseng,* Thermo Fisher Scientific, UK*; D. Marković, M. Radetić,* University of Belgrade, Serbia

Medical textiles are an indispensable component for a wide range of hygienic and healthcare products, such as disposable surgical gowns and masks, or personal protection equipment, with opportunities to provide further protection by engineering textiles with suitable medical finishing. While antibiotics are considered a viable option for their efficiency in treating bacterial infections, their abuse can result in adverse effects, e.g., bacteria resistance. Nanocomposites have emerged as a promising alternative to antibiotics, as the large surface-to-volume ratio and high activity helps attain the targeted antimicrobial efficiency by using tiny amounts of nanocomposites, and their biocompatibility and scalability are particularly advantageous for medical applications [1]. Thus, developing processing methods to integrate nanocomposites in the fabrics is essential for exploiting their properties for medical textiles.

In this study, polypropylene fabrics, alginate and copper oxides, were selected to develop novel antimicrobial nanocomposites based on various surface treatments, i.e. corona discharge and alginate impregnation, which led to improved fabrics hydrophilicity with functional groups introduced as binding sites for Cu(II), a precursor that formed Cu nanoparticles when reacted with reducing agents, i.e. NaBH4 and ascorbic acid. The composition of the fabrics after being treated with corona discharge and impregnation observed by XPS indicates the materials formed mainly consisted of C and O, attributed to the presence of a thin, hydrophilic layer and alginate, respectively, consistent with depth profiling measurements. Following Cu reduction, XPS mapping of the fabrics finds that, reacting with ascorbic acid resulted in formation of nanocomposites containing a mixture of Cu and Cu (II) oxides across the surface, which could be visualised by using SEM in the same locations. Excellent anti-microbial activity against Gram-negative bacteria E. coli, Grampositive bacteria S. aureus and yeast C. albicans was observed for the treated fabrics[2]. This result not only demonstrates a cleaner, and healthier approach for developing novel nanocomposites, but more importantly highlights the role of surface techniques in uncovering challenges in designing and engineering functional textiles.

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9:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-4 Multi-Modal Analysis in Photoelectron Spectroscopy: From High-Resolution Imaging to Operando Experiments***, **Olivier Renault**,* CEA-Leti, France*; A. Benayad,* CEA, France*; N. Gauthier,* CEA-Leti, France*; R. Charvier,* ST Microelectronics, France*; E. Martinez,* CEA-Leti, France

Over the past years, the field of surface and interface analysis has been greatly expanded by new developments made possible by lab-scale instruments enabling higher excitation energies. These new developments are directly serving technological advances especially in the area of technologies in renewable energies and nanoelectronics, which are adressing more and more complex system requiring to go beyond traditional ways of characterizing surfaces and interfaces. Different dimensions are to be explored in multi-modal surface analysis : the depth dimension, the lateral dimension, and the dynamic dimension.

After a short review of some of the achievements towards enhancing the depth dimension by lab-scale hard X-ray photoelectron spectroscopy (HAXPES) and the lateral dimension using X-ray PEEM, we will present different application cases of *operando* HAXPES. Here, the material is analyzed as being part of a device operated *in situ* during the experiment, in conditions that are as close as possible to the final applications and where the interfaces can be studied in dynamic conditions. We will first review some results of *operando* HAXPES on resistive memories obtained with synchrotron radiation [1, 2] before presenting various lab-scale experiments [3, 4] and the current limitations to such approaches.

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9:20am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-5 Multi-Modal Analyses of Ultrasonic-Spray-Deposited Ultrathin Organic Bathocuproine Films***, J. Chen, **Juliet Risner-Jamtgaard**, T. Colburn, A. Vailionis, A. Barnum, M. Golding,* Stanford University*; K. Artyushkova,* Physical Electronics*; R. Dauskardt,* Stanford University

Bathocuproine (BCP) is a small organic molecule that is typically used as an ultrathin hole blocking interlayer (< 10 nm thickness) in organic solar cells and perovskite solar cells. The film is typically deposited via low-throughput vacuum thermal evaporation with an *in-situ* Quartz Crystal Monitor to measure film thickness. Open-air ultrasonic spray deposition for low-cost and large-scale deposition is an attractive alternative method for solution processing of BCP films, but the process lacks a comparable *in-situ* metrology. Given that the BCP film is transparent to visible light and ultrathin, it is important to utilize a multi-modal approach to evaluate optoelectronic and physical properties of the sprayed film.

A suite of characterization techniques that span a range of equipment complexity, measurement time, and measurement sensitivity are used to analyze the BCP films. We begin by demonstrating the limitations of the singular ellipsometry model[1] for BCP found in literature and motivate a need to rely on other techniques. Multi-modal analyses including X-Ray Reflectivity, Angle-Resolved X-ray Photon Spectroscopy (AR-XPS), Auger Spectroscopy, Scanning Electron Microscopy, and Transmission Electron Microscopy with EELS are then performed on the sprayed BCP film. The advantages and disadvantages of each characterization technique are compared and discussed. We conclude that AR-XPS provides the most distinctive determination of individual layer thicknesses for a sample architecture consisting of silicon substrate/native SiO_x/BCP across the applicable range of AR-XPS from ~ 1-10 nm.

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9:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-6 Combinatorial Synthesis and High-Throughput Characterization of Pt-Au Thin Films Fabricated by Confocal Magnetron Sputter Deposition***, **David Adams**, R. Kothari, M. Kalaswad, C. Sobczak, J. Custer, S. Addamane, M. Jain, E. Fowler, F. DelRio, M. Rodriguez, R. Dingreville, B. Boyce,* Sandia National Laboratories

A few binary metal alloys are predicted to form thermally stable, compositionally segregated structures owing to the thermodynamic preference for minority species to collect and remain at grain boundaries established within the solid.(J.R. Trelewicz et al., PRB, 2009) When produced as a nanocrystalline thin film, these stable structures afford the potential to maintain excellent mechanical properties (e.g., high hardness) even after annealing to elevated temperature. Indeed, several systems, including Pt$_{.9}$Au$_{.1}$ thin films, are reported to develop thermally-stabilized, hard, nanocrystalline structures attributed to solute segregation at grain boundaries.(P. Lu et al., Materialia, 2019)

Future studies that seek optimal stoichiometry and/or preferred synthesis processes require access to a wide range of composition as well as an ability to vary key deposition parameters. Toward this end, our team reports on the challenges and the benefits of combinatorial synthesis for expediting the discovery of improved binary metal thin films. Our study utilized confocal sputter deposition wherein Pt and Au targets were individually sputtered via pulsed DC magnetron methods. Substrates (150 mm diameter wafers) were fixed in order to gain access to a wide compositional range for each deposition. The sputter power and cathode tilt orientation were then varied in subsequent depositions to access the nearly full binary metal compositional range. The binary collision Monte Carlo program SiMTra (D. Depla et al., Thin Solid Films 2012), which simulates the transport of sputtered atoms within the process gas, helped guide the selection of these process parameters in order to achieve compositional goals in relatively few depositions. Notably, the binary compositions predicted by SiMTra closely matched (within a few molar %) the measured compositions determined by Wavelength Dispersive Spectroscopy completed in 112 different areas across each wafer. The various combinatorial Pt-Au films were further characterized by high-throughput Atomic Force Microscopy, automated X-ray Diffraction, fast X-ray Reflectivity, mapping four-point probe sheet resistance, and automated nanoindentation. These studies reveal how hardness, modulus, film density, crystal texture, and resistivity of combinatorial films varied with composition as well the atomistics of film deposition. Attempts to correlate key film characteristics with the kinetic energies and incident angles of arriving metal species (estimated by SiMTra) are discussed with a goal of improving fabrication processes.

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11:00am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-10 Optical and X-Ray Characterization and Metrology of Si/Si(1-X)Ge(X) Nanoscale Superlattice Film Stacks and Structures***, **Alain Diebold**,* SUNY Polytechnic Institute **INVITED**

As traditional scaling of transistors comes to end, transistor channels and capacitors are being stacked to form new 3D transistor and memory devices.Many of these devices are fabricated using films stacks consisting of multiple Si/Si(1-x)Gex layers known as superlattices which must be fabricated with near atomic precision.In this talk, we discuss how Optical and X-Ray methods are used to measure the feature shape and dimensions of these structures.The use of X-Ray methods such as ω-2θscans and reciprocal space maps provide layer thickness and stress characterization. We will use simulations to show how a buried layer with a different thickness or Ge concentration alters the data. Recent electron microscopy studies have quantified the stress at the interfaces of these superlattices.We will also discuss how Mueller Matrix spectroscopic ellipsometry (MMSE) based scatterometry is used to measure feature shape and dimension for the nanowire/nanosheet structures used to fabricate nanosheet transistors and eventually 3D DRAM.The starting point for optical scatterometry is determining the optical properties of stressed pseudomorphic Si(1-x)Gex.MMSE can be extended into the infra-red and into the EUV.In addition, small angle X-Ray scattering has been adapted into a method knows as CDSAXS which can be used to characterize these structures.This talk will be an overview of these methods.

11:40am **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-12 Non-Destructive Depth Differentiated Analysis of Surfaces Using Ion Scattering Spectroscopy (ISS), XPS and HAXPES***, **Paul Mack**,* Thermo Fisher Scientific, UK

Recently there has been renewed interest in probing deeper into surfaces using HAXPES in addition to the more surface sensitive (soft X-ray) XPS. On modern XPS systems, with high sensitivity, the total sampling depth may be somewhere between 10nm and 15nm but HAXPES enables the analyst to look deeper, without having to destructively sputter the surface with ions. For a complementary, more comprehensive analysis, XPS and HAXPES can be combined with Ion Scattering Spectroscopy (ISS). ISS is far more surface sensitive than XPS, typically being thought of as a technique to analyse the top monolayer of a sample for elemental information.

In this work, the combination of XPS, HAXPES and ISS on a single tool has been used to give a non-destructive depth differentiated analysis of a range of samples, including a perovskite and an industrially relevant material containing multiple transition metals. The combination of all three techniques provides insight into the depth distributions of elements and chemical states, from the top monolayer to beyond 20nm into the surface.

12:00pm **AS+2D+CA+EL+EM+MS+NS+SE+SS+TF-WeM-13 Towards Measurement of Molecular Shapes Using OrbiSIMS***, **Gustavo F. Trindade**, J. Vorng, A. Eyres, I. Gilmore,* National Physical Laboratory, UK

An OrbiSIMS [1] instrument features a dual analyser configuration with a time-of-flight (ToF) mass spectrometer (MS) and an Orbitrap^{TM} MS, which confer advantages of speed and high-performance mass spectrometry, respectively. The ability to combine the MS performance usually found in a state-of-the-art proteomics and metabolomics MS with 3D imaging at the microscale and from nanolayers of <10 nm of material has proved popular in a broad field of application from organic electronics to drug discovery. For secondary ions to be efficiently transferred to the Orbitrap analyser, the sample is biased by a target voltage V_T necessary to match the acceptance window of the Orbitrap. Furthermore, the ions kinetic energy from the SIMS collision process must be reduced. Therefore, in the OrbiSIMS, a transfer system with helium gas at a pressure P_{He} slows the ions and reduces their kinetic energy distribution through inelastic collisions with gas atoms. Usually, an Orbitrap is used with an ambient pressure ion source and so here an extra gas flow of nitrogen is introduced that leads to an increase of pressure P_{N2} to compensate.

We conducted a systematic assessment of V_T and P_{He} and P_{N2} on the transmitted secondary ion intensities [2] and revealed a complex behaviour, indicating the possibility for additional separation of ions based on their shape, stability, and kinetics of formation. We showed that the V_T for maximum transmission of secondary ions will not be the same for all molecules of the same material and that sometimes multiple maxima exist. Here, we present recent progress towards the understanding of these phenomena and how we are leveraging it to measure molecular shape by using reference trisaccharides raffinose, maltrosiose and melozitose [3].

