## Atomic Scale Processing Mini-Symposium
## Room A107-109 - Session AP+PS+TF-MoM

### Thermal Atomic Layer Etching and Deposition

**Moderator: Jean-Francois de Marneffe**, IMEC, Belgium

8:20am **AP+PS+TF-MoM-1 Atomic Layer Etching of Aluminum and Aluminum Oxide for Optical Applications***, **John Hennessy**, R. Rodríguez, A. Jewell,* Jet Propulsion Laboratory **INVITED**

Thermal atomic layer etching can be utilized for the surface preparation of aluminum in order to improve its optical performance at ultraviolet wavelengths. In this work we report on the use of trimethyaluminum and anhydrous hydrogen flyoride to remove the native oxide of aluminum prior to encapsulation with fluoride dielectric materials. This ALE/ALD process is used for the fabrication of reflective coatings and bandpass filters operating at wavelengths shorter than 200 nm. The etch rate of aluminum oxide is observed to be dependent on chamber conditioning with a significant enhancement in etch rate observed when the cyclic etching is performed in the presence of alkali halide materials. This enhancement can reduce the temperature threshold where etching dominates the reaction cycle over deposition.

The reduction of the overall processing temperature can enhance the compatibility of the full coating process with some temperature-sensitive substrates, and limit the amount of etch damage experienced by aluminum surfaces. Etching into the aluminum surface is generally observed to result in non-conformal etching which greatly increases the surface roughness of films and degrades the optical performance of resulting structures. Reducing the etch temperature can mitigate this effect by increasing the selectivity of the native oxide removal over the underlying metal. Optimization of these processes may provide insight into achieving conformal ALE of aluminum surfaces. The extension of these atomic layer processing methods towards the fabrication of meter-class mirror coatings is also discussed in the context of future large UV space observatories for NASA astrophysics applications.

9:00am **AP+PS+TF-MoM-3 Thermal Etching of First Row Transition Metal Oxides using Acetylacetone and $O_3$: Pathway for Atomic Layer Etching***, **Jonathan Partridge**[1], S. George,* University of Colorado at Boulder

Etching metal oxides with halogen-free methods is important during processing to avoid corrosion.Acetylacetone (Hacac) is an organic hydrocarbon.Hacac can supply acac ligands that can form volatile metal complexes with most transition metals.Consequently, Hacac can spontaneously etch metal oxides to form $M(acac)_x$ and $H_2O$.One difficulty is that Hacac can also decompose on the metal oxide surface and block the spontaneous etching.However, this surface poisoning also leads to a self-limiting reaction. The $O_3$ exposure can then remove the carbonaceous decomposition species and produce a pathway for atomic layer etching.

Thermal etching of first row metal oxides was demonstrated using Hacac and $O_3$ at pressures of 2.5 Torr at 250 °C.A quadrupole mass spectrometer (QMS) reactor with molecular beam expansion and line-of-sight to the ionizer was employed to detect etch species with high sensitivity.Metal oxide nanopowders were used to maximize the surface area and signal intensity of the etch products. The reactant sequence used five sequential Hacac exposures, one $O_3$ exposure, and one final Hacac exposure to check for etch product enhancement after $O_3$ exposure.Etching was monitored by the production of $M(acac)_x$ etch products.

$M(acac)_x$ etch products were observed for $Sc_2O_3$, $V_2O_5$ and $VO_2$, $Cr_2O_3$, $Mn_2O_3$ and MnO, $Fe_2O_3$ and $Fe_3O_4$, $Co_3O_4$ and CoO, CuO and $Cu_2O$, and ZnO. No etching was observed for $TiO_2$, $MnO_2$, and NiO. The metal oxides that etched either displayed (1) spontaneous etching by Hacac with no self-limiting behavior or (2) etching that limited itself versus Hacac exposure.The metal oxides that were spontaneously etched by Hacac were $Mn_2O_3$ and MnO, $Co_3O_4$ and CoO, and ZnO.The metal oxides that displayed self-limiting behavior were $Sc_2O_3$, $V_2O_5$ and $VO_2$, $Cr_2O_3$, $Fe_2O_3$ and $Fe_3O_4$, and CuO and $Cu_2O$.ALE processes for these metal oxides that displayed self-limiting reactions are possible using Hacac and $O_3$.

A comparison between the $M(acac)_x$ etch products and the metal oxide also provided information about oxidation state changes during etching.The x in $M(acac)_x$ is both the number of acac ligands and the oxidation state of the M metal center.$Sc_2O_3$, $Cr_2O_3$, MnO, $Fe_2O_3$, CoO, CuO, and ZnO all formed $M(acac)_x$ etch products with the same oxidation state as the metal oxide.In contrast, the other metal oxides all displayed evidence for reduction during etching.This reduction may occur by oxygen loss during the combustion of Hacac.

9:20am **AP+PS+TF-MoM-4 Selectivity between Silicon-Based Materials for Thermal Atomic Layer Etching and Spontaneous Etching***, **Marcel Junige**, S. George,* University of Colorado at Boulder

Sub-10-nm technology nodes must overcome the limits of photolithography. This requires selectivity between various Si-based materials for thermal atomic layer etching (ALE) and spontaneous etching. This work examined selectivity between silicon dioxide ($SiO_2$) and silicon nitride ($SiN_x$) for thermal ALE using trimethylaluminum (TMA) and hydrogen fluoride (HF), as well as for spontaneous etching using HF alone, at 275℃. Distinct etch rates between $SiO_2$ and $SiN_x$ achieved inherent selectivity.

Experiments were conducted in a hot-wall, viscous-flow vacuum reactor with good control over the pressure during static reactant dosing to ensure reproducibility. *In situ* spectroscopic ellipsometry (iSE) was utilized to study etch-per-cycle (EPC), synergy, and selectivity characteristics. Sodium bifluoride ($NaHF_2$) was tested as an alternative HF source. $NaHF_2$ is a solid salt with negligible HF vapor pressure at room temperature, making $NaHF_2$ safer to handle than HF-pyridine. $NaHF_2$ delivered HF pressures up to 15 Torr when heated to 150℃ without releasing sodium. During thermal ALE of alumina ($Al_2O_3$), $NaHF_2$ exhibited diffusion-limited fluorination and EPC characteristics comparable with HF-pyridine.

For thermal ALE of $SiO_2$ alternating TMA and HF, the EPC and synergy were –0.2 Å and 88%, indicating minor spontaneous etching by HF alone. This moderate synergy for $SiO_2$ thermal ALE improved to 95% by ensuring water-free conditions during fluorination. On the other hand, the EPC for $SiN_x$ thermal ALE was –1.1 Å. The EPC for $SiN_x$ was expected to be much lower than for $SiO_2$ because no oxygen reactant was employed to oxidize $SiN_x$. However, iSE experiments revealed that repeated exposures of HF alone spontaneously etched $SiN_x$. Anhydrous HF vapor might form $F^-$ species at the surface that have been attributed to dominate $SiN_x$ etching. Spontaneous etching using static exposures of 45 s at 3 Torr HF alone obtained a high selectivity of ~50:1 for $SiN_x$ removal over $SiO_2$ retention.

For thermal ALE alternating TMA and HF in co-dose with ammonia ($NH_3$), the selectivity inverted to ~9,000:1 for $SiO_2$ over $SiN_x$. HF+$NH_3$ co-dosing led to rapid spontaneous etching of $SiO_2$. $NH_3$, similar to water, might facilitate the dissociation of HF into $H^+$ and $F^-$, where the increased $F^-$ concentration immediately produces $HF_2^-$ species. $HF_2^-$ species have been attributed to dominate $SiO_2$ etching.

In conclusion, this work demonstrated conditions for inherently selective gas-phase etching of either $SiO_2$ or $SiN_x$.

9:40am **AP+PS+TF-MoM-5 Thermal Atomic Layer Etching of $SnO_2$ by Fluorination and Ligand-Exchange Using HF and $Al(CH_3)_3$***, C. Li,* University of Colorado Boulder, China*; J. Partridge,* ***Steven George****,* University of Colorado Boulder

Thermal atomic layer etching (ALE) can be achieved with sequential, self-limiting surface reactions. One mechanism for thermal ALE is based on fluorination and ligand-exchange reactions. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming volatile products. Previous studies have successfully applied this thermal ALE strategy for $Al_2O_3$, $HfO_2$, and $ZrO_2$ ALE. However, no previous investigations have explored the thermal ALE of $SnO_2$ films.

This study demonstrated the thermal ALE of $SnO_2$ thin films using sequential, self-limiting thermal reactions with hydrogen fluoride (HF) and trimethylaluminum ($Al(CH_3)_3$, TMA) as the reactants. The initial $SnO_2$ films were grown by atomic layer deposition (ALD) using tetrakis(dimethylamino) tin and $H_2O_2$. The thermal $SnO_2$ ALE process was then studied using various techniques including quartz crystal microbalance (QCM), spectroscopic ellipsometry (SE), and quadrupole mass spectrometry (QMS).

In situ QCM experiments monitored $SnO_2$ ALE at temperatures from 250 to 300 ℃. The $SnO_2$ etching was linear versus the number of HF and TMA reaction cycles. The QCM studies also showed that the sequential HF and TMA reactions were self-limiting versus reactant exposures. The $SnO_2$ etching rates increased at higher temperatures. The QCM analysis measured mass change per cycle (MCPC) values that varied from −44.32 ng/(cm$^2$ cycle) at 250 °C to −123.5 ng/(cm$^2$ cycle) at 300 °C. These MCPCs correspond to $SnO_2$ etch rates from 0.64 Å/cycle at 250 °C to 1.78 Å/cycle at 300 °C.

SE measurements confirmed the linear removal of $SnO_2$ and the etching rates. QMS analysis also revealed the volatile etching products during the

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

sequential HF and TMA exposures on $SnO_2$ at 300 °C. These QMS investigations observed $Sn(CH_3)_3^+$, indicating $Sn(CH_3)_4$ as the etch product during TMA exposures. $Al_xF_y(CH_3)_z$ dimer and trimer species were identified as the ligand-exchange products. QMS analysis during multiple sequential TMA doses before HF/TMA cycling also revealed that fluorination was necessary for $Sn(CH_3)_4$ etch product evolution. This observation indicated that TMA does not convert $SnO_2$ to $Al_2O_3$. The results indicate that thermal $SnO_2$ ALE using sequential HF and TMA exposures occurs by fluorination and ligand-exchange reactions.

10:40am **AP+PS+TF-MoM-8 Reactivity and Volatility as Key Metrics for Classifying the Substrate Selectivity of Ligands in Atomic Level Processing**, ***Hadi Abroshan,*** Schrödinger, Inc.*; S. Lim,* Schrödinger, Inc., Republic of Korea*; A. Chandrasekaran,* Schrödinger, Inc.*; S. Elliott,* Schrödinger, Inc., Germany*; H. Kwak, M. Halls,* Schrödinger, Inc.

One of the main challenges in the area-selective deposition or etch for semiconductor processing is finding a single reagent that undergoes different chemistry on different substrates. The reagent may be an organometallic complex containing a particular ligand or may be the protonated version of that ligand. In this work we propose that examining just two properties of the organometallic complex across a series of metal cations is sufficient to give an indication of the area-selectivity that can be achieved with reagents based on the particular ligand chemistry.

The first property is reactivity towards the hydrolysis reaction, which gives information about oxide formation versus surface passivation or etching, and the second property is volatility of the organometallic reagent or etch by-product. Figure 1a shows the four limiting cases of the combination of these two properties. Using quantum chemical and machine learning methods to predict the properties, such reactivity-volatility maps can be plotted quickly for a wide range of ligands and metal-containing substrates. We validate our results on the chloro ligand (Figure 1b), thd, RCp and NR2 against area-selective experiments, including those using HCl as etchant [1], ruthenocene and ferrocene [2] as metal sources and β-diketonates as inhibitors [3]. While approximate, this approach provides a starting point for designing and understanding atomic-level processes that are area-selective with respect to a wide variety of substrates.

[1] M.F.J. Vos et al., Chem. Mater. 31, 3878 (2019).

[2] H. Nadhom et al., J. Phys. Chem. Lett. 12, 4130 (2021).

[3] A. Mameli et al., ACS Nano 11, 9303 (2017).

11:00am **AP+PS+TF-MoM-9 Etching of Silicon Nitride Using Vapor-Phase HF Exposures at Various Temperatures: Role of Ammonium Hexafluorosilicate Salt**, ***Vahid Ghodsi,*** *S. George,* University of Colorado Boulder

The etching of silicon nitride ($SiN_x$) was explored using vapor-phase HF exposures at various temperatures. The investigations were performed using *in situ* quadrupole mass spectrometry (QMS) and *ex situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to detect the volatile and non-volatile etch products, respectively. These QMS and ATR-FTIR studies provide valuable understanding of the $SiN_x$ atomic layer etching (ALE) process employing hydrofluorocarbon plasma to form $(NH_4)_2SiF_6$ salt at low temperatures and then thermal annealing at higher temperatures to desorb the salt [N. Miyoshi *et al.*, Jpn. J. Appl. Phys. **56,** 06HB01 (2017)].

At low temperatures, T≤60°C, QMS detected the evolution of $SiF_4$ from HF exposure at 0.5 Torr on $SiN_x$. $SiF_4$ formed concurrently with the formation of a $(NH_4)_2SiF_6$ salt layer on the $SiN_x$ surface according to: $Si_3N_4 + 16HF(g) \longrightarrow 2(NH_4)_2SiF_6 + SiF_4(g)$. To verify the presence of the salt, the temperature could be ramped up to 200°C in the absence of HF exposure. During this temperature ramp, QMS detected $SiF_4$ at higher temperatures T≥80°C corresponding to the thermal decomposition of the $(NH_4)_2SiF_6$ salt according to: $(NH_4)_2SiF_6 \longrightarrow 2NH_3(g) + 2HF(g) + SiF_4(g)$.