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[2] L. Matjacic *et al.*, “OrbiSIMS metrology part I: Optimisation of the target potential and collision cell pressure,” *Surf. Interface Anal.*, no. November 2021, pp. 1–10, 2021, doi: 10.1002/sia.7058.

[3] G.F. Trindade *et al.*, In preparation.

Thin Film Division
Room A105 - Session TF2+AP+SE+SS-WeM

Controlling Microstructure and Accessing Non-Equilibrium Phases in Thin Films

Moderators: Robert Grubbs, IMEC Belgium, **Richard Vanfleet**, Brigham Young University

11:00am **TF2+AP+SE+SS-WeM-10 Stabilizing Polar Polymorphs of Scandium Ferrite for Photovoltaics***, M. Frye, **Lauren Garten**,* Georgia Institute of Technology **INVITED**

Metastability is no longer synonymous with unstable or unattainable, but further work is needed to enable the next generation of electronics and photovoltaics. In this talk I will discuss the development of a stabilization route for the P63cm phase of ScFeO3 through precursor control and interface engineering. The P63cm phase has potential for lead-free piezoelectric, photo-ferroic, and ferroelectric applications. Unfortunately, this phase is in competition with four other known polymorphs that are similar in structure and energy and there is not a well matched epitaxial substrate. So we took a different approach by controlling the atomic layering of the precursor structure and the deposition timing to stabilize the P63cm phase under conditions that previously lead to the ground state. The film structure is verified by transmission electronic microscopy and x-ray diffraction. Ab initio calculations confirm that layered growth stabilizes the metastable phase and highlights the importance of the variable oxidation state of iron, the high activation energy against diffusion, and the surface termination of the substrate in designing a stabilization approach. This work highlights routes to access similar polymorphs on an array of different substrates, opening up new materials and new device architectures.

11:40am **TF2+AP+SE+SS-WeM-12 The Role of Thermal Vibrational Disorder in the Structural Phase Transition of VO₂ Probed by Raman Spectroscopy***, **Aminat Oyiza Suleiman**,* Institut National de la Recherche Scientifique, Canada*; S. Mansouri,* Institut National del a Recherche Scientifique, Canada*; N. Émond,* Massachusetts Institute of Technology, Canada*; T. Bégin, J. Margot,* Université de Montréal, Canada*; C. Mohamed,* National de la Recherche Scientifique, Canada

Vanadium dioxide (VO_2) is a typical correlated electron material which exhibits a first-order metal–insulator transition (MIT) at a near-room temperature of about 340 K. Upon heating, VO_2 switches from an insulating monoclinic phase (M1 or M2) to a metallic tetragonal rutile phase (R). The mechanism behind the MIT in VO_2 is still controversial: Is it a structure driven Peierls transition mechanism or a Mott transition where strong electron-electron correlations drive charge localization and collapse the lattice symmetry? By directly comparing the electrical and lattice–dynamic properties of VO_2, useful information about the MIT/SPT in VO_2 can be obtained.

Herein, we therefore present a detailed Raman study of undoped (M1) and Cr-doped (M2) VO2 thin films as a function of temperature. The studied VO_2 films with different thicknesses are deposited on c- and r-sapphire substrates. While their structural properties and morphology are examined by XRD and AFM techniques, respectively, Raman measurements are correlated to four-point probe resistivity measurements, giving an insight into the coupling between VO_2 structural phase (SP) and MI transitions. By distinctively combining the Raman data with information from reported EXAFS data, a relationship between the Raman intensities and the mean Debye-Waller factors (σ^2: the mean-square relative displacements) is established. The temperature dependence of the vanadium dimers Waller factor (σ_R^2 (V-V)), as calculated from the Raman intensity, was found to follow the temperature profile of the σ_{EXAFS}^2 (V-V) obtained from the reported EXAFS data. These findings provide an evidence on the critical role of the thermal vibrational disorder in VO_2 phase transitions, demonstrating that by correlating Raman data with EXAFS analysis, both lattice and electronic structural dynamics can be probed.

12:00pm **TF2+AP+SE+SS-WeM-13 Interplay of Lattice Distortion and Electronic Structure in Metastable Brookite TiO₂***, **Pritha Biswas**,* Oregon State University*; M. Choi, K. Koirala, M. Bowden, L. Strange,* Pacific Northwest National Laboratory*; H. Zhou,* Argonne National Laboratory*; J. Tate,* Oregon State University*; Y. Du, T. Kaspar, D. Li, P. Sushko,* Pacific Northwest National Laboratory

Controlling the coupling between lattice distortions and electronic properties is one of the promising routes toward enhancing the performance of materials used in energy technologies, such as photocatalysis, photovoltaics, and energy storage. Oxide semiconductors that exhibit polymorphism represent a convenient class of systems to study this coupling by investigating the effect of external stimuli on transition pathways between polymorphs. Among the oxide semiconductors, earth-abundant TiO_2 exists in several polymorphic forms, including rutile, anatase, and brookite, with distinctly different structural symmetries. Compared to the common rutile and anatase polymorphs, metastable brookite TiO_2 is the least studied one due to the difficulties associated with its synthesis in a phase pure form. At the same time, mechanisms of its transformation to the more stable anatase and rutile polymorphs are promising to provide a rich insight into the relationships between the character of the lattice deformations, defect content, and electronic structure. We have developed a recipe for phase selective TiO_2 polymorph formation, where tuning of oxygen vacancy concentration drives the crystallization of amorphous TiO_2 thin films towards a specific polymorphic structure. In this study, thermal treatment was used to control the evolution of as-deposited, sputtered amorphous TiO_2 thin films towards the brookite lattice. The crystallinity and phase purity of the resulting structures were investigated by lab-based grazing incidence XRD, synchrotron XRD, and transmission electron microscopy. The dependence of structural variations present in the sample on the details of the annealing treatments was evaluated using Rietveld refinement analysis. X-ray photoelectron spectroscopy (XPS), confocal Raman spectroscopy, and high-resolution transmission electron microscopy (HRTEM) were used to understand the effect of local deformation on the electronic structure of brookite. We found a correlation between the degree of lattice parameter deviation, shifts of the Raman vibrational modes, and the position of the brookite valence band. The effect of these lattice distortions at the atomic scale on the photocatalytic activity of brookite will be discussed.

Applied Surface Science Division
Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-WeA

Quantitative Surface Analysis I

Moderators: David Cant, National Physical Laboratory, UK, **Peter Cumpson**, University of New South Wales, **Christopher Moffitt**, Kratos Analytical Inc, **Lev Gelb**, University of Texas at Dallas

2:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-1 Status of Efforts to Upgrade the Quality of Surface Analysis Data in the Literature***, **Donald Baer**,* Pacific Northwest National Laboratory

Multiple efforts are being undertaken to address a growing presence of faultysurface analysis data and/or analyses appearing in the literature. Issues include bad data, incorrect analysis, and highly incomplete reporting of instrument and analysis parameters. This talk describes the status of four efforts to address some of the issues. Recognition of this problem within the surface analysis community has increased with an understanding that both inexperienced users and increased use of surface analysis methods outside the surface analysis community contribute to the problem. The current efforts build upon decades of development and efforts by standards committees, excellent books and journal publications, websites, short courses, and other efforts. A collection of guides, protocols and tutorials addressing reproducibility issues with a significant *focus on XPS* was published in JVSTA in 2020/21. A second collection, *Reproducibility Challenges and Solutions II,* with a more general focus on Surface and Interface Analysis was initiated in 2022 and is being finalized. The second collection addresses several techniques, including SIMS, SPM, and UPS, and includes topics such as theoretical modeling and machine learning in data analysis. A second effort focuses on a part of the community less interested in general understanding but needs to answer specific surface analysis questions. A new type of paper called Notes and Insights is being published in the journal Surface and Interface Analysis with the objective to provide incremental bits of useful information of importance to non-expert analysts. Two additional activities are underway to assist with reporting issues. Examination of papers in multiple journals found that instrument and analysis related information needed to assess or reproduce data is often incomplete or absent. To assist authors in reporting instrument parameters, papers describing in some detail related families of commercial instruments are being prepared for Surface Science Spectra. These papers describe the instrument, major components, geometry and provide example data related to common data collection modes. Authors will be able to reference these papers and identify specific modes of instrument operation used in their research. Another parameter reporting activity concerns sample handling before analysis. ISO Technical Committee 201 is developing a series of documents (ISO 20579 parts 1 to 4) on what needs to be reporting regarding sample handling, storage, processing, and mounting for analysis. These standards describe what needs to be reported and contain informative annexes that provide information regarding the needs and challenges to proper sample handling to produce reliable useful surface analysis data.

2:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-2 The behavior of the Shirley background of the Ti 2*p* spectra across the Ti 1*s* edge***, **Dulce Maria Guzman Bucio**,* CINVESTAV-Unidad Queretaro, Mexico*; D. Cabrera German,* Universidad de Sonora, Mexico*; O. Cortazar Martinez, J. Raboño Borbolla,* CINVESTAV-Unidad Queretaro, Mexico*; M. Vazquez Lepe,* Universidad de Guadalajara, Mexico*; C. Weiland, J. Woicik,* National Institute of Standards and Technology*; A. Herrera Gomez,* CINVESTAV-Unidad Queretaro, Mexico

A wide variety of photoemission spectra display a step-shaped background, called the Shirley-type background, which should be accounted for in the total background signal for reliably assessing chemical composition. However, it cannot be modeled with any method based on extrinsic processes like the inelastic dispersion of the photoelectrons (e.g., Tougaard-type backgrounds). Although its physical origin is still unknown, experimental data suggest that the Shirley-type background is due to phenomena occurring inside the atom [1,2]. To gain insights into those phenomena, we studied the behavior of the Shirley-type background for the Ti 2*p* photoemission spectra.

In this work, Ti 2*p* photoemission spectra were acquired with Synchrotron light (at Beamline 7-2 at the Brookhaven National Laboratory) from a clean metallic titanium film (sputtered on a Si (100) substrate) capped with an ultra-thin aluminum layer. The spectra were collected with 44 excitation energies around the Ti 1*s* edge. By simultaneously fitting Ti 2*p* photoemission spectra obtained with excitation energies higher than the Ti 1*s* edge, we robustly determined the peak structure of the Ti 2p spectra. Outstandingly, the parameter of the Shirley-type background associated with the Ti 2*p* peak structure is modulated as the photon energy crosses the Ti 1*s* edge. The relation of this phenomenon with the physical origin of the Shirley background will be discussed. The $KVL_{2,3}$ Auger peaks—which overlap with the Ti 2*p* peaks—do not have a step-shaped background for most of the excitation energies.

Acknowledgments:

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3:00pm **AS+CA+EL+EM+SE+SS+TF-WeA-3 Chemical Analysis of Multilayer System by Photoemission: The Binding Energy Reference Challenge***, **Thierry Conard**, A. Vanleenhove,* IMEC Belgium*; D. Desta, H. Boyen,* University of Hasselt, Belgium

XPS is a well-established technique used for non-destructive analysis of the chemical composition of thin layers and interfaces. It 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.

Increasing the number of analyzed (insulating) layers enhances the risk of significant vertical differential charging and makes the repeatability of binding energy determination more challenging. 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.

In this work, we will examine the influence of measurement conditions in single and multiple layers systems relevant to the microelectronic industry on the determination of precise binding energies.

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 oxide layers Si samples and metal/high-k/Si stacks including high-k materials as HfO_2 and Al_2O_3. The surface potential will be precisely set and monitored in situ by depositing a metallic layer (such as Ag) on top of the stack and applying an external potential instead of using an electron neutralization source. 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.

3:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-4 Where Are We on the Road-Map to Artificially Intelligent Interpretation of X-ray Photoelectron Spectra?***, C. Moffitt,* Kratos Analytical Inc*; A. Roberts, J. Counsell, C. Blomfield, **Kevin Good**, K. Macak,* Kratos Analytical Limited, UK

Robust peak identification is crucial for accurate sample analysis using X-ray photoemission spectroscopy (XPS). Automation of peak ID enhances this process by minimizing user error and bias. Current acquisition software offers improved computer-derived peak identification from unknown samples, instilling confidence in the correct identification of elements. Moreover, this forms the foundation for an automated sample analysis workflow known as Data-dependent Analysis (DDA). DDA involves identifying peaks in a survey spectrum and subsequently acquiring high-resolution spectra from major components. A recent User survey revealed that a significant majority of users rely on the large area survey acquisition mode as a starting point for analysis.

To provide a metric for confidence in the DDA process, existing spectral analysis data, which includes the element composition information, is used to generate reference spectra for testing purposes. These reference spectra serve as the basis dataset against which the performance of the automated analysis algorithm can be evaluated. By comparing the results of the algorithm with the reference spectra, statistical parameters can be calculated to assess the algorithm's precision, sensitivity, specificity, and accuracy in identifying elements of unknown spectra.

For experienced analysts, DDA serves as a time-saving acquisition method, while for inexperienced analysts, it provides assurance in accurate peak identification and appropriate high-resolution spectra acquisition. Here we highlight current status of automated XPS data acquisition in relationship to the 'expert system', championed in the early 2000's and full AI interpretation of XPS spectra of the future.

4:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-7 Thin Film Analysis by XPS: Quantitative Analyses Using Physics-Based and Machine-Learning Approaches***, **Lev Gelb**, N. Castanheira, A. Walker,* University of Texas at Dallas

We present progress towards quantitative analysis of XPS data using both model-based "fitting" approaches and machine learning methods. Two separate applications are considered.

The first concerns the simultaneous extraction of both compositional profiles and sputtering parameters from XPS sputter depth-profiles of multilayer films. Depth-profile data are routinely processed to provide "fractional composition vs ion dose" profiles, but such analyses typically assume the sample is homogeneous in the probed region, which is not true near interfaces, and cannot precisely convert between units of ion dose and depth without extensive calibration data. Our approach is to first construct analytical models for both the sample structure and for the sputtering process, and then to determine the model parameters (layer thicknesses, interfacial widths, material removal rates, etc.) that are most likely given the observed apparent fractional composition profiles. This is done numerically, by iteratively comparing simulated and observed apparent composition profiles. The only additional required inputs are the inelastic mean free paths for each tracked peak in each material present. The efficacy of this approach is demonstrated using both synthetic and experimental data sets, and various model improvements (sputter-induced mixing, *in situ* chemical reactions) are discussed.

The second application concerns the application of machine-learning tools to remove the inelastic scattering background from XPS spectra in order that accurate peak areas can be obtained. Our approach here is to generate a training data set which consists of a thousands of simulated XPS spectra with and without inelastic scattering included. This is accomplished using the SESSA software package[1]. This data set is then used to train a neural network algorithm to output a "no-background" spectrum from an input "with-background" spectrum; this output spectrum can then be used to compute peak areas for compositional analysis. The training set generation methodology and network structure are discussed, and application of the tool to both simulated and experimental spectra is demonstrated.

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4:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-8 Room Temperature Ionic Liquids as Reference Materials for Photoelectron Spectrometers***, **Benjamen Reed**,* National Physical Laboratory, U.K.*; J. Radnik,* BAM Berlin, Germany, UK*; A. Shard,* National Physical Laboratory, U.K.

Room-temperature ionic liquids (RTILs) are materials consisting of organic salts that are liquid below temperatures of 100°C and are used in several fields including electrochemistry,[1] pharmaceutics, and medicine.[2] RTILs have several notable properties that make them ideal for X-ray photoelectron spectroscopy (XPS) analysis. They have an extremely low vapor pressure and high surface tension, and so can be analysed using conventional XPS under ultrahigh vacuum without the need for near-ambient pressure instrumentation. Also, when deposited in a recessed sample holder, the meniscus of an RTIL will be perfectly flat meaning that there are no contributions from sample topographic effects. Finally, and most importantly, they are highly homogeneous and have well-defined stoichiometries.[3]

These properties make RTILs potential reference materials for validating the intensity calibration of a photoelectron spectrometer. RTILs with non-coordinating bistriflimide (NTf_2) anions (e.g. $PMIM^+NTf_2^-$) or dimethyl phosphate (DMP) anions (e.g. $MMIM^+DMP^-$) are such candidates, with core levels up to ~800 eV binding energy, making them apt for verifying the quantification of light elements, especially for organic materials.[4,5]

To accurately determine peak areas, however, requires the principal and secondary photoelectron signals to be deconvolved. Previous attempts by multiple laboratories using different quantification methods give a mean atomic composition within 1 at.% of the known stoichiometry, but some individual elements (such as fluorine) exhibit differences greater than 1 at.% because the elastic and inelastic secondaries are not suitably deconvolved. Attention must be paid to the energy loss function that defines the inelastic background over the full energy range of an XPS spectrum so that a suitable Tougaard background subtraction can be applied.[6] Here we present a study on several RTILs and discuss how they may be used to validate an XPS intensity calibration and provide confidence in measurements to XPS instrument operators.

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[5] X. Knigge and J. Radnik, *Surf. Sci. Spectra***30**, 014006 (2023).

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5:00pm **AS+CA+EL+EM+SE+SS+TF-WeA-9 Fractional Coverage Analysis of Monolayers with XPS and Non-Destructive Depth-Profiling with Combined Soft and Hard X-Rays***, **Norbert Biderman**, K. Artyushkova, D. Watson,* Physical Electronics USA

X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. Angle-resolved XPS (AR-XPS) has been used to determine composition of depth profiles and layer thicknesses, traditionally with Al Kα (1486.6 eV) X-ray beams for depths up to 5-10 nm below the surface. In recent years, new AR-XPS capabilities have been added to Physical Electronics XPS scanning microprobe instruments including Cr Kα (5414.8 eV) hard X-ray photoelectron spectroscopy (HAXPES) that can probe buried interfaces up to 15-30 nm below the surface. Coinciding with the HAXPES development, the StrataPHI analysis software was developed to reconstruct quantitative, non-destructive XPS/HAXPES depth profiles from angle-dependent and single-angle photoelectron spectra.

In this talk, we will show that the StrataPHI software has been further developed to combine Al Kα and Cr Kα XPS and HAXPES data within a single depth profile to enhance extracted analytical information from various depths below the surface. We will explore the method of the combined technique as well as its application to multilayered thin film samples. The updated StrataPHI software also includes a fractional coverage analysis mode, relevant in situations where ultra-thin films exist as discrete islands – commonly observed in early thin-film deposition stages on the substrate rather than as a continuous, uniform film. A model system of discrete molybdenum sulfide (MoS2) monolayer triangles deposited on SiO2/Si substrate will be discussed.

Such added StrataPHI capabilities allow for scientists and engineers in metrology and research & development to analyze multi-layered thin films and ultra-thin films rapidly and non-destructively without potentially damaging ion beam sputtering that might otherwise be required to depth-profile or sputter-clean adventitious contamination off the surface.

5:20pm **AS+CA+EL+EM+SE+SS+TF-WeA-10 Reassessing the Reduction of Ceria in X-Ray Photoelectron Spectroscopy**, ***David Morgan,*** Cardiff University, UK

Given its excellent redox abilities, the use of cerium dioxide (CeO_2, ceria) and related materials in catalysis is widespread [1]. This Ce^{3+}/Ce^{4+} redox shuffle allows for great catalytic ability and a method of correlation of catalytic activity to the state of ceria [2–4].Given that catalysis is a surface mediated process, XPS is critical in the analysis of pre- and post-mortem materials.

Over the years there has been debate on the degree of reduction of CeO_2 during XPS analysis. Therefore, in continuation of our work on understanding the reduction of materials in modern spectrometers [5], we have investigated different cerium oxide preparations and shown that not only is the rate of reduction dependent on instrument type and experimental configuration (and hence appropriate analysis protocols should be implemented), but is also related to the morphology of the cerium which may, at least in part, account for the discrepancies in the degree of reduction in the literature. It is postulated that reduction rates could be used to indicate likely ceria morphology where other analysis is unavailable.

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Acknowledgements

This work acknowledges the EPSRC National Facility for XPS (‘HarwellXPS’), operated by Cardiff University and UCL, under contract No. PR16195, and C.M.A. Parlett and X. Zhou for provision of nanostructured ceria materials.

5:40pm **AS+CA+EL+EM+SE+SS+TF-WeA-11 Using High Sensitivity – Low Energy Ion Scattering Spectroscopy (LEIS) to Unravel the Complex Nature of High Entropy Alloys**, ***Matthias Kogler,*** *C. Pichler,* Centre for Electrochemistry and Surface Technology (CEST GmbH), Austria; *M. Valtiner,* Vienna University of Technology, Austria

Complex metallic materials such as Multi-Principal Alloys (MPEAs) and High Entropy Alloys (HEAs) have emerged as a promising class of materials given their unique inherent characteristics. Excellent mechanical, thermal, and corrosion properties allow for a broad spectrum of applications. However, due to the multi-element nature of these alloys, characterisation of the composition and microstructure proves to be a challenging task.

Especially with regard to corrosion-protective passivation films, the complex correlations with the corrosion behaviour are fully unclear to date, and require an in-depth atomic level characterisation and rationalisation. However, the precise layer by layer structure of such passive films is particularly demanding to assess, since traditional techniques such as XPS (X-ray photoelectron spectroscopy) or AES (Auger electron spectroscopy) have analysis penetration depths of several nanometres and cannot reach atomic layer resolution. However, to fully understand and quantify the passivation layer structure, such an atomic layer resolution of the surface region is necessary, due to the complexity of HEAs.

In order to obtain an exact understanding of the atomistic mechanism at the monoatomic layer level, High-Sensitivity - Low Energy Ion Scattering Spectroscopy (HS-LEIS), was applied, which provides the required monolayer sensitive resolution to study the passivation layers of such complex multi-component alloys. The unique surface sensitivity combined with the implementation of in-situ treatment methods enabled the real-time study of oxide layer growth, as well as the analysis of temperature-dependent changes in the elemental surface composition. Due to the high resolution achieved by static and dynamic sputter depth profile modes, we could determine the exact composition of the HEA passivation layer with resolution on atomic monolayer scale.

The findings provide the potential to significantly advance the current understanding of the passivation behaviour of MPEAs and HEAs, and the development of novel metallic materials with superior properties. Valuable insights for understanding the material characteristics for those highly advanced materials could thereby be generated.

Applied Surface Science Division
Room B117-119 - Session AS+CA+EL+EM+SE+SS+TF-ThM

Quantitative Surface Analysis II

Moderators: Samantha Rosenberg, Lockheed Martin, **Thierry Conard**, IMEC, Belgium, **Benjamen Reed**, National Physical Laboratory, UK

8:00am **AS+CA+EL+EM+SE+SS+TF-ThM-1 OrbiSIMS: Signal, Noise and Transmission Are Three Sides of a Metrology Triangle***, G. Trindade, Y. Zhou, A. Eyres,* National Physical Laboratory, UK*; M. Keenan,* Independent*; **Ian Gilmore**,* National Physical Laboratory, UK

In metrology, the science of measurement, a “metrology triangle” approach is used to provide a secure foundation. For example, the Quantum Metrology Triangle links Voltage, Resistance and Current through the Josephson Effect and the Quantum Hall Effect.

The OrbiSIMS[1], introduced in 2017, has become increasingly popular for biological and material sciences studies owing to its ability to give high confidence in molecular identification (mass resolving power > 240,000 and mass accuracy < 2 ppm) simultaneously with high confidence in localisation (micrometre scale spatially and nanoscale in depth). With a growing number of instruments internationally there is an increased need for metrology for reproducible measurements. We will show how Signal, Noise and Transmission form three sides of a metrology triangle that combine to enable better measurement. In a recent comprehensive study of the noise in an Orbitrap mass spectrometer, a probabilistic model was developed.[2] A region of the intensity scale is described by Poisson statistics allowing the scaling parameter, *A*, that relates ion current to the number of ions in the trap to be determined. A true signal intensity scale is then established which allows the useful yield of atoms in an implant layer to be measured. Through comparison with time-of-flight and magnetic sector instruments the fractional ion transmission is determined.[3] We will discuss how Signal and Transmission combine to understand matrix effects in biological sample preparation and how understanding Signal and Noise are important for data analytical methods.