When the HF exposure was performed at higher temperatures T≥120°C, $SiF_4$ was again observed as an etch product. However, no secondary rise of $SiF_4$ was detected by QMS during the temperature ramp to 200°C in the absence of HF exposure. This behavior indicated that the $(NH_4)_2SiF_6$ salt did not form on the surface at temperatures T≥120°C. The spontaneous etching of $SiN_x$ with no salt on the $SiN_x$ surface is possible at these higher temperatures. ATR-FTIR studies corroborated the salt formation at lower temperatures and the salt decomposition at higher temperatures.

To demonstrate that HF exposures could achieve high $SiN_x$ etch rates without salt formation, experiments were conducted at T≥140°C with higher HF pressures. A four-fold increase in HF pressure to 2.0 Torr led to a ~five-fold increase in $SiF_4$ signal intensity measured by QMS. At these higher temperatures T≥140°C, $SiN_x$ etching can proceed with no inhibition from the salt.

11:20am **AP+PS+TF-MoM-10 Crystal Phase Transformations During Thermal Atomic Layer Etching of Hafnium–Zirconium Oxide (HZO) Using Hydrogen Fluoride and Dimethylaluminum Chloride**, ***Aziz Abdulagatov,*** *J. Partridge,* University of Colorado at Boulder*; M. Surman,* ASM Microchemistry Ltd., Finland*; S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) was previously demonstrated using hydrogen fluoride (HF) and dimethylaluminum chloride (DMAC) [1]. This current work focused on crystallographic transformations of HZO during ALE. Grazing incidence x-ray diffraction (GIXRD) analysis of initial 10 nm thick HZO film on 20 nm thick TiN on Si revealed orthorhombic (o-phase), tetragonal (t-phase), and monoclinic phases (m-phase). *Ex situ* spectroscopic ellipsometry and X-ray reflectivity (XRR) measurements showed that sequential exposures of HF and DMAC at 250 °C resulted in a linear decrease in film thickness with an HZO etch rate of ~0.45 Å/cycle.

GIXRD studies observed that the peaks associated with the o- and t-phases decreased faster in intensity than the m-phase peaks. As the number of ALE cycles increased, only the m-phase remained before the majority of the HZO film was removed by etching. Interestingly, as o- and t-phases were removed, the grain size of the m-phase crystallites increased in size according to the Scherrer equation. XRR investigations also monitored a decrease in the film density with ALE. In addition, atomic force microscopy (AFM) measurements observed that the density decrease was accompanied by an increase in film roughness.

Powder diffraction (PXRD) studies were also conducted to investigate the phase transformation of crystalline $ZrO_2$ powder at 250 °C. $ZrO_2$ powder was used as a model system since the chemical properties of $HfO_2$ and $ZrO_2$ are very similar. PXRD analysis of as-received $ZrO_2$ powder showed crystallographic planes of mostly m-phase with some cubic (c-phase) and t-phase. As expected, the etching of $ZrO_2$ powder resulted in a mass loss. PXRD also observed the loss of c- and t-phases and an increase in grain size of m-phase crystallites. The results for the HZO films and $ZrO_2$ powder are similar. There are crystal phase transformations that occur with loss of o- and t-phases and growth of m-phase during thermal ALE.

[1] J. A. Murdzek and S. M. George, J. Vac. Sci. Technol. A 38, 022608 (2020)

11:40am **AP+PS+TF-MoM-11 Novel Conversion Half-Cycle for Thermal ALD of High-Density $Hfo_2$ and Its Use in $HfO_2/Al_2O_3$ Nanolaminate Dielectric Barriers**, ***Dane Lindblad,*** Forge Nano

Hafnium dioxide, $HfO_2$, is an attractive material for use as a dielectric barrier in high-power SiC and GaN electronics, both MOSFET and HEMT, due to its high dielectric constant and thermal stability. Current techniques for depositing $HfO_2$ by thermal atomic layer deposition (ALD) tend to produce low density and performing films. While plasma enhanced ALD (PEALD) is employed to improve the performance, the high field and fast switching requirements of the device can make the barriers insufficient. In addition, not all applications can accommodate plasma. As such, a novel conversion process, referred to as the "CRISP" process, for the deposition of $HfO_2$ via thermal ALD has been explored. Utilizing the tool's unique ability to introduce a small amount of non-metal catalyst during the conversion half-cycle, the CRISP process employs surface catalysis to increase growth per cycle, improve stoichiometry, increase density, and modify crystal morphology compared to $HfO_2$ films grown with conventional conversion methods, $O_3$, as shown in Figure 1 and Table 1 below. A comparison of the $HfO_2$ films grown using the CRISP process and the conventional $O_3$ process, both deposited at 250°C, will be presented. Furthermore, due to the layer-by-layer growth of ALD, this deposition technique lends itself well to the fabrication of nanolaminate materials. Specifically, $HfO_2/Al_2O_3$ laminate stacks can be precisely manufactured to alter the bulk material properties and curate device performance, allowing one to choose improvements in leakage current or dielectric breakdown in the nanolaminate film. An initial investigation into the performance of various $HfO_2/Al_2O_3$ laminate stacks is presented, and this work, coupled with higher quality $HfO_2$ films, gives insight into the use of these materials for the next generation of high-power electronic devices.

## Plasma Science and Technology Division
## Room A106 - Session PS+TF-MoM

### Plasma Processing for Advanced Emerging Memory Technologies

**Moderators: Harutyun Melikyan**, Micron Technology, **Jeffrey Shearer**, TEL

8:20am **PS+TF-MoM-1 IBE Patterning and Characterization of High Density STT-MRAM at Pitch 50nm and MTJ CD 20nm***, **Romuald Blanc**, L. Souriau, K. Wostyn, S. Couet, F. Lazzarino,* IMEC, Belgium

Spin Transfer Torque Magnetic Random Access Memory (STT-MRAM) is a promising non-volatile memory technology that offers high-density storage, low power consumption, and fast read/write operations. One potential application of STT-MRAM is as a last level cache (LLC) in computer systems, since it can offer higher performance, lower power consumption, and higher scaling potential than traditional SRAM. However, the patterning of STT-MRAM with Ion Beam Etching (IBE) at CD 20nm and pitch 50nm presents several challenges such as high aspect ratio, damaged magnetic-tunneling junction (MTJ) and sidewall shorts[1,2]. IBE relies on physical ion sputtering which does not allow high selectivity to the hard mask, therefore the choice of the hard mask stack is crucial to avoid excessively high aspect ratio[3]. In this study, we use a hybrid hard mask composed of high-density diamond-like carbon (DLC) to increase etch selectivity and TiN which becomes the STT-RAM top electrode.

In this talk, we present the magnetic and electrical results obtained for STT-MRAM at pitch 50nm using multiple process conditions of IBE main etch, sidewall clean and post-oxidation. We demonstrate that the etch parameters have a significant impact on device yield, with the best condition leading to a wafer-level yield of 95% functional devices with Tunnel Magnetoresistance (TMR) higher than 100%. On the best devices, we measure a TMR of 170% which corresponds to the TMR value before MTJ patterning. Finally, we report a switching current of 20µA with low dependence on pulse width from 5 to 20ns which is consistent with a MTJ CD of 20nm.

**References:**

[1] Lei Wan et al, *Fabrication and Individual Addressing of STT-MRAM Bit Array With 50 nm Full Pitch*, IEEE TRANSACTIONS ON MAGNETICS, VOL. 58, NO. 5, MAY 2022

[2] Murat Pak et al, *Orthogonal Array Pillar Process Development for High Density 4F2 Memory Cells at 40nm Pitch and Beyond*, SPIE Advanced Lithography 2022, Paper 12051-45

[3] Kuniaki Sugiura et al, *Ion Beam Etching Technology for High-Density Spin Transfer Torque Magnetic Random Access Memory*, Japanese Journal of Applied Physics 48 (2009) 08HD02

8:40am **PS+TF-MoM-2 Cryogenic Etching by Physisorption of Neutrals for High-Aspect-Ratio Contact***, **Masahiko Yokoi**, R. Suda, K. Tanaka, M. Tomura, K. Matsushima, Y. Ohya, M. Honda, Y. Kihara,* Tokyo Electron Miyagi Limited, Japan

The most crucial challenge in High-Aspect-Ratio (HAR) dielectric etching is supplying both ions and etchants [1] at the same rate to the etch front. If a large amount of etchant supplied to bottom of the feature is consumed by sufficient ion bombardment, higher aspect ratio etching with superior etching rate can be achieved. Conventional HAR processes which rely on the formation of radicals utilize fluorocarbon and hydrofluorocarbon gases combined with high-applied bias power. However, the stable chemisorption of radicals on feature sidewalls decreases the radical flux at the etch front, which results in a lack of radical supply and a drastic etch rate attenuation in the high aspect region. A technological breakthrough has long been required to solve this problem.

In this work, we focus on neutral physisorption at cryogenic temperatures. There have been several reports on plasma etching in the cryogenic temperature regime [2, 3], but the mechanism has not yet been well understood nor implemented for HAR dielectric etching. We have evaluated a novel etchant in cryogenic temperature and discovered a synergy between hydrogen fluoride (HF) as the etchant and HAR etching process. The dielectric etch rate strongly correlates with the physisorption of the HF, enhanced in the cryogenic temperature regime. The direct injection of HF as the process gas yields higher partial pressure and increased flux compared to radical flux formed by plasma reaction in vapor phase. Furthermore, we confirmed that the phosphorous-containing gas acts as an effective catalyst in the HF reaction. The phosphorous-containing gas stabilizes the HF or etchant physisorption on the $SiO_2$ film, which provides an etch rate enhancement at cryogenic temperature. In this conference, we will present a detailed surface reaction model.

Applying this innovative process to HAR etching enables a higher etch rate, higher selectivity, and higher aspect ratio etching capability. This novel process will enable the manufacturing of next-generation 3D NAND flash memory devices.

[1] K. Ishikawa, et al., Jpn. J. Appl. Phys. Vol. 57, No. 6S2, 06JA01, (2018).

[2] T. Ohiwa, et al., Jpn. J. Appl. Phys. Vol. 31, p.405, (1992).

[3] R. Dussart, et al., J. Phys. D: 47123001, (2014).

9:00am **PS+TF-MoM-3 Plasma Etching Processes Challenges in Emerging Non-Volatile Memories***, C. Boixaderas, T. Magis, C. Socquet, A. Roman, B. Martin,* CEA-LETI, France*; B. Fontaine, P. Gouraud,* STMicroelectronics, France*; J. Dubois,* STMicrolectronics, France*; N. Posseme,* STMicroelectronics, France*; L. Grenouillet, C. Jahan, G. Navarro, G. Bourgeois, M. Cyrille, **Thierry Chevolleau**,* CEA-LETI, France **INVITED**

Since the appearance of flash memory in 1980s, the non-volatile memory (NVM) market is in constant evolution. Nowadays the random access memory (RAM) market is divided into two categories: standalone memories and embedded memories that are integrated into the core CMOS.Since the 2010s, new non-volatile embedded memories are emerging to achieve specific performances in terms of storage, speed, endurance and retention. Such advanced memories are based on resistive (RRAM), material phase change (PCRAM), magnetic (MRAM) and ferroelectric (FeRAM) properties. An overview of the main advanced memory technologies will be presented (operation principles, materials and investigated multilayers stacks).

We will address the patterning challenges that we are facing for the integration of the advanced non-volatile memories. We will mainly focus on the etching and stripping development in terms of scaling down, profile control and plasma induced damages on features sidewalls. The etch process optimization to control the profile and potential technological solutions to minimize plasma damages will be also presented and discussed in terms of plasma surface-interaction.

9:40am **PS+TF-MoM-5 Principle and Application of Etching Lag Mitigation in High Aspect Ratio Contact Process***, **Kyoungsoo Chung**, H. Kim, S. Park, J. Min, K. Yoon, B. Kuh,* Samsung Electronics, Republic of Korea

High Aspect Ratio Contact (HARC) etching is associated with various defects, such as random bending, global tilting, hole distortion, and vertical CD reduction. Depth loading, in particular, is significant and is intricately linked to all these issues. The implementation of a cryogenic process with specific gases has been verified to increase the initial etch rate by nearly threefold compared to the high-temperature process. Furthermore, this procedure has also amplified the patterned aspect ratio where etching lag is observable, in addition to increasing the etch rate. We engage in a comprehensive review and investigation of the mechanisms contributing to the improvement of etching lag. Firstly, it is essential to attain a substantial physisorption amount of neutrals, including radicals, while concurrently delivering highly directional ion energy to activate the surface. Additionally, the transport of neutrals within the hole is crucial for the etchant to be effectively adsorbed up to the etch front. We argue that elements such as a cryogenic environment, low-molecular-weight etchants, compounds that facilitate surface reactions, and a distribution of highly energetic ions are vital for overcoming depth loading. Ultimately, we propose advanced strategies for next-generation HARC etching, based on the lag reduction mechanisms.