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3. Y. Zhou, A. Franquet, V. Spampinato, G. F. Trindade, P. van der Heide, W. Vandervorst and I S Gilmore, in preparation.

8:20am **AS+CA+EL+EM+SE+SS+TF-ThM-2 Contribution of Imaging X-Ray Photoelectron Spectroscopy to Characterize Chrome Free Passivation Nano-Layer Deposited on Food-Packaging Tinplate: Composition and Chemical Environment***, E. Ros, **Vincent Fernandez**,* CNRS, France*; N. Fairley,* CASAXPS, UK*; B. Humbert, M. Caldes,* CNRS, France

To protect metal from corrosion, passivation layer are widely used in food-packaging industry. Those Nano-metric protections create a thin oxide Nano-layer on the metal surface, making it less oxidisable. Common passivation are composed by chromium oxide[1] , using hexavalent chromium as a reagent and reducing it. However, because of the toxicity of Cr(VI), European Union is gradually forbidding.Chromium Free Passivation Alternative is based on transitions metal oxides (Sn, Ti, Zr, Mn) and polymers. These samples present some roughness in few micron range observed by Atomic Force Microscopy.XPS Imaging were perform at different binding energy to allow extracting spectrum in each pixel over the eight (Mn 2p, O 1s, Sn 3d, Ti 2p,N 1s, C 1s, P 2s and Zr 3d) XPS core level process. This study show an anti-correlation between atomic concentration of Titanium and Tin Fig(1). We observe a ratio Sn oxide Sn metal homogeneous and independent of the Ti, Sn ratio More over using the vector method [2], [3] concurrently to height XPS core , we could extract two different chemical environments spectrum. The linear Least Square combination of theses 2 spectrum allow us to model 131072 regions. To extract information form XPS data on heterogynous sample the combination of XPS imaging energy scan measurement with the vector method is a promising way. These results bring the useful information about different thin layer deposition steps. Imagerie XPS results are in agreement with Raman imagerie analysis

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8:40am **AS+CA+EL+EM+SE+SS+TF-ThM-3 Cryo-Xps for Surface Characterisation of Nanomedicines***, **David Cant**,* National Physical Laboratory,, UK*; Y. Pei,* National Physical Laboratory, UK*; A. Shchukarev, M. Ramstedt,* University of Umea, Sweden*; S. Marques, M. Segundo,* University of Porto, Portugal*; J. Parot, A. Molska, S. Borgos,* SINTEF, Norway*; C. Minelli, A. Shard,* National Physical Laboratory, UK

Nanomedicines are an area of great interest for current and future pharmaceutical development. The use of nanoparticles to act as carriers for a therapeutic load has the potential to significantly improve medical outcomes, for example by allowing a therapeutic agent to circulate within the body for longer, or by allowing targeted delivery of a drug to a specific site. Such nanomedicines often rely on specific functional coatings to achieve their desired impact; for example the majority of nanomedicines currently available on the market utilise a poly-ethylene glycol (PEG) surface coating for its ‘stealth’ properties, helping nanomedicines evade the body’s clearance mechanisms. Accurate measurement of the surfaces of such nanomaterials is therefore of great importance, yet direct, quantitative surface chemistry measurements are not commonly available, and vacuum-based analysis methods such as XPS are unlikely to provide a representative measurement of the particles in their hydrated state.

Here we present to the best of our knowledge the first use of Cryo-XPS to provide direct, quantitative measurements of the surface chemistry of nanomedicines in a hydrated state. Two nanomedicine systems were measured: a drug-carrying polymer nanoparticle; and an mRNA loaded lipid nanoparticle. Both systems possessed a supposedly PEG-terminated surface, and were measured using XPS in both aqueous cryogenic state, and dry drop-cast onto a substrate. The results of these measurements clearly demonstrate that while the PEG surface cannot readily be observed in the dry state, the cryogenic measurements exhibit spectra that are consistent with the particle being measured in a hydrated condition.

9:00am **AS+CA+EL+EM+SE+SS+TF-ThM-4 Redox XPS as a Means to Address Some XPS Reproducibility Challenges***, **Peter Cumpson**,* University of New South Wales, Australia

The challenge of better understanding of increasingly-complex specimens in surface analysis has been highlighted recently[1,2,3,4]. Especially at a time of high throughput XPS instruments and broadening of the (non-specialist) user community. An AVS survey conducted in 2018 found that 65% of those responding identified reproducibility as a significant issue [5].

There is an analogy to be made with some radically–different technologies. Machine Learning makes more sense of a moving image than a single snapshot, even if the snapshot were to come from a larger, better calibrated camera. Yet somehow we expect greater calibration precision, reference data and rigorous procedures to be the only route to reliable understanding of single spectra.

Generating a sequence of spectra from a progressively chemically-modified surface can remove many ambiguities that can otherwise cause misinterpretation. Such sequences thereby help with rapid understanding of the unmodified surface. On the theme of “Two is Better than One: Breaking Barriers with Coupled Phenomena” we present results from coupled stepwise oxidation/reduction of the surface and XPS to resolve such ambiguities for a wide range of materials and problems. Gas-phase oxidation agents are used to move through the redox states of a specimen in a controllable way, taking advantage of the logarithmic growth of oxide thickness. What is more, this oxidation is easy to implement in the entry-locks of modern XPS instruments through the use of vacuum ultraviolet light (VUV) and the *in situ* generation of ozone and gas-phase hydroxide free radicals. In the past there have been many studies of how particular materials react to ozone exposure at their surfaces, often employing XPS. Here we reverse this, and use ozone (and VUV) exposure to simplify the interpretation of spectra from a wide range of unknown materials, we think for the first time.

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9:20am **AS+CA+EL+EM+SE+SS+TF-ThM-5 Sub-Nanometer Depth Profiling of Native Metal Oxide Layers Within Single Lab-XPS Spectra***, **Martin Wortmann**, N. Frese,* Bielefeld University, Germany*; K. Viertel,* Bielefeld University of Applied Sciences and Arts, Germany*; D. Graulich, M. Westphal, T. Kuschel,* Bielefeld University, Germany

Many metals form nanometer-thin self-passivating native oxide layers upon exposure to the atmosphere, which affect their interfacial properties and corrosion behavior. Such oxide layers are commonly analyzed by X-ray photoelectron spectroscopy (XPS). Here we propose a simple and accessible depth profiling approach for oxide layers with sub-nanometer depth resolution from single lab-XPS spectra. Metals and their oxides can be distinguished by a binding energy shift to quantify their distinct signal contributions. Analogous to the widely used Hill equation we utilize the known photoelectron's inelastic mean free path to calculate the characteristic oxide layer thickness. However, in contrast to the Hill equation we analyze not only one, but all orbital energies in the XPS spectrum to develop a model that accounts for a depth-resolved concentration profile at the oxide-metal interface. The proposed model not only improves the accuracy and reproducibility of earlier methods but also paves the way for a more holistic understanding of the XPS spectrum.

9:40am **AS+CA+EL+EM+SE+SS+TF-ThM-6 A Tag-and-Count Methodology Based on Atomic Layer Deposition (ALD) and Low Energy Ion Scattering (LEIS) for Quantifying the Number of Silanols on Fused Silica***, **Josh Pinder**,* Brigham Young University

The concentration of surface silanols governs many of the properties of glass and fused silica surfaces including surface wetting, surface contamination rates, and thin film adhesion. Indeed, the concentration of surface silanols is impactful for diverse fields such as atomic layer deposition (ALD), chromatography, catalysis, and displays. Accordingly, various analytical and theoretical methods have been employed to determine the number of silanols on surfaces, including density functional theory, FTIR, thermogravimetric analysis, and temperature programed desorption mass spectrometry. However, many of these methods are better applied to particulate materials than surfaces. In this presentation, we discuss a method for directly

measuring the concentrations of surface silanols on silica-containing surfaces via a tag-and-count methodology. This approach is based on tagging surface silanols by ALD via a single pulse of dimethylzinc or diethylzinc and then quantifying the number of tags (zinc atoms) using high

sensitivity-low energy ion scattering (HS-LEIS). Our method yielded the literature value for both fully hydroxylated fused silica and also fused silica that had been heated to 500, 700, and 900 C. We see this capability as enabling for all who work with glass, fused silica, and silicon wafers,

including for ALD.

11:00am **AS+CA+EL+EM+SE+SS+TF-ThM-10 ASSD Peter M. A. Sherwood Mid-Career Professional Awardee Talk: Providing Fundamental Mechanistic Insights Into Single-Site Catalytic Reactions***, **Jean-Sabin McEwen**[1],* Washington State University **INVITED**

The single atom limit achieves the ultimate degree of material efficiency for supported metal catalysts. To this end, the ability to create highly dispersed, single-site catalysts, which are highly efficient and have low cost, is very much desirable. While single atom sites can be created, there is still disagreement over whether the single atom sites are indeed catalytically active or if the observed catalytic activity of single-site catalysts is due to metal nanoparticles either unobserved during initial microscopy studies or formed upon exposure to catalytic conditions. Such disagreements create a crucial need for the development of well-defined single-site catalysts with an accurate theoretical model in order to correctly determine the chemical nature of the catalytically active sites. To this end, we provide new atomistic insights regarding the "44" Cu surface oxide through the integration of synchrotron-based X-ray Photoelectron Spectroscopy (XPS) measurements, Synchrotron X-ray Diffraction measurements (SXRD), Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT) techniques. We also quantify the low-temperature CO oxidation kinetics on Pt single-site catalysts supported on the "29" Cu surface oxide. The "29" Cu surface oxide is a high coverage chiral structure that arises when we further oxidize the "44" structure. Using STM, CO temperature programmed desorption (TPD), and DFT techniques, we determine that an accurate model for the "29" Cu oxide surface is formed from the growth of a Cu_xO layer formed from 6 fused hexagonal rings above the Cu (111) surface where 5 oxygen adatoms are added at the center of the Cu_xO rings. Furthermore, we determine the state of the Pt single atoms before, during, and after reaction through a combination of theoretical and experimental techniques. We also correlate ambient pressure experiments, surface science measurements and first principles-based calculations to demonstrate that Pt/Cu(111) single-atom alloys (SAAs) oxidized with varying degrees of O_2 exposure can be reduced with H_2 with reasonable kinetics (hours). This is in contrast to oxidized pure Cu(111) where such reduction is very slow (days). We further contrast the catalytic properties of Rh/Cu(111) SAAs with varying degrees of O_2 exposure to the those of Pt/Cu(111) SAAs. Finally, we report the effects of a copper oxide thin film toward the segregation of noble metal single-atoms on Cu (111) using DFT.

11:40am **AS+CA+EL+EM+SE+SS+TF-ThM-12 Beyond the Physical Origin of the Shirley Background in Photoemission Spectra: Other Predictions of the Interchannel Coupling with Valence Band Losses Mechanism***, **Alberto Herrera-Gomez**,* CINVESTAV-Unidad Queretaro, Mexico

The physical mechanism proposed in our 2017 paper about the origin of the Shirley background in photoemission spectra[1] es based on interchannel coupling[2] but with the important addition of energy losses in the valence band.[3] Besides the Shirley background, it is possible to derive other predictions of the interchannel Coupling with Valence Band Losses mechanism (ICLM). Two of them are discussed in this paper: 1) the quantitative relation between Auger peaks and the Shirley background and 2) the conduction-band-like structure of the extended region of the Shirley background.