10:00am **PS+TF-MoM-6 Etching Selectivities of $SiO_2$ and SiN Against *a*-C Films Using $CF_4/H_2$ with a Pseudo-Wet Plasma Etching Mechanism***, **Yusuke Imai**, S. Hsiao, M. Sekine, T. Tsutsumi, K. Ishikawa,* Nagoya University, Japan*; M. Iwata, M. Tamura,* Tokyo Electron Ltd., Japan*; Y. Iijima,* tokyo Electron, Japan*; T. Gohira, K. Matsushima, Y. Ohya,* Tokyo Electron Ltd., Japan*; M. Hori,* Nagoya University, Japan

With the advancement of cloud computing and AI technology, there is a growing demand for high-speed processing of large amounts of data and high-capacity storage. To manufacture 3D NAND, it is necessary to etch the layer structure where $SiO_2$ and SiN layers are alternately stacked, utilizing the amorphous C layer as a mask. A continuous increase of interest using cryogenic etching for high aspect ratio structure can be observed. Recently, etch selectivities among $SiO_2$, SiN and poly-Si with $CHF_3$/Ar and an ultra-high speed etch process at cryogenic temperature for 3D NAND have also been reported.[1,2] However, the cryogenic etching on variation of selectivities among SiN and $SiO_2$ over a-C have not been discussed yet. In this study, the etching selectivity among $SiO_2$, SiN and a-C was investigated by varying the hydrogen content (20 to 60 %) in $CF_4$/$H_2$ plasma at substrate temperature ($T_s$) of -60 and 20 °C. A capacitively coupled plasma reactor was used in the experiments, The total flow rate of gas mixture of $CF_4$ and $H_2$ was set at 150 sccm and the pressure during process was fixed at 4 Pa. As shown in the supplementary file, at $T_s$ = 20 °C, the both ER of $SiO_2$ and SiN films decreased with increasing the hydrogen content, which is consistent with previous studies. Contrarily, for $T_s$ = -60 °C the ER of $SiO_2$ reached its maximum at around 30-40% hydrogen additives, while the ER value of SiN decreased by nearly half compared to that at 20 °C. As a consequence, the etching selectivity of $SiO_2$/SiN at 20 °C was found to be less than 1 for all hydrogen contents, indicating that SiN was preferentially etched. For $T_s$ = -60 °C it exhibited values greater than unity with the same process. This demonstrates that surface reactions and etching mechanism were changed when substrate was cooled. On the other hand, for *a*-C films increasing the hydrogen content in the $CF_4$/$H_2$ plasma results in a transition from etching to deposition. The transition point was found to be $H_2$ additive of around 50% at 20 °C and around 30% at -60 °C, indicating a wider process window with infinite etching selectivities of $SiO_2$/SiN over *a*-C mask at low $T_s$. The etching characteristics at low temperature is correlated to the surface reactions between the films and neutral HF, based on the results of HF molecular density during plasma discharge using FTIR. A pseudo-wet etching mechanism was proposed to explain the obtained results. The bias power was also varied to investigate the etching behavior further at cryogenic temperature.

[1] R. Dussart *et.al.*, J. Appl. Phys. **133**, 113306 (2023).

[2] Y. Kihara *etal*., VLSI symposium T3-2 (2023)

10:40am **PS+TF-MoM-8 Enhancing Etching Processes at Lower Wafer Temperatures: New Insights into Chemical and Physical Mechanisms*, Thorsten Lill,*** Clarycon Nanotechnology Research, Inc. **INVITED**

Lower temperatures hold significant importance for etching advanced memory devices. In this presentation, we provide a comprehensive overview of the chemical and physical processes involved in etching at lower wafer temperatures. Traditionally, plasma etching techniques heavily rely on the generation of radicals that readily chemisorb onto the surface. However, at low temperatures, molecules tend to adsorb through physisorption, lacking the necessary energy to overcome the energy barrier required for a chemical reaction. However, the concentration of neutrals in typical plasma used for semiconductor manufacturing is notably higher (by one to two orders of magnitude) than that of radicals. At lower temperatures, the physisorption of neutrals becomes significant, increasing their concentration on the surface and contributing to the etching process once chemically activated by energy from the plasma [1].

Etching of high aspect ratio structures utilizes ions and neutral reactive species that must effectively traverse through high aspect ratio features to reach the etch front. We present computational results on neutral transport within such features, exploring the influence of aspect ratio, profile shape, and surface processes including adsorption, desorption, and diffusion of neutral species. Our findings indicate a substantial increase in the steady-state transmission probability with the introduction of surface diffusion [2]. While spontaneous and collision-induced desorption of adsorbed neutrals alone do not alter the steady-state transmission probability, they do impact the time required to reach it. However, in the presence of surface diffusion, spontaneous desorption enhances the transmission probability, whereas desorption resulting from collisions with co-flowing nonreactive gas reduces it. These results unveil the potential for enhancing neutral transport at low surface temperatures, facilitated by physisorption and surface diffusion mechanisms.

By shedding light on the intricate interplay between chemical and physical phenomena during etching processes at lower temperatures, this presentation provides insights into the optimization of etching techniques for advanced memory devices.

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11:20am **PS+TF-MoM-10 High Selectivity Etching via Pulsed Selective Deposition*, André Amend,*** *M. Yakushiji, K. Kuwahara,* Hitachi High-Tech, Japan

Semiconductor device structures are shrinking and increasing in verticality, thus requiring novel plasma dry-etching processes to manufacture high Aspect-Ratio (AR) profiles on nanometer scales. Fabrication of such devices requires hard masks (HM) with high etching resistance that have small Critical Dimension (CD) and large height, corresponding to the needs of the device dimensions. As a result, creating the HMs themselves becomes more expensive and requires costly multi-layer processes to deal with the relatively low etching resistance of the C-rich photomask, which transfers the device pattern via photolithography. HM fabrication could be significantly simplified by an etching process that selectively etches hard materials, such as $SiO_2$, even under soft C-rich masks.

Here, a Phase Mask Reconstruction Process (P-MRP) is introduced, that drastically increases the $SiO_2$ etching selectivity and is compatible with small CD structures. P-MRP allows control of the C-based mask shape while etching $SiO_2$ via a time-modulated bias voltage, that tunes separate selective mask deposition and sample etching phases with a frequency up to above 1000 Hz. While a high voltage is applied to the sample, high-energy ions promote etching, whereas deposition occurs during the low voltage phase. Preferential deposition on the mask is achieved via chemical selectivity and radical shading due to the mask AR.

By precise control of the time-modulated sample bias voltage to adjust etching and deposition phases, the etching selectivity, as well as the mask shape and stability, can be controlled, which is critical to processing small patterns. To achieve high selectivity, the net etching rate on top of the mask can be decreased by reducing average ion energy, while controlling the mask side-deposition rate via the maximum ion energy and duration of the deposition phase. Since P-MRP rapidly alternates mask etching and mask passivation (during the deposition phases) low pattern roughness is achieved as well. For Line/Space and Hole patterns with CD 16-26 nm, etching selectivity as high as 10 was demonstrated while etching a depth of up to 200 nm of $SiO_2$, with AR of up to about 10.

This result indicates that P-MRP could be used to simplify and accelerate HM fabrication. Furthermore, since deposition selectivity is also achieved through AR shading, it can be adopted to process materials other than C-masks and $SiO_2$ etching targets, as well.

## Quantum Science and Technology Mini-Symposium
## Room B110-112 - Session QS+EM+TF-MoM

### Materials for Quantum Computation and Quantum Information

**Moderators: Robert Grubbs**, IMEC Belgium, **Dave Pappas**, Rigetti Computing

8:20am **QS+EM+TF-MoM-1 High Stability Metal-Based Single Electron Transistors for Silicon Quantum Dot Charge Sensors*, Runze Li,*** University of Maryland College Park*; P. Namboodiri,* NIST-Gaithersburg*; Y. Hong, N. Ebadollahi,* University of Maryland College Park*; J. Pomeroy,* NIST-Gaithersburg

Extremely stable metal-based single electron transistors (SETs) are fabricated using a plasma oxidation technique, resolving the time stability problem that has been a major disadvantage for metal-based SETs. Metal-based SETs were studied extensively ~20 years ago, but were abandoned due to the much worse instability in the charge sensing results compared to Si-based SETs. The most severe instability was a low-frequency noise called “charge offset drift,” which causes random and unreproducible readout. Our goal is to produce high stability aluminum-based SETs using plasma oxidation and couple them to Si-based QDs as the charge sensor. The plasma oxidation reduces the two-level defects in the tunnel junction, and we consequently gain a significantly lower charge offset drift of $\Delta Q_0 = 0.13$ e ± 0.01 e in 7 days compared to $\Delta Q_0 > 1$ e in 1 day for thermally oxidized Al-SETs in the literature. However, we are only able to get an output current of ~4 pA during our measurements, which is insufficient as a charge sensor. Our current goal is to increase the output current to ~100 pA (similar to the level of Si-based SETs) by lowering the resistance of the AlOx tunnel junctions. Increasing the tunnel junction area will decrease the resistance, but also increase capacitance, so we are reducing the oxidation time from 7 seconds (which is the oxidation duration for the stabilized SETs being made) to 3 seconds, to reduce the resistance of the tunnel junction by ~10 times.

8:40am **QS+EM+TF-MoM-2 High-quality and High Deposition Rate Atomic Layer Deposition of NbN and TiN for Superconducting Quantum Applications***, H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; L. Bailey, D. Besprozvannyy, M. Powell,* Oxford Instruments Plasma Technology, UK*; **Russ Renzas**,* Oxford Instruments Plasma Technology

Due to the potential of excellent film control, uniformity, and conformality, atomic layer deposition (ALD) is seen as very promising for quantum devices where interface and material quality and their uniformities are a big challenge. Furthermore, for superconducting circuits, the deposition rate of ALD can be an issue, since a high enough film thickness (> 50 nm) is needed to minimize kinetic inductance effects on resonator frequency and where the shielding effectiveness of superconducting vias for crosstalk mitigation depends on film thickness and film conformality in the 3D structures. The challenge here is to deliver sufficiently fast processes while maintaining the desired film properties.

Here, we will share our recent development of a high-quality superconducting NbN and TiN for quantum applications, such as resonators and interconnects, capable of depositing > 50 nm film thickness in two hours. The RF-driven remote plasma source design and chamber of our system is optimized for ALD and allows for deposition rates which are > 3x faster than conventional substrate-biased plasma ALD deposition of similar materials.

The quality of the deposited films was demonstrated to be excellent, as measured by four-point probe electrical resistivity, conformality (100% on 8:1 trench for NbN, verified by SEM), and superconducting transition temperature ($T_c$). Good superconductive properties of the film were demonstrated by SQUID measurements. Thickness uniformity of < ±5% across a 150 mm Si wafer was achieved with good repeatability. We will also show how stress can be tuned as a function of process parameters, such as the RF source power.

Emerging quantum technologies based on superconducting nitride materials are showing great promise and will benefit not only from the uniformity of the deposition, conformality and film quality, but also from the speed and control provided by this ALD process.

9:00am **QS+EM+TF-MoM-3 Navigating MBE Growth of Atomically Precise Complex Oxides using Source Chemistry***, **Bharat Jalan**,* University of Minnesota, USA **INVITED**

From its beginnings as a successful method for III–V semiconductor growth to today for the growth of many contenders for next-generation electronics, spintronics and quantum devices, molecular beam epitaxy (MBE) has been very successful. However, several challenges exist for metal oxide growth where a metal is hard-to-oxidize and/or difficult to evaporate/sublimate. In this talk, I will review these issues and will present my group’s effort to address these challenges using a novel solid-source metal-organic MBE approach. We show, for the first time, controlled synthesis of metal and metal oxides of these “stubborn” elements with the ***same ease and control*** as afforded by III-V MBE. We will present detailed growth study utilizing chemistry of source materials as a controlling knob to navigate synthesis. With the goal to understand and control electronic ground states in defect-managed complex oxide films and nano-membranes, we will discuss how chemistry of source materials can be used to navigate synthesis on-demand.

9:40am **QS+EM+TF-MoM-5 Atomic Layer Deposition of Superconducting Titanium Nitride for Through-Silicon-Via Structures and Photon Detection***, **John Femi-Oyetoro**, H. LeDuc, P. Day, M. Dickie, F. Greer,* Jet Propulsion Laboratory (NASA/JPL)

Superconducting detectors (SDs) play a crucial role in solving various problems in astronomy and cosmology, including dark matter, exoplanet transit spectroscopy, quantum computing and information. An example of such devices is the microwave kinetic inductance devices (MKIDs). This device has been employed in answering questions about the first light emitted after the big bang approximately 14 billion years ago. SDs make use of thin films of superconducting materials, such as titanium nitride (TiN), because of their high intrinsic kinetic inductance (KI) and large London penetration depth, which makes them particularly interesting and useful. In this study, we demonstrate the atomic layer deposition (ALD) of high-quality TiN with high transition temperature ($T_c$) and KI suitable for large photon detector arrays and high-density through-silicon-via (TSV) structures. ALD-TiN provides an alternative and reliable source of high-quality films for scarce high-quality sputtering targets. Additionally, these films are expected to be more uniform than reactive sputtered films, which is crucial for cm-scale detector arrays, increasing the absolute detector yield on each wafer. We explored various precursors, gas chemistries, techniques, and deposition conditions, including temperatures as low as 200°C. In particular, we also employed ion bombardmentvia RF biasing for our deposition process. This is a unique method for removing oxygen impurities, a major contributor to low-quality and high-resistivity films. Furthermore, this energy supply facilitates film densification, efficient elimination of precursor ligand residues, and surface adatom diffusion. We are able to repeatedly deposit a film of ~ 54 nm on a planar 6-inch wafer that transitions and superconducts at $T_c = \sim 4.35$ K. Overall, our goal is to produce SC films with spatial uniformity, highly conformal, and high $T_c$ to overcome the challenges of large detector arrays and interconnect density using 3D integration. The results aiding these efforts will be discussed further.

10:40am **QS+EM+TF-MoM-8 Molecular Beam Epitaxy of Superconducting ZrN Thin Films on GaN Substrates***, **Brelon May**, K. Vallejo, D. Hurley, K. Gofryk,* Idaho National Laboratory

Group III-Nitride materials have found applications in optoelectronics and photonic devices due to the large variation in direct bandgap spanning from the infrared to the deep ultraviolet. Recent research has pursued the integration of this well-established material system with transition-metal nitrides to create complex heterostructures with additional magnetic or superconducting functionality. ZrN is a well-known refractory conductor with high oxidation resistance, high hardness, and has been shown to be a superconductor at low temperatures. The estimated lattice mismatch of ZrN with InN, GaN, and AlN is 8.5%, -1.5%, and -4.2%, respectively, suggesting strain free as well as strain-tunable growth on the ternary III-Ns. This work focuses on the epitaxial growth of ZrN on c-plane GaN substrates via molecular beam epitaxy. An electron beam evaporation source and an RF-plasma source were used to supply the Zr and active nitrogen, respectively. Reflection high energy electron diffraction (RHEED) and X-ray diffraction (XRD) did not reveal any crystallographic texture of ZrN deposited on fused silica at temperatures >700°C. However, growth of ZrN on c-plane GaN substrates at similar temperatures was epitaxial. RHEED revealed that the ZrN maintains the symmetry of the underlying GaN throughout the entire deposition, and post-growth examination via XRD showed (111) oriented ZrN thin films. RHEED patterns during the regrowth of GaN directly on thicker layers of higher symmetry ZrN suggest a preference for twin formation and a slight degree of surface faceting. A physical property measurement system was used to measure electrical transport as a function of temperature and magnetic field. Initial results of uncapped ZrN thin films reveal a superconducting phase with a critical temperature of <10 K and a critical field of 2 T. Because the critical temperature is lower than expected, the presence of off stoichiometry or structural disorder is suspected. These results pave the way for integration of superconductors and quantum phenomena in existing III-N photonic systems.

11:00am **QS+EM+TF-MoM-9 Enhancing Quantum Circuits Through Biased Plasma-Enhanced ALD of Ultrathin Superconducting $TaC_xN_{1-x}$***, **Silke Peeters**,* Eindhoven University of Technology, Netherlands*; C. Lennon, V. Seferai, R. Hadfield, M. Weides,* University of Glasgow, UK*; M. Verheijen, E. Kessels,* Eindhoven University of Technology, Netherlands*; H. Knoops,* Eindhoven University of Technology, Oxford Instruments, Netherlands

Superconducting quantum circuits are one of the leading architectures in quantum computing platforms. Recent experiments [1,2] demonstrating up to 0.5 ms coherence time in superconducting Ta transmon qubits mark a six order of magnitude improvement in superconducting qubit coherence over the past two decades [3,4]. However, major material challenges, such as uncontrolled oxides and disordered interfaces, still stand in the way of realizing large-scale, fault-tolerant quantum computers.

In this contribution, material properties of ultrathin $TaC_xN_{1-x}$ are extensively characterized and coupled to cryogenic superconducting quantum device performance. In this way, we aim to clarify the roles of various processing aspects in achieving high-quality-factor devices. $TaC_xN_{1-x}$ films with thicknesses of 7 – 40 nm were prepared by plasma-enhanced atomic layer deposition (PEALD) with radiofrequency substrate bias. Because of its atomic-scale growth control PEALD is a promising technique for growth of thin films with high-quality interfaces. Ion energy control in the ~25 – 250 eV range is provided by the substrate bias.

We have observed that energetic ions can counteract oxygen impurity incorporation and promote a larger grain size, while minimizing ion-induced material damage. Increasing the ion energy from ~25 eV to ~150 eV yields a hundredfold decrease in room-temperature resistivity to 239 μΩ cm for an 18 nm film. Smooth, dense, polycrystalline $TaC_xN_{1-x}$ films of the fcc crystal structure are obtained, which are stable in ambient atmosphere.These films maintain a high critical temperature of superconductivity ($T_c$) of 7 K down to 11 nm film thickness.

The high ultrathin-film quality achieved by PEALD with substrate bias is promising for ultrathin, low-loss superconducting quantum devices. Specifically, superconducting resonators were fabricated from 20 - 35 nm $TaC_xN_{1-x}$ films on high-quality silicon and sapphire substrates, with preliminary measurements showing internal quality factors of at least $2x10^5$ in the single-photon regime. Furthermore, we provide practical pointers for quantum device compatibility of ultrathin superconducting films. Through the high level of control in PEALD with substrate bias, this work contributes to the understanding of material loss mechanisms in superconducting quantum circuits.

References

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2. C. Wang *et al.* npj Quantum Inf. **8**, 3 (2022).
3. W. D. Oliver and P. B. Welander *MRS Bulletin***38**, 816 (2013).
4. D. Gill and W. M. J. Green *IEEE ISSCC* 30 (2020).

11:20am **QS+EM+TF-MoM-10 Characterization of Ultra-Thin Superconducting TaN Nanowires with Integrated Heatsink Capabilities for SNSPD Applications***, **Ekta Bhatia,*** NY CREATES*; T. Nanayakkara, C. Zhou,* Center for Functional Nanomaterials, Brookhaven National Laboratory*; T. Vo,* American Institute for Manufacturing Integrated Photonics*; W. Collison, S. Schujman, A. Biedron, J. Nalaskowski, S. Olson,* NY CREATES*; S. Kar,* American Institute for Manufacturing Integrated Photonics*; H. Frost,* College of Nanoscale Sci. & Eng., SUNY Polytechnic Institute*; J. Mucci, B. Martinick, I. Wells, T. Murray, C. Johnson, V. Kaushik,* NY CREATES*; C. Black, M. Liu,* Center for Functional Nanomaterials, Brookhaven National Laboratory*; S. Papa Rao,* NY CREATES

Tantalum nitride (TaN) has emerged as a promising candidate for superconducting nanowire single-photon detectors (SNSPD) due to its favorable properties such as lower $T_c$ that enables easier Cooper-pair breaking and a longer wavelength cut-off [1]. TaN is also attractive because it is widely used in the CMOS IC industry enabling TaN SNSPDs to be readily made at a large scale, on 300 mm wafers. While the body of knowledge about superconducting TaN has been growing, its knowledge at 300 mm scale is limited. In this work, we report on the superconducting properties of 300 mm scale TaN and its dependence on process variables. We then discuss the impact of novel integration schemes on the thermal characteristics of TaN nanowires for SNSPD applications.

Copper encapsulated damascene TaN nanowires (with a N/Ta ratio of 0.53 set by room temperature reactive sputtering conditions) have a coherence length of ~8 nm. This is in rough agreement with prior literature on TaN thin films deposited at 750°C on sapphire substrates [2]. Extracted values of effective penetration depth, critical magnetic field, and critical current density are reported. We also studied the $T_c$, $I_c$ dependence on varying thicknesses and line widths (100 nm to 3000 nm). Our TaN nanowires exhibit a $T_c$ of ~3.45 K (at a thickness of ~35 nm) with <5% variation across the 300 mm wafer. Sheet resistance (at 300 K) and $I_c$ vary by < 5% across the 300 mm wafer for all the line widths measured, similar to the < 5% across-wafer non-uniformity of thickness (XRR) and N/Ta ratio (SIMS & XPS). We also investigated the superconducting properties of different in-film N/Ta ratios varying from 0.35 to 0.7 using 20 nm thick nanowires.

We explored the efficacy of Cu as a heat transport material that is integrated with TaN nanowires in various schemes (damascene Cu above the nanowire, and a blanket underlayer of Cu) and compared to a control case with no Cu. We used the ratio of retrapping current to $I_c$ as the metric of heat transfer efficiency. This study demonstrates a novel way to increase heat transport away from the nanowire, hence improving the reset times of SNSPDs. We discuss one possible design of a focal plane array of fast SNSPDs based on the findings of this work. This study further strengthens the case for scalable fabrication of TaN nanowires using state-of-the-art 300 mm process tools, with applications ranging from arrayed detectors for cosmology to single photon detection in photonic quantum computing and superconducting optoelectronic neuromorphic computing.

[1] A. Engel *et al.* Appl. Phys. Lett. **100**, 062601 (2012).

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Authors 1 and 2 contributed equally.

11:40am **QS+EM+TF-MoM-11 Cryogenic Microwave Loss Measurements of Metal-Oxides using 3D Superconducting Cavities***, **Nicholas Materise,*** Colorado School of Mines, USA*; J. Pitten,* University of Colorado Boulder*; W. Strickland, J. Shabani,* New York University*; C. McRae,* University of Colorado Boulder/National Institute for Science and Technology (NIST)

Reports of high performance tantalum-based qubits has stimulated interest in comparing the quality of tantalum pentoxide with niobium pentoxide and suboxides of niobium. Here, we present a high participation cavity capable of resolving differences in losses due to oxides grown on Ta and Nb thin films. We distinguish losses of the oxide from the other interfaces using in a multi-step measurement process, first measuring the substrate with its native oxide, then repeating the measurement with the film deposited on the same substrate with oxide grown on the surface. Participation ratio calculations estimate the losses due to each interface, with their thicknesses measured by cross-sectional transmission electron microscopy. This measurement capability opens possibilities to screen candidate materials, and their oxides, for use in superconducting qubits and devices.

## 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.

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

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.

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[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 °C 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 ( 2.6-2.7x$10^{13}$ $cm^{-2}$). 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.

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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.

## Spectroscopic Ellipsometry Technical Group
## Room C124 - Session EL1+TF-MoA

### Thin Films & Novel Materials

**Moderators: Mathias Schubert**, University of Nebraska - Lincoln, **Megan Stokey**, Milwaukee School of Engineering

1:40pm **EL1+TF-MoA-1 Enhancement of Electron Effective Mass in Semiconductor Materials and 2DEGs Revealed by THz Optical Hall Effect**, ***Nerijus Armakavicius,*** Linköping University, Sweden*; S. Knight,* Linköping University*; P. Kuhne, H. Zhang, R. Carrascon,* Linköping University, Sweden*; S. Richter,* Linköping University, Lund University, Sweden*; V. Stanishev,* Linköping University, Sweden*; M. Schubert,* Linköping University, Sweden, University of Nebraska-Lincoln*; P. Paskov,* Linköping University, Sweden*; V. Darakchieva,* Lund University, Sweden **INVITED**

Progress in semiconductor material technology continues to enable significant advances in nearly all scientific endeavors and lies at the heart of modern information and communication networks. Wide band gap semiconductors, such as GaN and SiC transpire as key materials to address the demands of next-generation quantum technology and green electronics.Understanding transport in semiconductor materials is a prerequisite for their implementation in advanced device architectures with improved functionalities. Electron effective mass is a fundamental material parameter defining the free charge carrier transport but it is very challenging to be directly determined at high temperatures and frequencies relevant for device operation.

With the advent of the optical Hall effect (OHE), which consists of performing generalized spectroscopic ellipsometry at long wavelengths in magnetic field the determination of the electron effective mass tensor at variable temperatures has became possible without the need to invoke any additional electrical measurements [1,2]. The OHE describes the external magnetic field induced anisotropic charge displacement in materials when interacting with electromagnetic waves and allows for the determination of the charge carrier sign, concentration, mobility and effective mass parameters [2].

In this work, we present a comprehensive investigations of the electron effective mass parameters in GaN bulk and epitaxial layers, as well as in two-dimensional electron gas (2DEG) in GaN based high-electron mobility transistor structures [3,4] by THz and MIR OHE [5]. OHE analysis allows to extract the free charge carrier concentration and mobility in the various structures as a function of temperature and the results are found to be in a good agreement with the respective parameters obtained by electrical Hall effect and capacitance-voltage measurements. In addition, the electron effective mass parameter is determined from the OHE at temperatures from 10K to 370K. At low temperatures (< 100 K) an electron effective mass of approximately $0.20m_0$ is obtained in agreement with the well accepted value. Unusual enhancement of the electron effective mass is discovered with increasing temperatures to room temperature and above for both bulk, epitaxial and 2DEG GaN systems. We evaluate and discuss various mechanisms such as band gap nonporabolicity, magnetic field, strain and polaron effects,that could potentially contribute to the observed increase. We propose a frequency-dependentscattering time to be at the origin of the effective mass enhancement. We also discuss possible deviations of the free electron behavior from the classical Drude model and its implications for transport and devices operating at high temperatures (room temperature and above) and frequencies (100 GHz to 1THz).