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12:00pm **AS+CA+EL+EM+SE+SS+TF-ThM-13 Aging of Hydrophilicity in a Nano-Textured SS316 Thin Film Fabricated by Magnetron Sputtering***, **Pakman Yiu**,* Ming Chi University of Technology, Taiwan*; J. Chu, J. You,* National Taiwan University of Science and Technology, Taiwan

According to the structural zone model by J.A. Thronton[1], we may manipulate the surface morphology of a thin film by altering the deposition temperature and vacuum. Therefore in this study, we prepared a series of SS316 thin film by magnetron sputtering under different Argon working pressure. Resultant thin film possessed a pressure dependent nano-textured surface which was dependent on working pressure. Furthermore, we discovered that the textured surface was highly hydrophilic (water

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[1] **ASSD Peter Sherwood Award**

contact angle <15 degrees). The hydrophilicity could be attributed to the combinitorial contribution of surface roughness and capillary effect. However, we also discovered that the hydrophilicity aged with time, where after 21 days the surface turned hydrophobic with water contact angle >90 degrees. XPS studies on both as-deposited and 21-days stored sample films revealed that there was a Carbon-rich surface layer on the surface which grew with time. Interestingly when we tried to clean the surface with Argon atmospheric plasma, the hydrophilicity was almost fully restored. Results revealed that the aging of hydrophilicity may due to the fact that nano-surface texture gathers hydrocarbons in the atmosphere, which eventually formed an extra film that altered the surface wetting property. Understanding the aging mechanism and method of ecovery may contribute to the development of a long-lasting hydrophilic surface, which is very useful in applications such as self-cleaning surface and medical apparatus[2,3]

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Applied Surface Science Division
Room B117-119 - Session AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM

Industrial Applications

Moderators: Marko Sturm, University of Twente, Netherlands, **Alan Spool**, Western Digital Corporation, **Yundong Zhou**, National Physical Laboratory, UK

8:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-1 Correlative Analysis Using Time-of-flight Secondary Ion Mass Spectrometry for Beam Sensitive Samples***, **Jean-Paul Barnes**, C. Guyot, P. Hirchenhahn, A. De Carvalho, N. Gauthier, T. Maindron, B. Gilquin, D. Ratel, C. Gaude, O. Renault,* Univ. Grenoble Alpes, CEA, Leti, France*; A. Galtayries,* Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, France*; G. Fisher,* Physical Electronics USA*; C. Seydoux, P. Jouneau,* Univ. Grenoble Alpes, CEA, IRIG-MEM, France **INVITED**

Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) is now widely used for materials analysis in domains such as semiconductor and energy applications. These challenging applications also provide access to well-controlled, custom made samples that have allowed the limits of TOF-SIMS analysis to be identified and helped in the development of correlative analysis approaches. Recent examples include combining AFM measurements with TOF-SIMS depth profiling to correct for sputter rate differences [1] or to measure mechanical or electrical properties and performing X-ray tomography prior to FIB-TOF-SIMS analysis to allow morphological and compositional data from the same volume to be visualized [2]. Currently we are working on two aspects. Firstly improving the quantification and chemical sensitivity of the technique by combining TOF-SIMS with photoemission techniques (XPS or XPEEM), and secondly trying to improve the lateral resolution by correlation with SEM and AFM measurements. Recent examples will be shown for the analysis of beam sensitive organic samples such as OLED devices, brain tissue samples after medical device implantation [3] and symbiotic microorganisms [4]. As well as the correlative aspects between techniques, we will show how tandem mass spectrometry can help in analyzing complex organic samples. In all cases the importance of sample preparation is paramount, especially for biological samples. For example, for the correlation between TOF-SIMS and XPS on OLED samples, a wedge crater protocol has been developed to allow analysis on exactly the same area of the sample whilst minimizing beam damage to the sample. Wedge crater preparation and transfer between instruments is performed under a protected environment (vacuum or inert gas) to avoid unwanted surface modifications.

Part of this work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the “Recherches Technologiques de Base” and the “CARNOT” program of the French National Research Agency (ANR).

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9:00am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-3 Secondary Ion Mass Spectroscopy of Battery Surface and Interface Chemistry – Metrology and Applications***, **Yundong Zhou**, S. Marchesini, X. Yao, Y. Zhao, I. Gilmore,* National Physical Laboratory, UK

Batteries are very important to achieve carbon net zero. Understanding battery materials change, electrode surfaces, solid electrolyte interphase (SEI) evolution and novel solid-state electrolyte structures is very helpful for developing better batteries. Surface chemical analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are often used but they have their limitations. XPS analysis cannot always resolve overlapping binding energies for some key SEI elements. The SEI often has poor Raman signal intensity. These are all hurdles for battery applications.

Secondary ion mass spectrometry has great potential to study interfacial chemistry in batteries owing to high sensitivity and high-resolution imaging in 2D and 3D.In this study, we use an OrbiSIMS instrument which is equipped with two complementary mass spectrometers (MS). A time-of-flight (ToF) MS has the capability for 2D and 3D imaging using a Bi_3^+ liquid metal ion gun with a spatial resolution of up to 200 nm but with modest mass resolving power. The Orbitrap MS offers high mass resolution and mass accuracy (> 240,000 at m/z 200 and < 2 ppm, respectively). The instrument is equipped with low energy Cs and O_2 sputter beams for high resolution depth profiling of inorganic materials. It also has a Leica docking station enabling samples to be transferred using a vacuum sample transfer chamber from an argon glove box without atmospheric exposure. To improve the quality of measurements on battery materials, we have used ion implanted materials to determine relative sensitivity factors for relevant elements. We have also conducted a systematic study to optimise the OrbiSIMS depth profiling capability. These findings along with recommendations to reduce effects of signal saturation will be discussed and examples of the application to batteries will be provided. We will provide examples of the application of ToF MS and Orbitrap MS. (1,2)

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9:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-4 Characterizing Ion Distribution at the Solid-Electrolyte Interface in Solid-State Lithium Ion Batteries with ToF-SIMS***, **Teodora Zagorac**,* University of Illinois - Chicago*; M. Counihan, J. Lee, Y. Zhang,* Argonne National Laboratory, USA*; L. Hanley,* University of Illinois - Chicago*; S. Tepavcevic,* Argonne National Laboratory, USA

Interest in solid state lithium-ion batteries as the next generation of energy storage devices has led to intense study of the chemistry, structure, and manufacturing processes for polymer electrolytes. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) salt is often used to introduce Li ions into the solid-state electrolyte. Lithium bis(fluorosulfonyl)imide salt (LiFSI) and lithium nitrate ($LiNO_3$) are less expensive salts with the potential to improve performance characteristics over pure LiTFSI in certain electrolyte formulations. The differences in distribution and reactivity of these different salts are still unknown but are critical to battery performance. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging and depth profiling was performed to compare the distributions of Li^+ cations and $TFSI^-$, FSI^-, and NO_3^-anions across the solid-electrolyte interface (SEI) formed between the polymer electrolyte and thin lithium metal electrode. Experiments were performed on ~600 nm salt-rich poly(ethylene oxide) electrolytes with ~10 nm overlayers of vapor-deposited Li metal. Samples were probed with 30 keV Bi_3^+ from a liquid metal ion gun while depth profiling with 10 keV Ar_{1400} gas cluster ion beam to collect both positive and negative ion mass spectra. Ion distributions from the three salts and their 3D images will be presented and discussed in terms of the relative composition of their SEI layers. Chemical differences from ToF-SIMS analysis help explain the differences in electrochemical SEI formation and half cell cycling: LiTFSI and LiFSI are similar, but $LiNO_3$ presents much different electrochemical properties.

9:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-5 A Perspective on X-ray Photoelectron Spectroscopy (XPS) Peak Fitting, and Reporting of XPS Data Acquisition and Peak Fitting Parameters in the Literature***, **Matthew Linford**, G. Major, J. Pinder,* Brigham Young University

We recently reported that a rather large fraction (ca. 40 %) of the XPS peak fitting in the literature is at best suspect. In a recent Perspective article (doi: 10.1116/6.0002437) we argue that the various stake holders of the problem can act together to improve the current situation. This Perspective begins with representative examples of poor XPS peak fitting. The purpose of showing these examples is to demonstrate to the reader that we are not quibbling or arguing over subtle interpretations of the data. Increasingly, we see errors that might be classified as egregious. We argue that science is in a state of ‘pre-crisis’ more than in a state of ‘crisis’. We suggest that if too much incorrect data analysis enters the literature it may cease to be self-correcting. We note the very large number of surface and material characterization techniques available today and how this presents a challenge for scientists. Consequently, it is likely that many manuscripts are incompletely reviewed today. Graduate students and post-docs at research institutions are often given minimal training on acquiring and analyzing XPS data. High fees for instruments can limit access to them and student training. Prisoner’s dilemmas may help explain situations in science that lead to suboptimal outcomes for the community. Authors are primarily responsible for the quality of the research in their papers, not reviewers or editors. We question the wisdom of placing the names of reviewers and editors on papers. In some cases, staff scientists are not adequately recognized for their intellectual contributions to projects. Selective reviewing may allow more reviews to be performed without overtaxing the community. Reviewing at some open access journals may be inadequate.

Collaboration needs to be encouraged to a greater extent at some institutions.

10:00am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-6 Unsupervised and Supervised Machine Learning Applied to ToF-SIMS of an Organic Matter-Rich Mudstone with Molecular Biomarker***, M. Pasterski,* University of Illinois Chicago*; M. Lorenz,* Oak Ridge Natinal Laboratory*; A. Ievlev,* Oak Ridge National Laboratory*; R. Wickramasinghe,* ***Luke Hanley****, F. Kenig,* University of Illinois Chicago

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging has been used to detect organic compounds including molecular biosignatures (biomarkers) in geologic samples (R.C. Wickramasinghe, *et al.,* Anal. Chem., 2021, 93, 15949). The spatial distribution of these biomarkers can help determine when and how these organics were incorporated into the host rock. ToF-SIMS imaging can rapidly collect a large amount of data, but molecular and fragment ions of different species are mixed together in complex mass spectra that are difficult to interpret. Here, we apply unsupervised and supervised machine learning (ML) to help interpret the mass spectra obtained by ToF-SIMS of an organic-carbon-rich mudstone from the Middle Jurassic of England (UK). It was previously shown that the presence of sterane molecular biomarkers in this sample can be detected via ToF-SIMS (M.J. Pasterski, *et al.*, Astrobiol., in press). We use unsupervised ML on field emission scanning electron microscopy – electron dispersive spectroscopy (SEM-EDS) measurements to define compositional categories based on differences in elemental abundances. We then test the ability of four ML algorithms - k-nearest neighbors (KNN), recursive partitioning and regressive trees (RPART), eXtreme gradient boost (XGBoost), and random forest (RF) - to classify the ToF-SIMS spectra using the categories assigned via SEM-EDS, using organic and inorganic labels, as well as using presence or absence of detectable steranes. KNN provided the highest predictive accuracy and balanced accuracy. The feature importance, or the specific features of the ToF-SIMS data used by the KNN model to make classifications could not be determined, preventing post-hoc model interpretation. However, the feature importance extracted from the other three models was useful for interpreting spectra. We determined that some of the organic ions used to classify biomarker containing spectra may be fragment ions derived from kerogen.

10:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-8 Probing Thin Film Interfaces at the Nanoscale by Low Energy Ion Scattering***,* ***Marko Sturm****, A. Chandrasekaran, A. Valpreda, A. Zameshin, R. Van de Kruijs, A. Yakshin, F. Bijkerk, M. Ackermann,* University of Twente, Netherlands **INVITED**

The growth of thin films with nanometer range thickness is of great importance for application topics as nanoelectronics, oxidation protection of thin films and optical coatings for X-ray applications. The performance of these coatings often critically depends on the sharpness of the interfaces between different layers. In this talk I will outline how we use Low-energy ion scattering (LEIS) to study interface formation between layers of different transition metals (TMs) and between TMs and Si.