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2:20pm **EL1+TF-MoA-3 In Situ and Real Time Spectroscopic Ellipsometry of Polycrystalline $CuInSe_2$ Co-Evaporation for Narrow Bandgap Photovoltaic Absorbers***, D. Sapkota,* ***Balaji Ramanujam****, M. Alaani, A. Shan, N. Podraza, R. Collins,* University of Toledo

Deposition processes for narrow bandgap ($E_g$ = 1.02 eV) polycrystalline $CuInSe_2$ (CIS) thin films with intended applications as photovoltaic (PV) absorbers have been developed and studied using various techniques of in situ and real time spectroscopic ellipsometry (SE). Real time SE analyses of two series of sequentially deposited Cu and $In_2Se_3$ thin films on the same substrates, but at different Cu and In evaporation source temperatures, serves as an accurate source calibration method. This calibration enables co-evaporation of CIS films at independently controllable deposition rates and compositions, the latter characterized by the [Cu]/[In] molar ratio which establishes their p-type character as PV absorbers. In situ SE analyses of the starting crystalline Si substrates provide an accurate substrate temperature calibration, and real time SE of CIS co-evaporation on such substrates provides insights into polycrystalline nucleation and grain coarsening processes. In contrast to earlier studies of hydrogenated amorphous silicon PV absorbers, the highest device quality CIS absorbers are obtained in processes leading to the most extensive increases in the surface roughness layer thickness with bulk layer thickness, characteristic of crystallites of increasing size protruding from the film surface. Real time SE provides the time evolution of the surface roughness layer, bulk layer, and effective thicknesses for the deposited film, where the effective thickness is the volume per planar area of substrate and, thus, includes the surface roughness contribution. The effective thickness is used to evaluate the deposition rate for the desirable situation in which the roughness thickness increases continuously with bulk layer thickness. For substrate temperatures of 500°C and below in CIS co-evaporation, the roughness thickness is relatively stable with increasing bulk layer thickness at values controlled by the initial nucleation. At higher temperatures, in contrast, the surface roughness thickness increases rapidly and continuously with bulk layer thickness, well above that observed in the initial nucleation process. Such grain growth enhancement is also reflected in the following variations in the final film properties with increasing substrate temperature: (i) an increased grain size as determined by the widths of the peaks in the X-ray diffraction pattern, (ii) a reduction in the bandgap critical point broadening parameter from ex situ SE, consistent with an increase in the grain boundary scattering time for excited carriers, (iii) a steeping of the Urbach tail, and (iii) higher performance PV devices for absorbers incorporated into cell structures.

2:40pm **EL1+TF-MoA-4 Anisotropic Optical Properties of $GdScO_3$***,* ***Prabin Dulal****, E. Miller,* University of Toledo*; D. Sotir, M. Barone, D. Schlom,* Cornell University*; N. Podraza,* University of Toledo

$GdScO_3$ is a wide-band gap semiconductor with a high dielectric constant, the potential to replace $SiO_2$ in silicon-based transistors, and use as a substrate for epitaxial thin film growth. It has an orthorhombic crystal structure resulting in crystallographic and optical anisotropy. The optical properties in the form of complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra for each principal direction of single crystal $GdScO_3$ are investigated using generalized spectroscopic ellipsometric spectra collected over the photon energy range from 0.70 to 8.50 eV. Multiple sets of generalized ellipsometric spectra are collected from (001) and (110) surface plane oriented single crystals of $GdScO_3$ as a function of rotation about the surface normal. A divided spectral range analysis is used to determine the structural parameters of the $GdScO_3$ including bulk and surface layer thicknesses and the azimuthal Euler angle for each measurement while the remaining Euler angles are fixed based on known lattice parameters and the respective surface plane cut. In divided spectral range analysis, the full measured spectra range is subdivided into nominally transparent, weakly absorbing, and highly absorbing regions. A common structural model is used to describe the transparent and the highly absorbing spectral region to obtain common structural parameters while separate physically realistic models are applied to describe spectra in ε in each direction and both of these spectral regions. The weakly absorbing region is initially ignored as the line shape describing ε is not initially known. After obtaining structural parameters, numerical inversion is then used to extract ε corresponding to electric fields oscillating parallel to each crystallographic axis over the full spectral range, including the initially ignored weakly absorbing region. Critical points transition in *ε* corresponding to each direction are identified by simultaneously fitting each numerically inverted spectra in $\varepsilon_2$ and $d\varepsilon_2/dE$ using a sum of critical point parabolic band (CPPB) oscillators. A piecewise parameterization is developed that includes an Urbach tail below the band gap energy and CPPB behavior at and above the band gap energy to parameterize the numerically inverted optical response. The lowest direct transition is identified at 6.46 eV for electric fields oscillating parallel to a-axis, and above gap critical transitions at 6.72, 6.78, 6.95, 7.40, 7.92, and 8.25 eV are identified from all spectra in ε.

3:00pm **EL1+TF-MoA-5 Combined Density Functional Theory and Spectroscopic Ellipsometry Studies of Anisotropic Materials***, **Rafal Korlacki**, M. Hilfiker, M. Stokey, M. Schubert,* University of Nebraska-Lincoln **INVITED**

The ability of spectroscopic ellipsometry (SE) to resolve all components of the dielectric tensor combined with the predictive power of density functional theory (DFT) and related first-principles methods, is a particularly useful combination of techniques to study anisotropic materials. In recent years, a wide-bandgap gallium oxide $Ga_2O_3$ is a promising candidate for applications in high-power electronic devices. The most stable *β* phase, which can be grown as a high-quality bulk crystal is highly anisotropic, thanks to the low-symmetry monoclinic lattice [1,2]. In order to further increase the bandgap, the alloys of gallium oxide and aluminum oxide, $(Al_xGa_{1-x})_2O_3$, can be epitaxially grown on gallium oxide substrates. Heteroepitaxial films are inherently strained. The dependence of material properties on the components of the strain tensor for monoclinic crystals have been obtained from symmetry analysis [3], and the linear deformation potentials for energies of phonon modes and band to band transitions in $Ga_2O_3$ - from DFT calculations [3,4]. The same principle can be applied to the monoclinic phase of $Al_2O_3$, and Vegard's rule can then be used to construct a simple universal model of strain and composition dependencies of various material properties, including band-to-band transitions, refractive indices, components of the dielectric tensors, and effective mass parameters. Thus, these dependencies can be fully resolved for actual heterostructures under specific strain patterns [5,6].

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## 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.

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## Surface Science Division
## Room D136 - Session SS+AS+TF-MoA

### Mechanisms at Surfaces and Interfaces

**Moderators: Florencia C. Calaza**, Instituto de Desarrollo Tecnológico para la Industria Química, **Jun Nakamura**, UEC Tokyo

1:40pm **SS+AS+TF-MoA-1 Spin- and Alignment-Controlled $O_2$ Chemisorption and Catalytic CO Oxidation on Stepped Pt and Pt/Co Alloy Surfaces*, Mitsunori Kurahashi,*** National Institutes for Materials Science, Japan **INVITED**

$O_2$ chemisorption and catalytic oxidation on Pt and its alloy surfaces have been studied intensively due to the relevance to important processes such as car exhaust gas purification and oxygen reduction reaction (ORR) in fuel cell. Since $O_2$ is a linear diatomic molecule with an electron spin, the alignment of the $O_2$ axis relative to the surface local structure is a key to understand the elementary processes of $O_2$ chemisorption. If the surface is magnetic, the spin correlation between $O_2$ and the surface also plays an important role. A single spin-rotational state-selected [(J,M)=(2,2)] $O_2$ beam allows us to investigate the effects of molecular alignment and spin on $O_2$/surface interactions [1].

In this talk, I will firstly present the alignment-controlled $O_2$ chemisorption and CO oxidation on curved Pt(111). The use of a curved crystal surface and a local probe allows us to monitor the step-density dependence in surface properties or reactivity[2,3]. In this study, by scanning the aligned $O_2$ beam with a dimension of 0.2mmW x 2mm across a curved Pt(111) surface, the step-density and structure dependence in alignment-resolved $O_2$ chemisorption probability and CO oxidation rate were measured. The results indicate that step affects the reactivity of the neighboring terraces, and that the low temperature CO oxidation rate at step site is much lower than at (111) terrace.

Secondly, I will present the spin-dependent catalytic CO oxidation on Pt/Co/Pt(111). Pt/Co alloy has attracted much attention since it shows a higher ORR activity than pure Pt [4]. The higher reactivity has been attributed to the charge transfer from the subsurface Co to the surface Pt layer while how the spin of the subsurface Co affects the reactivity of the surface Pt remains unclear. Spin-resolved $O_2$ chemisorption and CO oxidation experiments on a perpendicularly-magnetized Pt/Co(2ML)/Pt(111) film indicate that the $O_2$ chemisorption probability and the catalytic oxidation rate depend strongly on the spin orientation between $O_2$ and the Pt surface. The magnitude of the spin orientation dependence was larger than that observed for $O_2$/Ni [1,5]. An SPMDS measurement and DFT calculation show that the surface Pt layer is spin-polarized at around $E_F$. The present experiments indicate that the catalytic activity of Pt is strongly affected by the magnetism of neighboring atoms.

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2:20pm **SS+AS+TF-MoA-3 Atomic-Scale Insights Into the Sintering Resistance and Oxidation of Single-Atom Alloys*, Audrey Dannar*[1]*,*** Tufts University*; J. Finzel,* University of California, Santa Barbara*; V. Cinar, E. Sykes,* Tufts University

Copper-based catalysts are used in a wide range of heterogeneous catalytic processes that can take place in oxidizing environments, where Cu is known to readily oxidize to form CuOx, and reducing environments, where Cu is known to deactivate via sintering. Single-atom alloys (SAAs) are a new type of catalyst in which isolated atoms of dilute reactive dopants such as Pt and Rh are present in more inert host metals such as Cu. Despite their great promise for hydrogenation and dehydrogenation reactions, there exists limited understanding of these materials under oxidizing conditions. Similarly, SAAs have shown exceptional long-term stability with anecdotal reports of sintering resistance in industrial conditions that are not presently fundamentally understood. This work aims to develop atomic-scale structure-function relationships for Cu-based catalysts that span oxidizing and reducing conditions and understand how single dopant atoms stabilize the undercoordinated Cu atoms responsible for sintering and involved in CuOx formation upon O2 exposure.

First, we used a specialized method for measuring the surface diffusion of metal atoms that leads to sintering with scanning tunneling microscopy (STM) experiments which reveals that single Pt atoms in a Cu(110) surface significantly reduce the rate of Cu atom detachment from undercoordinated surface sites. Thus, the origin of sintering resistance exhibited by SAA is hypothesized to be due to dopant atom stabilization of undercoordinated Cu atoms at the step edge. This is validated by DFT and paired with collaborator work that shows PtCu/SiO2 dilute alloy catalysts are significantly more stable than monometallic Cu/SiO2 in methanol synthesis experiments via EXAFS and TEM.

Next we used STM experiments to elucidate atomic-scale details of the oxidation processes of both PtCu(111) and RhCu(111) SAAs. STM images reveal that on Cu(111), oxidation occurs below Cu step edges, consistent with literature reports. Interestingly, for the RhCu(111) SAA, oxidation occurs both below the step edges and also above, where the Rh atoms are located, but this is not the case for the Pt brim on PtCu(111). For both Rh and Pt SAAs the oxidation below the step edge is reduced compared to Cu, which we hypothesize is due to the stabilization of Cu step edge atoms, which are required to restructure during CuOx formation below the step. The reduced rates of sintering and oxidation of PtCu SAAs compared to Cu originate from Cu step edge atoms being kinetically stabilized by dilute dopants. Together, these results begin to shed light on the role of single dopant atoms in the mechanisms Cu nanoparticle sintering and Cu oxidation.

2:40pm **SS+AS+TF-MoA-4 Visualization of the Local Dipole Moment at the Si(111)-(2x2) Surface Using DFT Calculations*, Akira Sumiyoshi,*** *J. Nakamura,* The University of Electro-Communications (UEC Tokyo), Japan

Understanding the polarization state of a sample is essential in the development of devices and functional materials. Recently, the spatial distribution of the surface polarization has been observed using new microscopy techniques, such as SNDM[1-3]. However, there have yet to be any reports regarding the theoretical simulation of surface polarization. Here, we focused on the dipole moment (DM), an essential aspect of polarization, and developed a method to visualize the distribution of surface DM using theoretical calculations. In this study, we report on the surface DM distribution of Si(111)-(2x2) with the characteristic motif of the Si(111)-(7x7) DAS structure. Furthermore, we confirmed that the surface dipole distribution can be explained consistently with the surface stabilization mechanism.

We defined and calculated the DM using the following formula;

$\mu_{(x,y,z)} = \int \rho_{(x,y,z')} * (z'-z_0)\, dz'$

Here, μ is the DM, $\rho_{(x,y,z')}$ is the total charge density, and $z_0$ is the origin in the vertical direction. In order to eliminate the effect of the backside surface of the Si(111) slab, we adopted the midpoint of the deepest bulk layer of the slab as the origin and integrated the above formula from $z_0$ to the vacuum position z sufficiently far from the topmost surface. The total charge density was calculated using DFT-based first-principles calculations.

Upon optimizing the structure, the restatom was lifted compared to the original bulk position, suggesting the larger orbital electronegativity[4] of the surface orbital of the restatom[5]. This change in orbital electronegativity leads to an electron transfer from the adatom to the restatom, resulting in no surface dangling bond. We calculated the electron localization function (ELF) map and the band diagram to confirm the surface electron transfer. We confirmed the presence of the electron pair on the restatom from ELF. It was revealed that the Si(111)-(2x2) surface has a finite energy gap. As a result, it was clearly shown that the electron transfer occurs from the adatom to the restatom, emptying the dangling bond at the adatom and forming a lone pair at the restatom.

Furthermore, we simulated the surface DM distribution. As a result, an upward DM was observed at the adatom position, which is explained by the depletion of electrons just above the adatom due to the electron transfer at the surface.

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3:00pm **SS+AS+TF-MoA-5 Mechanism Study of a Chemisorbed $O_2$ Molecule on Ag(110) Induced by High-Order Overtone Excitation Using STM*, Minhui Lee,*** *E. Kazuma,* The University of Tokyo, Japan*; C. Zhang,* Tongji University, China*; M. Trenary,* University of Illinois at Chicago*; J. Takeya,* The University of Tokyo, Japan*; J. Jung,* University of Ulsan, Republic of Korea*; Y. Kim,* The University of Tokyo, Japan

The dissociation pathway of chemisorbed $O_2$ on Ag(110) was elucidated by single-molecule microscopic and spectroscopic studies using a scanning tunneling microscope (STM). The dissociation reaction was found to be predominantly triggered by inelastically tunneled holes from the STM tip due to the significantly distributed density of states below the Fermi level of the substrate. A combination of action spectroscopy with the STM and density functional theory calculations revealed that the $O_2$ dissociation reaction is caused by direct ladder-climbing excitation of the high-order overtones of the O-O stretching mode arising from anharmonicity enhanced by molecule-surface interactions.

3:20pm **SS+AS+TF-MoA-6 Characterization of Oxygen Evolution from Rh(111)*, Maxwell Gillum,*** *E. Jamka, F. Lewis, D. Killelea,* Loyola University Chicago

Due to the importance of oxide surfaces in heterogeneously catalyzed reactions, it is critical to gain a fundamental understanding of the reactivity and behavior of oxygen on these transition metal surfaces. In previous studies we have been able to establish that the reactivity and thermodynamic stability of oxygen on Rh(111) relies in part on the concentration of oxygen present in the subsurface. However, more research needs to be conducted in order to gain a better understanding of the relationship between surface reactivity and subsurface concentration. In addition to the techniques used in our previous studies, namely temperature programmed desorption (TPD) and scanning tunneling microscopy (STM), the experiments herein will include simultaneous infrared (IR)/TPD techniques to gain more information on these critical interactions.

4:00pm **SS+AS+TF-MoA-8 Spin-Polarized VLEED from Au(111): Surface Sensitivity of the Scattering Process*, Christoph Angrick,*** *A. Reimann,* University of Münster, Germany*; J. Braun,* Ludwig-Maximilians-University of Munich, Germany*; M. Donath,* University of Münster, Germany

Low-energy electron diffraction from Au(111) shows the well-known threefold symmetry of the diffracted electron beams despite the sixfold symmetry of the surface layer. This is due to the influence of the second and deeper layers and the probing depth of the electrons. In this work, we

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[1] **SSD Morton S. Traum Award Finalist**

investigated Au(111) with spin-polarized very-low-energy electron diffraction (VLEED) [1,2,3] experimentally and theoretically. We monitor the reflected specular beam at a fixed polar angle of incidence of $\Theta=45°$ while the azimuthal orientation of the crystal is varied. This puts the surface sensitivity of the VLEED scattering process to a test.

Our results show that the electron reflection and the spin-orbit-induced reflection asymmetry along ΓM and ΓM' are equivalent. The observed sixfold symmetry suggests a sensitivity to one atomic layer only. At azimuth angles deviating from the high-symmetry directions ΓM and ΓM', however, the VLEED signal from Au(111) shows a threefold symmetry. To reveal the origin of this effect, we varied the parameters in the calculation. The results indicate a non-negligible influence of the second atomic layer in the VLEED scattering process.

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4:20pm **SS+AS+TF-MoA-9 Unravelling the Chemisorption Mechanism of Epoxy-Amine Coatings on Zr-Based Converted Galvanized Steel by Combined Static XPS/ToF-SIMS Approach***, **Vanina Cristaudo**, K. Baert, P. Laha,* Research Group Electrochemical and Surface Engineering (SURF), Vrije Universiteit Brussel, Belgium*; M. Lim, L. Steely, D. Clingerman, E. Brown-Tseng,* Coatings Innovation Center, PPG*; H. Terryn, T. Hauffman,* Research Group Electrochemical and Surface Engineering (SURF), Vrije Universiteit Brussel, Belgium

In the automotive industry, the corrosion protection of hot-dip galvanized (HDG) steel is of primary importance. To this purpose, a Zr oxide-based conversion pre-treatment of the metal surface for passivation and improved adhesion [1], in combination with the application of a polymeric primer coating is often performed. Usually, organic and inorganic additives are used in the acidic conversion bath for a large variety of purposes. For instance, Cu(II) salts are employed to accelerate the deposition of zirconium oxide [1]. Recently, the heterogeneity and multi-metal nature of the resulting surface has been demonstrated in our laboratory [2]. Now, it is of pivotal importance to study the efficiency and durability of such hybrid (hydr)oxide-polymer systems, which depend on the formation and degradation of the chemical bonds at the buried interface.

This work aims at the elucidation of the interfacial interactions established between an epoxy-amine coating and HDG steel [3]. The influences of the Zr-based conversion treatment of the substrate and the use of Cu(II) additive on interfacial bonding will be studied [3]. To this purpose, an amine-functionalized molecule – diethylenetriamine (DETA), a common curing agent – will be adsorbed and used as an indicator of the acid-base properties of the metal oxide surface. The complex multi-metal oxide surface of the Cu-modified Zr-based converted substrate will be decomposed in derivative (simpler) systems, such as pure Zn, Zr, and Cu. The resulting DETA-adsorbed model and multi-metal surfaces will be investigated by X-ray photo-electron spectroscopy (XPS), and by examination of the N 1s peak, the interfacial bond densities will be determined. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) will be performed to discriminate between the different metal oxide contributions present on the substrate surface. Preferential adsorption of the DETA molecule on the zinc atoms is found on converted substrates. SIMS also points out the interfacial bonding with the Cu cationic sites when the copper additive is used, highlighting the extreme usefulness of this analytical technique in the assessment of interfacial interactions of “diluted” adsorption sites.

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[3]V. Cristaudo, *et al.* Unravelling the chemisorption mechanism of epoxy-amine coatings on Zr-based converted galvanized steel by combined static XPS/ToF-SIMS approach. Appl. Surf. Sci. (2022), 599, p.153798.

4:40pm **SS+AS+TF-MoA-10 Fermi Surface Emergence and Valence Band Maximum Formation During $Li_xCoO_2$ Insulator-to-Metal Transition***, **Elena Salagre**,* Dpto Física Materia Condensada, Universidad Autónoma de Madrid, Spain*; P. Segovia,* Dpto Física Materia Condensada, Universidad Autónoma de Madrid. IFIMAC (Condensed Matter Physics Center), Spain*; M. González-Barrio,* Dpto Física de Materiales, Universidad Complutense de Madrid, Spain*; J. Pearson, I. Takeuchi,* Materials Science and Engineering, Univ. Of Maryland*; E. Fuller, A. Talin,* Sandia National Laboratories*; M. Jugovac, P. Moras,* Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Italy*; A. Mascaraque,* Dto. Fïsica de Materiales, Univ. Complutense de Madrid, Spain*; E. Garcia Michel,* Dto. Física Materia Condensada, Univ. Autonoma de Madrid, IFIMAC (Condensed Matter Physics Center), Spain

Despite the great interest in $LiCoO_2$ (LCO) and related materials for their applications in batteries, catalysis and resistive memory devices, uncertainties regarding the valence band structure, charge compensation and the nature of the insulator-to-metal transition (IMT) remain controversial [1][2]. In addition, the use of chemical and electrochemical methods on heterogeneous materials, including cathode binders and solid electrolyte interfaces, pushes research further away from a fundamental understanding of the processes involved in ion deintercalation.

We have developed a surface science-based approach to vary the Li content, based on $Ne^+$ sputtering and performed entirely in situ under ultra-high vacuum (UHV) conditions on epitaxial LCO thin films, without interactions between the material and any electrolyte.

This has allowed us to obtain high-resolution angle-resolved photoemission (ARPES) data of the valence band structure in LCO for a wide range of Li molar fractions, directly observing the IMT at x=0.95 and the regions of phase coexistence and phase dominance. X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) were used to characterize the material during Li deintercalation and to investigate the mechanisms of charge compensation in the absence of electrolyte. Li removal is accompanied by the formation of $Co^{4+}$ from the initial $Co^{3+}$ in the LCO structure. Oxygen holes were also observed, related to the hybridization of Co 3d and O 2p orbitals. The valence band was interpreted using reported theoretical calculations [3] and limited previous experimental work [4]. We identify the Co 3d $t_{2g}$ energy levels as those involved in the IMT and locate the valence band maxima (VBM) with a clear 3-fold symmetry and band renormalization, suggesting a Mott character of the transition.

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5:00pm **SS+AS+TF-MoA-11 Nanoscale Hydrogen Detection Using Time-of-Flight Secondary Ion Mass Spectrometry***, B. Paudel, J. Dhas, M. Choi, Y. Du, **Zihua Zhu**,* Pacific Northwest National Laboratory

Hydrogen in materials attracts tremendous interest as its incorporation leads to significant alterations in structure, composition, and chemistry, which in turn impacts functional properties. Additionally, it has been integral to nuclear fusion reactors and is regarded as the major source of clean energy. However, nanoscale manipulation and characterization of hydrogen in materials are challenging as only a selected few analytical technique can readily detect hydrogen, among which time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a unique and powerful technique due to its excellent detection limit along with decent spatial and depth resolutions. In our lab, ToF-SIMS has been used for hydrogen detection for more than 15 years, and it became more and more important in the last several years. In this presentation, we will discuss, using selected examples, how the detection and quantification of hydrogen in materials by ToF-SIMS has been utilized to reveal the hydrogenation/protonation-induced novel functional states in different classes of materials along with some tricks on sample preparation, optimized experimental conditions to achieve reasonable detection limits of hydrogen, and future prospects. We emphasize the unique capabilities of ToF-SIMS which can potentially unlock new functional states and answer some outstanding scientific questions in materials science.

## Atomic Scale Processing Mini-Symposium
## Room A107-109 - Session AP+EM+PS+TF-TuM

### Area Selective Processing and Patterning

**Moderators: Eric A. Joseph**, IBM Research Division, T.J. Watson Research Center, **Adrie Mackus**, Eindhoven University, Netherlands

8:00am **AP+EM+PS+TF-TuM-1 Area-Selective Deposition in Nanoscale Patterns*, Annelies Delabie,*** Imec Belgium, and KU Leuven Belgium*; J. Clerix,* IMEC Belgium*; K. Van Dongen,* IMEC, Belgium*; J. Sinha,* IMEC Belgium*; L. Nyns,* IMEC, Belgium*; R. Nye,* LAM Research*; G. Parsons,* North Carolina State University*; J. Swerts,* IMEC Belgium **INVITED**

Manufacturing nano-electronic devices becomes more and more complex as the device dimensions reach the nanoscale and a wide range of new materials is being implemented to achieve high device performance. Additional complexity comes from the use of three dimensional (3D) structures to reduce the active footprint. Area-Selective Deposition (ASD) provides a promising avenue to assist and/or even simplify device manufacturing processes. ASD is a technique to deposit material only on a pre-defined area of a patterned surface (the growth area), while no deposition is intended on other areas of the same surface (the non-growth area). As such, ASD can be used to replicate patterns on 3D substrates and to (partly) fill narrow trenches or holes from the bottom up. ASD can be achieved by tuning the adsorption and diffusion kinetics in atomic layer deposition (ALD) and chemical vapor deposition (CVD) processes. Insight in the chemical and physical processes is essential to enable rational design of new ASD processes for nano-electronic device manufacturing for advanced technology nodes.

This presentation will discuss the growth mechanisms during ASD on substrates that contain nanoscale patterns, where the geometry of the nanopatterns can affect the growth behavior, selectivity and uniformity. An aminosilane small molecule inhibitor can enable ASD on a wide range of materials with $SiO_2$ as the non-growth surface [1]. The selectivity of $TiO_2$ ALD relies mainly on adsorption. Selectivity loss during $TiO_2$ALD occurs via a nucleation site generation mechanism: small $TiO_2$ nanoparticles are continuously generated during ALD by slow, unintentional adsorption on the passivated non-growth surface area [2]. ASD super cycles consisting of inhibitor adsorption, $TiO_2$ ALD and etch effectively improve the selectivity, but may compromise the height uniformity in nanoscale patterns. The selectivity of Ru and $Ge_2Sb_2Te_5$ ALD relies on a complex interplay of adsorption, diffusion and aggregation. We reveal a pattern-dependent selectivity for Ru ALD, which is explained by aggregation of Ru adspecies at the pattern edges [3]. We conclude that the selectivity and uniformity of ALD processes can change when pattern dimensions reach the nanoscale.

[1] K. Van Dongen et al, *J. Vac. Sci. Technol. A* 2023, 41, 032404.

[2] R. A. Nye et al, *Appl. Phys. Lett.* 2022, 121, 082102.

[3] J.-W. J. Clerix et al, *Appl. Surf. Sci.* 2023,626, 157222.

8:40am **AP+EM+PS+TF-TuM-3 N-Heterocyclic Carbenes as Small Molecule Inhibitors in AS-ALD*, Cathleen Crudden,*** Queen's University, Canada **INVITED**

A unique carbon-based SMI, called an N-heterocyclic carbene (NHC), has been developed as a small molecule inhibitor using carbon as the heteroatom. NHCs have been used in organometallic and catalysis chemistry for decades, where they are renowned for their ability to form strong bonds to metal surfaces. We have developed a suite of organic SMIs with high volatility and thermal stability enabling deposition in an ALD tool. We demonstrated strong binding of the SMI to Ru, Co, Mo and Cu and selectivity for binding to metal surfaces in the presence of insulators. These results are informed by surface science studies including microscopy and spectroscopy.