LEIS with noble gas ions as projectiles yields surface peaks that indicate the composition of the outermost atomic layer of a sample. This makes the technique excellently suited to study whether deposition of a thin films leads to a closed layer. However, deposition of an overlayer on top of an underlayer may result in surface segregation of underlayer atoms (driven by surface energy differences or stress), such that the surface composition is not directly representative for the in-depth concentration profile. We analyzed the evolution of surface coverage versus deposited thickness for a large set of TM/TM film combinations, deposited by magnetron sputtering in a system that allows LEIS analysis without vacuum break after deposition. By applying a model that takes into account surface segregation, the interface profiles were derived from these layer growth profiles, which we call deposition depth profile. In addition, we demonstrated that the sharpness of interfaces in TM/TM film systems can be predicted by a phenomenological model with the crystal structure and surface energy of the materials as input parameter. This model in principle predicts the sharpness of the interface in any TM/TM thin film combination! [1]

Apart from surface peaks, LEIS spectra typically also contain so-called tails, caused by projectiles that, after sub-surface scattering, are reionized when leaving the sample. It was demonstrated before that LEIS tails can be used to determine thickness of various thin film systems, when the stopping power of the projectiles is known. Here, we show that LEIS tails can also be used to determine the sharpness of interfaces of few nm Si-on-W and Si-on-Mo films, by comparing LEIS measurements with Monte Carlo simulations with the TRBS code, which takes into account multiple scattering and stopping in the target. This approach allows interface characterization from a single sample, without the need to make a deposition depth profile.

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11:20am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-10 The Effect of Instrument Settings, Sample Distance, and Tilt on TofsimsSecondary Ion Intensities***,* ***Alan Spool****, L. Finney,* Western Digital

Experiments were performed to explore the effects of various instrument settings and sample placements on secondary ion intensities to better understand what factors have the greatest effect on repeatability and replicability in TOF-SIMS. A batch of magnetic recording disks used in hard disk drive manufacture, natively flat and homogeneous, were used as test samples for the purpose. As expected, by far the largest variable altering raw intensities was the LMIG tip stability. LMIG tips can have stable emission currents while still producing variable pulsed LMIG beam currents with resultant variable secondary ion counts. This variability sometimes is seen in slow current drift, but is sometimes so rapid that measurements taken directly before each measurement are not close enough in time to properly scale the measurement results. In these cases, normalization is the only solution. Secondary ion intensities were remarkably insensitive to small variations in sample height (position relative to the extractor). Far more interesting were the changes to the secondary ion intensities that resulted from tilting the sample. These effects varied amongst the secondary ions detected such that normalization did not remove them. Secondary ion emission as a function of emission angle has long been understood to be like a cosine function and to vary somewhat from ion to ion. These different angular profiles explain the differences seen in ion detection as a function of tilt. Some of these differences proved to be asymmetrical, varying depending on whether the sample was tilted toward or away from the primary ion source, an indication that in some situations some residual momentum from the initial primary ion impact onto the surface is carried into the secondary ion emission. These results have implications for attempts to do quantitative analysis on any sample that is not completely flat.

11:40am **AS+2D+CA+EM+MS+NS+SE+SS+TF-FrM-11 Evaluation of Unaltered and Irradiated Nuclear Graphite Surfaces through Integrated Traditional XPS and HAXPES Techniques***,* ***Jonathan Counsell****, L. Soomary, K. Zahra,* Kratos Analytical Limited, UK*; B. Spencer, A. Theodosiou,* University of Manchester, UK

Graphite-moderated reactors have been operational worldwide for several decades. There exists a substantial body of research in this domain, with particular emphasis on investigating the impact of irradiation damage on the graphite matrix. In order to satisfy the design and regulatory requisites of these advanced reactors, it becomes imperative to gain a deeper comprehension of the retention and transportation mechanisms of fission products within graphite.

This study outlines a technique for the precise assessment of the surface chemistry of highly-oriented pyrolytic graphite (HOPG), serving as a representative model akin to the current graphite grades utilized in the nuclear sector. We delve into the process of surface etching aimed at eliminating surface adsorbates and contaminants. This process involves the utilization of both monatomic and cluster ions, the former inadvertently causing undesirable damage to the graphite structure. Such damage is evidenced by a significant reduction in the sp2 component of C 1s. We introduce the use of UPS analysis as a straightforward means of determining the presence of sp2 characteristics in the uppermost atomic layers.

Moreover, we examine the consequences of high-energy ion implantation (Cs+) and the ensuing damage to the HOPG surface. This examination is carried out using XPS (1486eV) and HAXPES (2984eV), thereby showcasing the capability to characterize the resulting surface damage and the associated alterations within the probed depths.

Plasma Science and Technology Division
Room A106 - Session PS+SE-FrM

Atmospheric Pressure Plasmas and Their Applications

Moderators: Michael Johnson, Naval Research Laboratory, USA, **Floran Peeters**, LeydenJar Technologies

8:20am **PS+SE-FrM-1 Electrolyte Engineering for Nitrogen Fixation by Plasma Electrolysis***, **Brandon Kamiyama,*** University of Illinois at Urbana Champaign*; M. Eslamisaray,* University of Illinois Urbana-Champaign*; R. Pierrard, R. Sankaran,* University of Illinois at Urbana Champaign

The fixation of nitrogen is critical to our most basic need, the growth of plants for food. Industrially, nitrogen is fixed to ammonia (NH_3) by the Haber-Bosch process which has a large physical and environmental footprint. The development of alternative methods that are sustainable and deployable at a small scale has become one of the active areas of research. Among the different approaches being explored, plasma-based electrolytic reactors have shown the most promise, capable of activating nitrogen in air or with water as a source of hydrogen at atmospheric pressure and near room temperature without any catalyst and using only electricity which could in the future come from renewable sources. However, a key challenge is selectivity of products with typical processes producing NH_3, nitrates (NO_3^-), and nitrites (NO_2^-).

In this work, we studied direct-current plasma in contact with an electrolyte solution. Various products were characterized in the liquid phase including NH_3, NO_3^-, NO_2^-, as well as hydrogen peroxide (H_2O_2). To control the product selectivity, various conditions were mapped including gas feed, cathodic vs. anodic polarity, and pH. Our most promising result was that the pH and more generally, the electrolyte composition, was found to greatly influence the product distribution. At low pH, the product distribution shifted more to the reduced form, NH_3, and at high pH, the distribution shifted more to the oxidized form, NO_3^-, We also found a strong effect on the presence of O_2 (in air) and humidity. These results can be used to selectively synthesize nitrogen products, elucidate product formation mechanisms, or to inform scale up of similar plasma-liquid systems for sustainable nitrogen fixation.

8:40am **PS+SE-FrM-2 Two Atmospheric Pressure Plasma Jets Driven by Phase-Shifted Voltages: A Method to Control Plasma Properties at the Plasma–Surface Interface***, **Michael Johnson,*** Huntington Ingalls Industries*; G. Brown,* University of Texas, Austin*; D. Boris, T. Petrova, S. Walton,* Naval Research Laboratory

Atmospheric pressure plasma jets project plasma away from their electrodes, enabling the treatment of remotely located surfaces, and making them appealing for a diverse range of surface treatment applications. However, their small effective areas pose a challenge to broader adoption and utilization. To circumvent this limitation, multiple plasma jets can be used in tandem to increase their effective area. The objective of this study is to examine the interactions between two plasma jets and leverage this relationship to manipulate plasma properties at the plasma-surface interface. The jets are positioned at a 130° angle from each other, converging at the surface of a glass substrate. Each jet is driven by an individual piezoelectric transformer, powered by identical but phase-shifted voltage waveforms, which provides precise control over their relative timing and influence plasma properties. As phase difference between the two jets is varied the jet behavior changes from a regime where the two jets repel each other to a regime of enhanced jet interaction, resulting in an expanded effective area for the plasma. Interestingly, increasing this phase difference led to reduced power consumption while simultaneously enhancing electron density at the intersection point. Consequently, this technique of utilizing phase-shifted jets presents a method for increasing the effective area of the plasma and controlling plasma properties at an interface, potentially benefiting a wide array of applications.

This work supported by the Naval Research Laboratory Base program

9:00am **PS+SE-FrM-3 Plasma Chemistry in Atmospheric Pressure Gases and Liquids: Fundamentals and Novel Applications***, **Alexander Fridman,*** Drexel University, Nyheim Plasma Institute **INVITED**

The presentation is focused on fundamental and applied aspects of the non-equilibrium plasma chemical processes performed in high pressure gases and liquids. As an example of the gas-phase processes, the plasma synthesis of NO from atmospheric pressure air is considered, with especial attention on minimizing energy cost of the process. As an example of the plasma-chemical processes in liquid water, the PFAS abatement in considered with especial attention to complete mineralization of these important impurities. As an example of plasma chemistry in cryogenic liquids, the plasma synthesis of polymeric nitrogen is considered. The process is accomplished in liquid nitrogen using the nanosecond-pulsed discharges organized with creation of bubbles during the synthesis.

9:40am **PS+SE-FrM-5 Integrated Circuit Manufacturing with Plasma Activated Chemical Treatment (IMPACT): Effect of Plasmas on Photoresist and Cleaning Solutions in Semiconductor Processing***, **Christian Williams**, S. Dubowsky, D. Curreli, M. Sankaran, D. Ruzic,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas open various chemical and material applications because of their ability to be in contact with temperature-sensitive surfaces such as plastics and liquids. In this work, we investigated the potential of plasmas to modify two key components of semiconductor processing [1]: the photoresist and cleaning solution used to remove the photoresist after lithographic exposure. Two different plasma sources were used in experiments, a dielectric-barrier discharge and a pulsed direct current discharge jet. Characterization of the gas phase was performed by optical emission spectroscopy (OES) and the chemical modification of the treated solutions was examined using ion chromatography (IC). Ultraviolet-visible (UV/Vis) spectroscopy was also used to measure OH radical concentrations in the treated samples. In parallel, a reaction network was constructed using CRANE, a MOOSE-based tool for plasma chemistry modeling. Simulations provided the concentrations of species which could then be compared to experiments to understand potential reaction mechanisms.

10:00am **PS+SE-FrM-6 Increasing Adhesion of Polyurethane Painting on Aluminum by Atmospheric Pressure Plasma Jet Treatment***, **Jorane Berckmans**, C. Tubier,* Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium*; R. Revilla Castillo,* Research Group Electrochemical and Surface Engineering (SURF), Department of Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium*; C. Poleunis,* Unité Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, Louvain-la-Neuve, Belgium*; H. Terryn,* Research Group Electrochemical and Surface Engineering (SURF), Department of Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium*; A. Delcorte,* Unité Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, Louvain-la-Neuve, Belgium*; F. Reniers,* Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium

Nowadays, industries are looking for replacement of chromium VI in aluminum pretreatment. In this quest, plasma treatments could represent an interesting approach. Indeed, atmospheric plasmas enable a wide range of possible modifications of materials (etching, grafting, surface functionalization) but also allow an easy industrial upscale.[1,2]

In this work, aluminum 99,99% surfaces were modified by an atmospheric pressure plasma jet (APPJ) and the effect on polyurethane paint adhesion was studied. The difference in wettability, chemistry and roughness induced by plasma treatments were investigated by water contact angle, X-ray photoelectron spectroscopy and atomic force microscopy respectively. In parallel, optical emission spectroscopy (OES) was used to characterize the plasma phase. The correlation between plasma species, identified by OES, and the resulting surface modification was investigated. Then, the adhesion of the polyurethane coatings on the plasma-modified surfaces was studied by a tape test according to ASTM D3359. The coating – aluminum substrate interface has been also characterized by Tof-SIMS, to identify specific fragments characteristics for bonding.