9:20am **AP+EM+PS+TF-TuM-5 Unraveling Precursor Blocking Mechanisms in Area-Selective Atomic Layer Deposition Using Small Molecule Inhibitors*, Olaf Bolkenbaas,*** *M. Merkx,* Eindhoven University of Technology, Netherlands*; P. Yu,* eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Area-selective atomic layer deposition (ALD) has garnered significant attention as a potential technique for enabling the further miniaturization of semiconductor devices. One method for achieving area-selective ALD is through the use of small molecule inhibitors (SMIs) that selectively block deposition on certain materials. Previous research has indicated that precursor blocking by SMIs involves two components: the chemical removal of reactive surface sites and the physical blocking of the surface, also referred to as chemical passivation and steric shielding respectively [1]. However, it is difficult to differentiate between these two factors as they occur simultaneously. In this work we attempt to unravel the steric shielding and the chemical passivation contributions by the SMI acetylacetone (Hacac) with the use of reflection adsorption infra-red spectroscopy (RAIRS) on dehydroxylated $Al_2O_3$ surfaces obtained through annealing.

When comparing Hacac adsorption on an as-prepared and an annealed $Al_2O_3$ surface using RAIRS, a lower amount of Hacac adsorbates was observed on the annealed surface. Furthermore, a higher fraction of the Hacac adsorbates was present in the more strongly bonded chelate configuration. This difference in the distribution of the binding configurations demonstrates that the density of surface sites affects the SMI adsorption behavior. We expect that this different adsorption behavior is caused by a lower amount of steric hindrance between the SMIs on the annealed $Al_2O_3$ surface. Furthermore, the increase in the amount of adsorbates in the chelate configuration will result in a higher contribution of chemical passivation on the dehydroxylated surface, since only the adsorbates in the chelate configuration chemically passivate the surface [2]. From this we can conclude that the removal of surface sites can be used to obtain a better understanding of the two precursor blocking mechanisms. This better understanding will create opportunities for the development of new area-selective ALD strategies involving the removal of reactive surface sites before the functionalization with SMIs to improve selectivity.

[1] Merkx, et al., Chem. Mater. **32**, 3335–3345 (2020).

[2] Mameli et al., ACS Nano **11**, 9303–9311 (2017).

9:40am **AP+EM+PS+TF-TuM-6 Topographically-Selective Deposition Using Amorphous Carbon as Inhibition Layer*, Thijs Janssen,*** *M. Merkx, W. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

To accommodate the increasing complexity of device architectures in nanoelectronics, new nanoscale processing techniques are required. Selective deposition techniques have been developed in recent years to enable bottom-up and self-aligned processing[12]. While traditional area-selective deposition distinguishes between areas depending on their chemical character, topographically-selective deposition (TSD) distinguishes between areas based on their orientation within a 3D structure[2,3]. Such TSD approaches offer new fabrication opportunities, for example when the growth and non-growth areas possess similar material properties, or when too many different materials are present within the device structure. Previously reported TSD methods have been demonstrated only for specific materials.

In our work, we develop a versatile TSD strategy that is potentially suitable for a broad range of materials. Our approach utilizes a pulsed Ar/$CH_4$ plasma to selectively apply an amorphous carbon (aC) inhibition layer on horizontally-oriented surfaces by relying on the directional ions from the plasma. The vapor-phase selective deposition of aC is integrated together with existing ALD processes and plasma treatments into a TSD supercycle recipe.

The highly inert surface of aC lacks suitable absorption sites for ALD precursors and co-reactants, making it an effective inhibition layer. It was found that only the horizontally-oriented surfaces are covered by the aC layer, thus subsequent ALD of target materials proceeds exclusively on vertically-oriented surfaces.

Successful ALD inhibition on the aC surface is established for several different target materials such as $TiO_2$ using TDMAT and $H_2O$, $Nb_2O_5$ using TBTDEN and $H_2O$, and $NiO_x$ using $Ni(BuAMD)_2$ and $H_2O$. In particular 90% selectivity was maintained for 35 cycles $TiO_2$ deposition (1.09 ± 0.01 nm selective growth), 70 cycles $Nb_2O_5$ deposition (4.38 ± 0.02 nm) and 40 cycles of $NiO_x$ deposition (1.28 ± 0.01 nm). It is demonstrated for $NiO_x$ that the supercycle can be repeated, which effectively resets the nucleation delay, such that a thicker film (nominally ~5 nm after 4 supercycles) can be deposited selectively.

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2. Parsons, G. N. & Clark, R. D. Area-Selective Deposition: Fundamentals, Applications, and Future Outlook. *Chem. Mater.***32**, 4920–4953 (2020).

3. Chaker, A. *et al.* Topographically selective deposition. *Appl. Phys. Lett.* **114**, (2019).

11:00am **AP+EM+PS+TF-TuM-10 A ReaxFF Study for Hacac Interaction on $Al_2O_3$ Surface in Area-Selective ALD***, **Naoya Uene,*** Tohoku University, Japan*; I. Tezsevin, W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands*; A. van Duin,* Pennsylvania State University*; T. Tokumasu,* Tohoku University, Japan

An area-selective ALD process of $SiO_2$ was developed comprising acetylacetone inhibitor (Hacac), bis(diethylamino)silane precursor (BDEAS), and $O_2$ plasma reactant pulses. Hacac inhibitors lead to delayed $SiO_2$ growth on the $Al_2O_3$ surface for about 15 ALD cycles, after which the selectivity is lost. Two chemisorption configurations of Hacac inhibitors on $Al_2O_3$ surfaces have been reported: monodentate and chelate configurations. (Merkx et al. 2020) Density functional theory (DFT) calculations have shown that the monodentate configuration is relatively reactive with incoming BDEAS, causing the loss of selectivity due to precursor-inhibitor reactions. Therefore, exploration of the relative densities of the chelate/monodentate configurations on the surface is crucial for the understanding of the selectivity loss mechanism. We aim to understand the reaction mechanisms of Hacac inhibitor adsorption on $Al_2O_3$ surfaces at the atomic scale.

Up to now, the investigation of the adsorption of inhibitor molecules has been studied via DFT calculations. Thereactive force-field molecular dynamics (ReaxFF MD), which can simulate chemical reactions and physical dynamics at the atomic scale, has been used for gas-surface systems. (van Duin et al. 2001) We performed ReaxFF MD simulations to consider the chemical reactions of Hacac inhibitor molecules with dislocation effects on the surface. An initial force field has been developed for the Hacac interaction on $Al_2O_3$ surface based on the two existing force fields: Li/Si/Al/O force field for $Al_2O_3$ structure and protein force field for carbohydrate interactions. (Kim et al. 2016; Monti et al. 2013) The initial force field is trained for Hacac geometry, and their reaction on an OH-terminated $Al_2O_3$ surface is also modeled.

We performed ReaxFF MD simulations using the developed force field. The simulation consists of three steps. First, the $Al_2O_3$ surface is pre-thermally relaxed. Then, the Hacac inhibitor is supplied on the relaxed surface, followed by post-thermal relaxation of the Hacac-adsorbed surface. We first confirmed the temperature stability of the $Al_2O_3$ surface with different temperatures. Our force field can control the temperature of the $Al_2O_3$ surface ranging from 300 K to 1500 K. Next, sequential adsorption of 20 Hacac inhibitor molecules was simulated on the temperature-controlled $Al_2O_3$ surface, as shown in the supplemental document. The findings from our ReaxFF simulations provide in-depth insights into the mechanisms of Hacac adsorption and saturation on the surface. These insights will be used for the investigation of precursor blocking and blocking selectivity loss in our future work.

11:20am **AP+EM+PS+TF-TuM-11 Enhancement of TMSDMA Passivation on SiO2 by Surface Fluorination***, **Anthony Valenti,*** SUNY College of Nanoscale Science and Engineering*; C. Vallée,* SUNY College of Nanoscale Science and Engineering, France*; C. Ventrice,* SUNY College of Nanoscale Science and Engineering*; K. Tapily, K. Yu, S. Consiglio, C. Wajda, R. Clark, G. Leusink,* TEL Technology Center, America, LLC, USA

With the ever-shrinking scale of semiconductor devices, area-selective atomic layer deposition (AS-ALD), a bottom-up and self-aligned patterning process with atomic-scale control has been in development in order to meet the demands of industry. This technique is typically conducted by promoting growth on specific surface termination types, while inhibiting growth on the other surface types of the substrate via selective chemisorption of molecules that are inert to the deposition process. With its affinity for chemisorbing to hydroxylated oxide surfaces, specifically SiO2, but not on Si or non-oxidized metal surfaces, N-(trimethylsilyl)dimethylamine (TMSDMA) has been of recent interest for its use as a small molecule inhibitor (SMI) for area selective deposition (ASD). Upon interaction with a surface hydroxyl group, the TMSDMA molecule dissociates, resulting in a trimethylsilyl group bonded to the chemisorbed oxygen atom of the hydroxyl group. Although TMSDMA-passivated SiO2 typically remains inert over several ALD cycles, nucleation of the growth precursor can eventually occur. This may be due to hydroxyl groups on the surface that did not interact with TMSDMA molecules and/or non-hydroxylated sites that were not passivated by trimethylsilyl groups. For instance, surface siloxane bridges do not dissociate TMSDMA and can act as nucleation sites for the ALD growth precursor. In order to enhance the passivation of SiO2 surfaces, the use of co-passivants has been explored. In particular, a remote NF3 plasma has been studied as a means for forming a co-inhibitor. Dosing before or after TMSDMA treatment has been investigated. The deposition of the small molecules were carried out on 10 Å SiO2/Si(100) substrates. Water contact angle measurements were taken to determine relative surface passivation of each sample. Angle-resolved X-ray photoelectron spectroscopy and attenuated total reflection/Fourier transform infrared spectroscopy were performed in order to characterize the chemical state of each surface. Our results indicate that exposure of the substrate to the NF3 plasma after passivation with TMSDMA, results in damage to the passivating layer. However, exposure of the surface to the NF3 plasma before TMSDMA exposure maintains the passivation of the SiO2 surface. In addition, temperature programmed desorption (TPD) measurements are being conducted to assess the relative coverage of the inhibiting film on each sample and its thermal stability.

11:40am **AP+EM+PS+TF-TuM-12 A Study of Elucidation and Improvement of $TiO_2$ Selectivity by First-Principles Based Thermodynamic Simulation***, **Yukio Kaneda,*** Sony Semiconductor Solutions Corporation, Japan*; E. Marques, S. Armini, A. Delabie, M. van Setten, G. Pourtois,* IMEC, Belgium **INVITED**

Area-selective deposition (ASD) enables the deposition of materials in a targeted area, typically a pre-patterned surface, while preventing the growth on adjacent surfaces.[1] The technique is appealing for both academia and industry as it offers a vehicle to simplify material developments in nanoelectronics. Consequently, numerous efforts have been dedicated to investigate the factors driving the selectivity mechanisms and to identify optimal process deposition conditions, including surface treatments, that enable highly selective processes.

The “selectivity” dimension results from the identification of the right combination of precursors (including co-agents), surface treatments, and reactor operating conditions. This is typically a complex and laborious process that requires many systematic and tightly controlled experiments. As a result, the development of highly selective ASD processes is often a slow and challenging task where any form of guidance provided by modeling insights can be precious.

In this context, we studied, by combining thermodynamic considerations and first principle simulations, the reactivities of complex surface chemical reaction networks and the factors impacting on selectivity. In this talk, we will discuss the case of the ASD of $TiO_2$ on $SiO_2$ substrates terminated with either “reactive” (-OH) or “passivated” alkyl-silyl groups. First, we will first briefly discuss the validation of our approach by comparing our model prediction with experimental measurements for the case of the ALD of $TiO_2$ using the precursors $TiCl_4$ and $Ti(OMe)_4$ and then report the insights gained for the identification of optimum Ti precursor and inhibitor for the ASD of $TiO_2$. We will then extend the discussion to the case of the ASD supercycles of $TiO_2$, where the interaction of some Ti precursors (or of their ligands) leads to the degradation of the surface “passivation” and then requires restoring the surface by injecting of alkyl-silyl functional groups. We will review the strategies that worked with their drawbacks.

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## 2D Materials Technical Group
## Room C123 - Session 2D+TF-TuA

## 2D-Materials: Synthesis

**Moderators: David Johnson**, University of Oregon, **Peter Liljeroth**, Aalto University

2:20pm **2D+TF-TuA-1 High-Order Van Der Waals Superlattices and Artificial Quantum Solid Beyond Mechanical Exfoliation and Restacking*, Xiangfeng Duan,*** UCLA **INVITED**

The advent of two-dimensional atomic crystals (2DACs) and van der Waals heterostructures (vdWHs) has inspired a new thinking on heterostructure construction beyond the limits of lattice matching requirement. However, the vdWHs explored to date have been largely limited to relatively simple systems with a small number of building blocks. The preparation of high-order vdW superlattices with a larger number of alternating units is exponentially more challenging due to the limited yield and scalability of the commonly used exfoliation-and-restacking strategy. Here I will discuss strategies to create high-order vdW superlattices (vdWSLs). First, by exploiting a capillary-force-driven rolling-up process, we show a series of synthetic VDWHs can be transformed into high-order vdWSLs with alternating atomic layers of widely variable material compositions, electronic band offset dimensions, chirality and topology. Alternatively, we further discuss a molecular intercalation approach to prepare a new family of hybrid superlattices consisting of alternating layers of covalently bonded 2D atomic layers and self-assembled molecular layers, which opens the door to exploit highly versatile molecular design strategies to tailor solid-state materials, enabling artificial materials with designable structural motifs and tunable electronic properties beyond the reach of conventional crystalline solids. We will particularly highlight a recent example of a new class of chiral molecular intercalation superlattices with robust chiral-induced spin selectivity. The formation of high-order vdW superlattices defines a rich artificial materials platform to unlock previously inaccessible physical limits and enable new device concepts beyond the reach of the existing materials.