Different plasma sources were used, with different plasma conditions (PlasmaTreat Openair FG5001, 2 bars of dry air, at varying distances from 5 mm to 10 mm and treatment times of 0,5 to 60,0 s by tuning the number of scans and the scan rate of the APPJ over the surface, SurfX Atomflo 600, with 30,0 L/Min of Ar at varying flow of oxygen from 0,00 to 0,60 L/ Min, distance from 5 mm to 30 mm and treatment times of 0,04 s to 25 s by tuning the number of scans and the scan rate of the APPJ over the surface). Varying humidity containing in plasma, by water injection, was also studied with the SurfX Atomflo 600.

It is shown that, for most of the plasma treatments used, an increase of the adhesion of polyurethane coatings is observed (Fig. 1) and associated with the surface modification of the aluminum and with the plasma chemistry.

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[2] K. G. Kostov, T. M. C. Nishime, A. H. R. Castro, A. Toth,L. R. O. Hein, Appl. Surf. Sci. 2014, 314, 367.

Acknowledgements

This work is partly supported by the ULB-VUB “joint research group” fund.

10:40am **PS+SE-FrM-8 Fundamentals of Atmospheric Pressure Discharges for Plasma Catalytic Applications**, ***Judith Golda***, *D. Steuer, R. Labenski, H. van Impel, M. Böke, V. Schulz-von der Gathen,* Ruhr-University Bochum, Germany **INVITED**

A central challenge of our time is the energy transition from fossil energy sources to renewable ones. Plasma catalysis is one of the promising techniques that has been proposed to contribute to this transition. Research shows that synergies between classical catalysis and plasma processes can be obtained due to the distinct non-equilibrium character of atmospheric pressure plasmas and their interaction with surfaces. However, the underlying mechanisms are hard to entangle as typical reactor designs for plasma catalysis are packed bed reactors. While advantageous for industrial processes, the diagnostics of these reactors is challenging.

In this talk, we give an insight into the diagnostic challenges of plasmas for catalysis as well as possible approaches to overcome them. We will discuss alternative reactor designs for fundamental studies such as micro-structured surface dielectric barrier discharges. We will give an overview of global and local diagnostic techniques: Current-voltage characteristics for dissipated plasma power and estimation of electron densities, emission-based techniques for reactive species densities such as atomic oxygen (state-enhanced actinometry) or temperature (rotational bands), and electric field estimation (Stark splitting and shifting).

This research is funded by the German Research Foundation within CRC 1316 in project A6.

11:20am **PS+SE-FrM-10 Atmospheric Pressure Inductively Coupled Torus Torch System for 3D Printing the Silicon-Nanofiber (Si/CNF) Anodes for Li-ion Batteries**, ***Yuri Glukhoy,*** Nanocoating Plasma Systems Inc*; M. Ryaboy,* UC Berkeley

Our approach to environmentally-friendly manufacturing low-cost Si anodes with the core-shell heterostructure includes 3D plasma beam printing. Excitingly, because of the merits of low price, high doping content, and no toxic emission during the process, Si sawdust, which is a waste of the solar cell industry, can be a fascinating raw material for Si shells with well-tailored functions and electrical properties. However, the transition of the Si sawdust requires a long resident time in the high-temperature plasma and a high RF power to sustain it. We offer a new method of generation of Si vapor and the simultaneous lamination of CNFthrough the recirculation of both Si and CNF in the high-temperature torus plasma torch. It allows the incremental sublimation of Si particles, while Si vapor is deposited in the fly on the fibers' preheated surfaces. This torus torch recirculated in the high-temperature doughnut-like reactor is generated by two tangentially injected in the opposite direction axial atmospheric plasma beams in the swirling mode. Besides the high-temperature plasma species, these beams are designed to bring the liquid Si droplets from the melted Si powder injected into the high-temperature plasma discharge generating such a beam.Two inductors with transversal RF fields are positioned on the opposite sides of the doughnut and surround this profile. They boost this torus plasma torch, increasing the plasma density and current until its magnetic field pinches into the high-temperature plasma cord. But RF power applied to the inductor should be limited to avoid melting the CNF at 3550 °C. This recirculation process in the high-temperature plasma reactor should provide a conformal Si lamination of CNF in the fly to achieve the Si shell's thickness of around 1 um. Two outlets are welded to this doughnut to extract the Si/CNF composites and generate the plasma sprays. Ended with the nozzles and directed to the opposite sides of the copper tape serving as a current collector, they provide 3D printing of the Si/CNF anodes in the roll-to-roll mode.

11:40am **PS+SE-FrM-11 Design and Functionality of a Low-Frequency Pulsed Plasma System**, *M. Gulan,* Technological University Dublin, Ireland*;* ***Vladimir Milosavljevic***, Technological University Dublin, Ireland & Faculty of Physics, University of Belgrade, Serbia, Ireland

This study presents the design and functionality of a kHz pulsing plasma generator at atmospheric pressure, which can be used for a range of applications, such as sterilization in food processing or plasma-based treatments for biological samples. This next generation plasma system is developed to operate in ambient air or on an argon/helium/oxygen/nitrogen gas mixture at atmospheric pressure, making it suitable for a range of applications such as surface modification, plasma-based sterilization, and material processing. The system's unique design allows for improved efficiency, higher plasma density, and greater control over plasma parameters compared to previous systems. The plasma tool is particularly suitable for sensitive and fragile materials. This work describes the development and operation of a non-thermal, dielectric-free atmospheric plasma system designed for use in surface treatment and modification applications. The system was developed in-house to meet the specific technological needs, and includes detailed information on the design and operating parameters of the system. The new plasma system allows an increase in the plasma-surface interaction selectivity and reduces plasma induced damages to the surface. The innovative design of our plasma system led to the development of unique plasma parameters that are not currently available on the market. Specifically, the system allows for precise control of plasma temperature, density, and composition, which are essential for effective plasma treatment of a range of materials. These unique parameters were designed with the goal of simplifying plasma treatment in industrial applications such as surface modification, cleaning, and sterilization, where precision and efficiency are critical factors for success. The system creates a plasma discharge in gap from 5 to 60 mm in space of hundreds of cm^2. The plasma source is based on a pulse resonance circuit which allows the creation of high voltage pulses with the ability to control and reduce a current of the plasma discharge. The study also includes different setting of plasma source to control the ion flux, the ion energy and the plasma chemistry. Plasma pulsing allows new domains of ion energy and radical fluxes to be reached, thereby extending the operating range of plasma generators. The plasma diagnostics in this work include the absorption spectra of oxygen and nitrogen based molecules and their dependence on the process parameters such as duty cycle, discharge frequency, pick-to-pick voltage, etc.

Thin Film Division
Room A105 - Session TF+SE-FrM

Metal-Organic Frameworks and Other Network Materials

Moderators: Christophe Vallee, SUNY College of Nanoscale Science and Engineering, **Junjie Zhao**, Zhejiang University

8:20am **TF+SE-FrM-1 Membrane Design by Atomic Layer Deposition***,* ***Mikhael Bechelany,*** CNRS/European Institute of Membranes, France **INVITED**

Atomic layer deposition (ALD) is a technology offering the possibility to prepare thin films of high quality materials on high aspect ratio substrates with precise thickness control, high uniformity and excellent conformality, a unique capability. Therefore, this route is particularly suited for the structural modification and pore tailoring of synthetic membranes. ALD coatings have been prepared on a wide variety of membrane substrates, from inorganic templated supports to porous polymers. In this talk we aim to provide an extensive summary of the advances of ALD applied to membranes. A selected list of our studies will be used to illustrate how the ALD route can be implemented to improve the operational performance of different inorganic, organic, hybrid or composite membranes. We will show examples how ALD [1], could be used for the design of membranes in which the geometry can be tuned accurately and the dependence of the physical-chemical properties on the geometric parameters can be studied systematically in order to investigate their performances in renewable energy (gas separation [2,3] and osmotic energy harvesting [4]), environmental (water treatment [5], and sensors [6,7] as well as health applications.

Furthermore, the challenges and opportunities of the route for this specific membrane application are also discussed. This talk comprehensively shows the benefits of ALD and its application in various facets of membranes and membrane associated engineering processes, and will help exploiting the numerous prospects of this emerging and growing field.

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9:00am **TF+SE-FrM-3 Ultrathin Transferable MOF/Polymer Janus Thin Films with Tunable Turing Morphologies***, **Xinyu Luo**[1], J. Zhao,* Zhejiang University, China

Janus thin films are known for their distinct asymmetric structures that bring unique properties for energy harvesting, mist collection and membrane separation applications. Decorating Janus thin films with Turing patterns could enlarge the surface area and generate stretchability. However, these delicate structures are particularly difficult to synthesized by conventional methods and not easily transferrable for integration of composites and devices. Here, we report a novel interfacial synthesis method using an atomic layer deposited (ALD) ZnO template and a nanoscale polymer topcoat for Janus thin films with the intricate Turing patterns. Through confining the reaction at the interface between the ALD ZnO layer and the polymer topcoat, a continuous micron-scale MOF film, acting as the Turing morphogen, was rapidly formed and anchored onto the bottom side of the polymer topcoat, thus leading to a Janus structure. We obtained Turing patterns in the MOF/polymer Janus thin films that agree well with the prediction by the Gray-Scott diffusion-reaction model. Our Turing Janus film remained flexible even with 96wt% MOF loading and can be transferred onto various substrates for membrane separation and sensing applications. Gas permeation tests confirm the absence of pinhole defects in the Turing Janus films transferred onto porous alumina support. Additionally, the Turing structures provide strechability to the Janus films that allows repeated bending on flexible electrodes for gas sensors. The reported Turing Janus film demonstrated a proof-of-concept handy transferable thin film product for versatile functions.

9:20am **TF+SE-FrM-4 Growth of Metal-Organic Framework Thin Films by a Vapor-Assisted Conversion Method***, D. Speed, A. Bajpai, **Greg Szulczewski,*** The University of Alabama

Metal-organic frameworks (MOFs) are a class of highly porous materials that can be synthesized using a variety of inorganic nodes and organic linkers, which enable MOFs for applications in gas sensing, gas storage, and gas separations. In this talk, we will describe the synthesis of MOFs thin films via a hot vapor-assisted conversion method on a variety of substrates. In general, the precursor components to the MOF are dissolved in an appropriate organic solvent and transferred to the substrate as a small droplet. The reaction is initiated by heating the droplet in the presence of the hot vapor from the organic solvent. Specifically, we describe the results for UiO-66 and UiO-67 thin films and Co-MOF-74 and Ni-MOF-74 thin films. The thin films were characterized by x-ray diffraction, IR/Raman spectroscopy and scanning electron microscopy. The growth of UiO-67 is interesting. Quasi-octahedral crystals appear to grow from the surface, which is in contract to the other MOFs we studied. The role of precursor concentration appears to strongly effect the film growth mechanism. The porosity of the films was assessed by measurement adsorption isotherms using aromatic hydrocarbons as the probe molecules. In all cases the films show saturation adsorption uptake comparable to bulk samples. Overall, the vapor-assisted conversion method is a convenient way to grow thin films at low temperatures within a few hours.

9:40am **TF+SE-FrM-5 Enhancing the Electrical and Optical Properties of Thermochromic VO_2: The Impact of Nanostructuring and Gold Nanoparticles***, **Gregory Savorianakis**, S. Konstantinidis, M. Voué,* Université de Mons, Belgium*; N. Martin,* FEMTO-ST, France

Monoclinic VO2 (m-VO2) exhibits a Metal-Insulator Transition (MIT) at approximately 67°C, making it a thermochromic material of interest. In this study, we initially show the optimization of magnetron sputtering using a vanadium target within an Ar/O2 mixture to synthesize films that are 200 nm thick and contain m-VO2 crystals. Our synthesis process involves precise control of the oxygen flow rate and subsequent annealing of the films in O2 for 120 minutes at 500°C.

In the first segment of our research, we validate our numerical findings obtained through the CAvity Modelling Framework (CAMFR) by comparing them to the optical properties of the synthesized films. Our simulations demonstrate how nanostructuring via ribbon-like structures can be adjusted to enhance film properties for potential applications in smart windows. By varying parameters such as the width of VO2 nano-ribbons, periodicity, and film thickness, we can achieve improved energy efficiency and a less opaque appearance compared to a dense film with the same thickness.

Secondly, we conducted experimental research where we combined m-VO2 films with gold nanoparticles (AuNPs) to achieve tunable plasmonic signals in response to temperature variations. Our study demonstrates the successful grafting of AuNPs onto the surface of the VO2 film using (3-aminopropyl) trimethoxysilane (APTMS) linkers. We observed a noticeable shift in the wavelength of the plasmonic peak, which was quantified as a function of temperature for two distinct platforms: one with NPs positioned on top of the VO2 film and another with NPs embedded within the film. Additionally, our investigations into resistivity and optical hysteresis revealed that the presence of AuNPs amplifies the resistivity drop by one order of magnitude and enhances the transmission drop by 15%. Furthermore, it reduces the critical temperature by 5°C and narrows the hysteresis width.

In a subsequent development, we have successfully synthesized thermochromic VO2 nanostructures, including tilted nanocolumns, zig-zags, and helices, utilizing the GLancing Angle Deposition (GLAD) technique. Our optical and ellipsometry analyses have revealed a significant anisotropy that correlates with the sample's rotation during measurement. This unique type of sample introduces a new dimension of control beyond temperature alone, allowing us to fine-tune its optical response. By combining both factors, we can achieve multi-dimensional tunability.

The here-mentioned work may pave the way towards the elaboration of thin film materials with high optical accordability which can potentially be used in applications as colour display, protection against counterfeiting, opto-electronics chips or energy-saving smart windows.

10:00am **TF+SE-FrM-6 Atomic Layer Deposition of Sn-doped MoO_2 Electrode Films with Distorted Rutile Structure for High-performance TiO_2-based DRAM Capacitors***, **Jae Hyeon Lee**, J. Han, J. Shin, W. Kang,* Seoul National University of Science and Technology, Republic of Korea

Traditional DRAM capacitor electrodes, typified by TiN, confront performance deterioration attributed to their low work function and the formation of low-k TiO_xN_y interfacial layers. As device scaling progresses, these issues become increasingly critical, driving recent research efforts to explore alternative electrode materials to replace TiN. Molybdenum dioxide (MoO_2) emerges as a promising candidate, boasting a low resistivity of 150 µΩ·cm, a high work function (>5 eV), and excellent thermal stability, outperforming TiN. Furthermore, MoO_2 exhibits a distorted rutile structure similar to rutile-TiO_2 which is a next-generation DRAM capacitor high-k material, enabling the low-temperature growth of rutile-TiO_2 on MoO_2 bottom electrode. However, MoO_2 deposition presents challenges due to its metastable nature compared to the stable phase molybdenum trioxide (MoO_3).

In this study, we successfully fabricated distorted rutile MoO_2 films through atomic layer deposition (ALD) by incorporating SnO into MoO_3. The ALD process was performed using a super-cycle method consisting of the MoO_3 ALD sub-cycles and SnO ALD sub-cycles. The optimal sub-cycle ratio of MoO_3 to SnO was determined by varying the ratio from 100:1 to 100:5 After post-deposition annealing, MoO_2 films with resistivity of 0.254 Ω·cm and an RMS roughness of 0.48 nm were obtained. Finally, to assess the feasibility of Sn-doped MoO_2 films as DRAM capacitor electrodes, metal-insulator-metal capacitors were fabricated using Sn-doped MoO_2 as bottom electrodes. Through this, it was confirmed that ALD TiO_2 film was crystallized into the rutile phase on the Sn-doped MoO_2, and a high dielectric constant of 130 was obtained despite the relatively low TiO_2 deposition temperature. Consequently, this study confirmed the viability of Sn-doped MoO2 as a promising DRAM capacitor electrode material.

10:40am **TF+SE-FrM-8 Area Selectivity and Crystallographic Orientation of Zif-8 Films Deposited by Molecular Layer Deposition***, **Jorid Smets**, V. Rubio-Giménez,* KU Leuven, Belgium*; S. Armini,* IMEC, Belgium*; R. Ameloot,* KU Leuven, Belgium

Integrating metal-organic frameworks (MOFs) into electronic devices would benefit from controlled vapor-phase thin film deposition. In this study, we investigate the molecular layer deposition (MLD) of zeolitic imidazolate framework 8 (ZIF-8). Thin films were deposited on various substrates through consecutive self-limiting reactions of diethyl zinc, water, and 2-methyl imidazole, employing an all-vapor-phase process in an atomic layer deposition reactor. Two-step ZIF-8 MLD was utilized in this study, in which an amorphous layer is first deposited via MLD, followed by crystallization during a linker post-treatment step.[1] The degree of crystalline orientation of the resulting MOF layers can be tuned by changing the surface termination of the substrate. Moreover, these surface groups influence the mobility of the building blocks on the surface, allowing control over the

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

surface coverage. We exploited this phenomenon to perform direct area-selective deposition of ZIF-8. The mechanisms behind these observations were elucidated using various imaging techniques, synchrotron GIXRD, and in-situ ellipsometry.

[1] Smets, J.; Cruz, A. J.; Rubio-Giménez, V.; Tietze, M. L.; Kravchenko, D. E.; Arnauts, G.; Matavž, A.; Wauteraerts, N.; Tu, M.; Marcoen, K.; Imaz, I.; Maspoch, D.; Korytov, M.; Vereecken, P. M.; De Feyter, S.; Hauffman, T.; Ameloot, R. Molecular Layer Deposition of Zeolitic Imidazolate Framework-8 Films. Chem. Mater. 2023, 35 (4), 1684–1690.

11:00am **TF+SE-FrM-9 Electron-Beam Assisted Solvent-Free Bottom-Up Patterning of Zeolitic Imidazolate Frameworks***, **Dennis Lee**, Y. Miao,* Johns Hopkins University*; M. Dorneles de Mello,* Brookhaven National Laboratory*; M. Ahmad,* Stony Brook University/Brookhaven National Laboratory*; M. Abdel-Rahman, P. Eckhert,* Johns Hopkins University*; A. Boscoboinik,* Brookhaven National Laboratory*; H. Fairbrother, M. Tsapatsis,* Johns Hopkins University

For many years, researchers have been trying to develop a way to create patterns in porous materials like metal-organic frameworks (MOFs) for use in electronic and optical devices.[1] Recent progress has been made in understanding how irradiation with X-rays[2] and electron beams (e-beams)[3,4] causes amorphization in MOFs and zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs. Researchers have also found that certain types of ZIFs with halogen atoms on their structural linkers undergo a solubility switch when exposed to irradiation, allowing for selective removal of either the exposed or non-exposed regions to create ZIF patterns.[5]

In this presentation, I will describe our work on a bottom-up approach to patterning non-halogenated ZIFs using an e-beam-assisted solvent-free technique.[6] By pretreating metal oxide precursors (i.e., ZnO for ZIF-8 and CoO_x for ZIF-67) with 2-methylimidazole (2mIm) linker vapor, we were able to sensitize the oxide surface to e-beam exposure, delaying the conversion of the oxides to ZIFs in irradiated areas while allowing growth in non-irradiated areas. This all-vapor phase technique resulted in well-defined patterns with features as small as 150 nm width and 150 nm gap, making it a promising method for micro and nanofabrication processes.

During the presentation, I will focus on our primary approach to enable the creation of ZIF patterns without solvents or masks. It will also be discussed in our systematic investigation of the 2mIm-sensitized oxide film, which involves the use of various characterization methods, such as atomic force microscopy, transmission electron microscopy, grazing incidence X-ray diffraction, and X-ray photoelectron spectroscopy.

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11:20am **TF+SE-FrM-10 Al_2O_3 Atomic Layer Deposition on a Porous Matrix of Carbon Fibers (FiberForm) for Oxidation Resistance***, **Jack Widmer**, S. George,* University of Colorado Boulder

Atomic layer deposition (ALD) was used to coat a porous matrix of carbon fibers known as FiberForm with Al_2O_3 to improve oxidation resistance. Static trimethylaluminum (TMA) and H_2O exposures for Al_2O_3 ALD were used to obtain the uniform coating of this high porosity material. The carbon surfaces were initially functionalized for Al_2O_3 ALD by exposure to sequential exposures of nitrogen dioxide and TMA. A gravimetric model was developed to predict the mass gain per cycle under conditions when the ALD reactions reach saturation during each reactant exposure. The uniformity of the Al_2O_3 ALD coating on FiberForm was confirmed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis. The SEM, EDS and gravimetric model were all consistent with a uniform Al_2O_3 ALD coating on the porous carbon fiber network when the ALD reactions reach saturation on the entire surface area. In contrast, the profile of the Al_2O_3 ALD coating on the FiberForm was also characterized using undersaturation conditions when the ALD reactions do not reach saturation throughout the FiberForm sample. These Al_2O_3 coverage profiles were consistent with diffusion-limited Al_2O_3 ALD. The oxidation of the FiberForm and the Al_2O_3 ALD-coated FiberForm was also investigated by thermogravimetric analysis (TGA). TGA revealed that a 50 nm thick Al_2O_3 coating deposited using 400 Al_2O_3 ALD cycles enhanced the oxidation resistance. The Al_2O_3 ALD coating increased the oxidation onset temperature by ~200 ℃ from 500 °C to 700 °C and decreased the oxidation rate by ~30%. The oxidation rate of the Al_2O_3 ALD-coated FiberForm samples was also constant and independent of the thickness of the Al_2O_3 ALD coating. This behavior suggested that the oxidation is dependent on the competing O_2 diffusion into the FiberForm and CO_2 diffusion out of the FiberForm.

11:40am **TF+SE-FrM-11 Mesoporous UiO-66-NH$_2$ Thin Film Growth on TiO_2 Coated Fabrics Using Atomic Layer Deposition (ALD) for Enhanced Organophosphate Degradation***, **Mai Abdelmigeed**,* North Carolina State University

Nowadays, most of the UiO-66-NH$_2$ research focuses on the capabilities of the microporous UiO-66-NH$_2$-fabric composites for organophosphate degradation via hydrolysis.Unfortunately, microporous UiO-66-NH$_2$ suffers from diffusion limitation of the bulky organophosphates accessing the active sites. As a novel solution, we are introducing the aqueous phase synthesized mesoporous UiO-66-NH$_2$ thin film on fabric coated with »20 nm TiO_2 using ALD. The mesoporous version of UiO-66-NH$_2$ overcomes the mass transfer limitation issues while the TiO_2 layer works as nucleation centers to form a dense, robust, and homogeneous MOF thin films. The mesoporosity of the solvothermally synthesized UiO-66-NH$_2$-fabric composites is mainly due to the utilization of an amphoteric surfactant, CAPB, as a template to construct these mesochannels.[1] Fig.(1,a) shows the benign MOF synthesis process avoiding the common toxic solvents and highly acidic medium at elevated temperatures. Importantly, Fig.(1,b) shows the pore size distribution of mesoporous UiO-66-NH$_2$ has both characteristic pore width peaks corresponding to the microporous range and a new peak at »28 Å corresponding to the mesoporous range. The benign synthesis approach allows mesoporous UiO-66-NH$_2$ growth on a range of fabrics. Fig.(1,c) shows a MOF thin film on PP coated with TiO_2 using atomic layer deposition that achieves BET SA up to »360m^2/g$_{comp}$. Fig.(1,d) shows that these mesoporous UiO-66-NH$_2$ compositeenhanced the paraoxon methyl (DMNP) degradation with a half-life time of less than a minute compared to a half-life time of 2.5 minutes for microporousUiO-66-NH$_2$. Similar trends were found for live nerve agent degradation. To conclude, the benign synthesis process of the mesoporous UiO-66-NH$_2$ thin film improves the growth of this MOF on a large range of fabrics and enhances the organophosphates degradation, respectively. These thin film MOF-fabric composites have great potential in filtration, protection, and catalysis applications.

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