3:00pm **2D+TF-TuA-3 Understanding the Sequential Growth of Bilayer MoS2 on SiO2 Substrate by Mo Isotope Labeling*, Kai Xiao,*** Center for Nanophase and Materials Sciences Oak Ridge National Laboratory*; Y. Yu,* School of Physics and Technology, Wuhan University, China*; J. Hachtel,* Center for Nanophase and Materials Sciences Oak Ridge National Laboratory*; M. Yoon,* Material Science and Technology Division, Oak Ridge National Laboratory*; A. Puretzky, A. Ievlev, C. Rouleau, D. Geohegan,* Center for Nanophase and Materials Sciences Oak Ridge National Laboratory

Bilayer 2D materials and heterostructures with different stacking configurations have attracted interest due to their emerging optical and quantum properties. Usually, it can be synthesized by the two-step chemical vapor deposition (CVD) method. Here we utilized isotope labeling method to study the CVD growth of bilayer $MoS_2$ on $SiO_2$/Si substrates. The stacking configuration and growth sequence were characterized by Raman spectroscopy, time-of-flight second ion mass spectroscopy (ToF-SIMS), and scanning transmission electron microscopy (STEM). We found that the growth of bilayer $MoS_2$ follows a sequential growth process which the second growth layer of $MoS_2$ goes underneath the fist growth layer. The AB and AA stacked bilayer $MoS_2$ are formed by templating the first growth single crystal $MoS_2$ layers. The embedded antiphase grain boundaries were characterized by atomic-resolution z-contrast STEM. Density functional theory (DFT) with molecular dynamic (MD) simulation were performed to understand the sequence growth pathway of bilayer $MoS_2$. This new understanding of the growth mechanism for bilayer $MoS_2$ can provide a new strategy for synthesis of 2D materials with controllable layer numbers and stackings.

Synthesis science was supported by the U.S. Dept. of Energy, Office of Science, Materials Science and Engineering Division. This work was performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

4:20pm **2D+TF-TuA-7 The Transformation from Dendritic to Triangular $Ws_2$ Growth via Nacl-Assisted Low-Pressure Chemical Vapor Deposition*, Himal Pokhrel,*** *J. Duncan, S. Pollard,* The University of Memphis

Monolayer tungsten disulfide (WS2) is one of the promising two-dimensional materials in the transition metal dichalcogenide family due to its remarkable optical, electronic, and electrocatalytic behavior. However, the structure of this material varies significantly with growth conditions. In this work, we use the salt-assisted low-pressure chemical vapor deposition (LPCVD) method to grow monolayer $WS_2$ crystals reaching over 50 µm in size on the SiO2/Si substrates. We observe a transition from large, dendritic to triangular growth by systematically varying the amount of promotor material (NaCl), growth temperature, and source-substrate distance. The synthesized material is characterized by Raman spectroscopy, scanning electron microscopy, and X-ray photoemission spectroscopy in order to understand the role of each parameter during the growth process. The results of this work provide a framework for the synthesis of large-area $WS_2$ growth with variable morphology through salt-assisted LP-CVD.

Kay words: Chemical vapor deposition, dendrites, $WS_2$

4:40pm **2D+TF-TuA-8 Hybrid Pulsed Laser Deposition Growth of Layered Chalcogenides*, Mythili Surendran,*** *H. Chen, J. Ravichandran,* University of Southern California

Mythili Surendran[1], Huandong Chen[1],Shantanu Singh[1], Boyang Zhao[1] and Jayakanth Ravichandran[1]

1. Mork Family Department of Chemical Engineering and Materials Science, University of Southern California

Chalcogenides, especially layered transition metal dichalcogenides, have emerged as an exciting class of materials that host several novel physical phenomena suitable for a broad range of electronic and photonic applications. High-quality thin film growth of these chalcogenides is critical to enable investigations into their fundamental properties and also for device applications. The thin films of layered chalcogenides are mostly grown using chemical vapor deposition, although molecular beam epitaxy, metal-organic vapor deposition, pulsed laser deposition (PLD) and several other techniques have been exploited. However, large area and high-quality growth with precise and uniform thickness control and low defect densities still remain a challenge due to a large cation-chalcogen vapor pressure mismatch, corrosive and reactive nature of most chalcogen precursors, high synthesis temperatures and the propensity to oxidize easily in the presence of oxygen at these high temperatures. In case of metal disulfides, most growth techniques utilize $H_2S$ as the sulfur source. However, $H_2S$ is a toxic, hazardous, and flammable gas and require high temperatures for efficient decomposition and sulfurization, resulting in high defect densities.

Here, we report an alternative hybrid PLD approach wherein we employed organo-sulfur precursors as sulfur source to grow chalcogenide thin films. This novel method enables low temperature growth (~500°C) of chalcogenides as the precursors decompose at a lower temperature (~250-400°C) to provide dissociated sulfur species. To demonstrate the efficacy of this approach, we have demonstrated large area epitaxial growth of Group IV 2D chalcogenides such as $TiS_2$ (metallic), $ZrS_2$ and $HfS_2$ (semiconducting). Structural and electrical characterization, along with low temperature transport studies reveal low defect densities and high carrier mobilities in these thin films. These results emphasize the importance of development of low temperature growth techniques for high mobility refractory metal-based chalcogenides for electronic applications, especially with back-end-of-line (BEOL) compatibility. The potential of these chalcogenides as suitable candidates for transparent and conducting layers in chalcogenide-based optoelectronic devices will be discussed. Further, we will also briefly discuss about the epitaxial growth of a variety of other chalcogenides such as 3D metal chalcogenides, chalcogenide perovskites, thus establishing the versatility of this novel method to grow chalcogenides for next-generation electronics and photonics.

5:00pm **2D+TF-TuA-9 Effect of Several Growth Parameters on Graphene Growth on Four Types of Supported Cu Films Using Cold Wall Cvd and Perspective on Growth Mechanism of Graphene from Scaling Functions of Graphene Island Size Distribution*, Shantanu Das,*** Intel Corporation

Graphene growth was explored on solid electrodeposited, recrystallized, sputter deposited and liquid Cu films supported on W or Mo refractory substrates under ambient pressure using Ar, H2 and CH4 mixtures using a custom-automated LabVIEW controlled graphene growth method in a custom-modified multi-chamber UHV chamber transformed into a cold wall CVD system. Among these films, electrodeposited Cu film was chosen to study the effect of total flow rate, CH4:H2 ratio and dilution of the CH4/H2 mixture by Ar at a fixed substrate temperature of 1000 °C and total pressure of 700 Torr, on the nucleation density and average size of graphene crystallites. The resulting morphological changes correspond with those that would be expected if the precursor deposition rate was varied at a fixed substrate temperature for physical deposition using thermal evaporation. The evolution of graphene crystallite boundary morphology with decreasing effective C deposition rate indicates the role of edge diffusion of C atoms along the crystallite boundaries, in addition to H2 etching on graphene crystallite shape. The results indicate that graphene grown on Cu films using cold wall CVD follows a classical two-dimensional nucleation and growth mechanism. Following nucleation at the earliest growth stages, isolated crystallites grow, impinge and coalesce to form a continuous layer. During the pre-coalescence growth regime, the size distributions of graphene crystallites exhibit scaling which is a function of island area, graphene coverage, average island area and areal density. For graphene grown on Cu surfaces that have been annealed in a reducing Ar+H2 ambient, excellent data collapse onto a monotonically decreasing universal Avrami scaling function is observed irrespective of graphene coverage, surface roughness or Cu grain size. This result is interpreted to indicate attachment limited growth and desorption of C-containing species. Graphene grown on Cu surfaces that were annealed in a nonreducing environment exhibits a qualitatively different bimodal scaling function indicating diffusion-limited growth with a lower attachment barrier combined with C detachment from the graphene edges. Graphene growth on molten Cu films supported on custom-designed Mo substrates demonstrate a similar 2D nucleation and growth mechanism. The roles of temperature gradient, chamber pressure and rapid thermal heating in C precursor-rich environment on graphene growth morphology on thin sputtered Cu films are explained. I anticipate that applying the study of pre-coalescence size distribution method to other 2D material systems may be useful for elucidating atomistic mechanisms of film growth that are otherwise difficult to obtain.

5:20pm **2D+TF-TuA-10 Decoupling of Graphene from Metal Substrate via Interface Epitaxy*, Abdullah Al-Mahboob*, *J. Sadowski,* Center for Functional Nanomaterials, Brookhaven National Laboratory

The research on two-dimensional quantum materials (2DQM) received significant attention in both, theoretical and experimental physics. Among 2DQM systems, graphene (Gr) remains a material of special interest since its discovery three decades ago. The interest in 2DQM research further evolved beyond Gr and its analogs (called Xenes) as these materials have potential for technological applications including quantum computing and quantum information.

The interest on Gr originated not only from well-known Gr stability in ambient conditions, massless Dirac carrier characteristics and feasibility of roll-to-roll production, but also successful use of Gr as a template for other 2DQMs. Despite the interest in Xenes other than Gr, such as silicene, antimonene, borophene, these materials are generally unstable at ambient conditions. In order to protect reactive Xenes and stabilizing their structure, Gr can also be also used as a protective inert coating. In the present study we explored a method of interfacial 2D growth under the inert overlayer, graphene.

We employed in-situ real-time low-energy electron/photoemission electron microscopy (LEEM/PEEM), micro-beam LEED, XPS/UPS and micro-spot ARPES for the study of interface chemistry of silicon allotropes and 2D silica structures grown at the Gr/Ru interface.

In this report, we show how the Si interface epitaxy can decouple Gr electronically from the catalyst Ru substate, and a successful scalable synthesis of Gr/√3-Silicene and Gr/Si/$SiO_2$ heterostructures can be realized. Tuning the growth conditions also provided means to control the growth of 2DQM at large scale. The strategy of interface epitaxy could be more general and opens the avenue of growing and stabilizing other atomically thin 2D materials.

Research was carried out at the Center for Functional Nanomaterials and the National Synchrotron Light Source II at Brookhaven National Laboratory under Contract No. DE-SC0012704.

5:40pm **2D+TF-TuA-11 Wafer-Scale, Phase-Selective Growth of Two-Dimensional Indium Selenides by Metal-Organic Chemical Vapor Deposition***, **Seunguk Song**, S. Jeon, M. Rahaman, J. Lynch, D. Rhee, P. Kumar, S. Chakravarthi, G. Kim, X. Du,* University of Pennsylvania*; E. Blanton,* KBR Inc.*; K. Kisslinger,* Brookhaven National Laboratory*; M. Snure,* Air Force Research Laboratory, Sensors Directorate*; N. Glavin,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA*; E. Stach, R. Olsson III, D. Jariwala,* University of Pennsylvania

The two-dimensional (2D) indium selenides (InSe and $In_2Se_3$) have garnered attention as a highly desirable ultrathin III-VI semiconductor, possessing favorable qualities akin to III-V semiconductors and 2D van der Waals transition metal dichalcogenides. However, due to the complexity of the In-Se system and challenges related to promoting lateral growth, large-area, phase-selective synthesis of 2D InSe and $In_2Se_3$ has proved difficult. Here, our work presents a successful method for the growth of high-quality and thickness-controlled 2D InSe and $In_2Se_3$ thin films using vertical, cold-walled metal-organic chemical vapor deposition. By interrupting the Se source periodically, we create an environment deficient in Se that favors the nucleation of InSe over $In_2Se_3$. Additionally, pulsing the Se precursor promotes lateral growth of InSe at low temperatures (360-500 °C), allowing us to produce highly stoichiometric, crystalline thin films on 2-inch sapphire substrates. Importantly, these growth temperatures are compatible with back-end-of-line integration in Si microelectronics. The resulting 2D domains are oriented along the crystal structure of the substrate, and the thickness can be controlled by growth time. We also demonstrate the fabrication of few-layer InSe transistors with high on-to-off current ratios (~$10^4$-$10^5$) and field-effect mobility (~2.8 $cm^2V^{-1}s^{-1}$) comparable to that of mechanically exfoliated single crystals of InSe. In the case of a few-layer $In_2Se_3$, its inherent ferroelectric nature allows us to evaluate its potential as a ferroelectric semiconductor field-effect transistor with non-volatile memory. Our work offers a promising approach for creating phase-pure 2D InSe and $In_2Se_3$ films at the wafer scale, which can be adapted for other material systems with multiple polymorphs.

## Atomic Scale Processing Mini-Symposium
## Room A107-109 - Session AP1+2D+EM+PS+TF-TuA

### Atomic Layer Processing: Integration of Deposition and Etching

**Moderator: John F. Conley, Jr.**, Oregon State University

2:20pm **AP1+2D+EM+PS+TF-TuA-1 Combination of Plasma-Based Atomic-Scale Deposition and Etching Processes for Advanced Patterning*, Marceline Bonvalot*,** LTM - MINATEC - CEA/LETI, France*; C. Vallée,* SUNY College of Nanoscale Science and Engineering*; r. gassilloud, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France*; N. Posséme,* STmicroelectronics, France **INVITED**

Selective Deposition processes have gained increased research interest in recent years, because they enable the accurate placement of a thin film on a specific substrate surface (in the case of area selective deposition ASD) or on specifically oriented surfaces (in the case of topographical selective deposition TSD). Such processes require atomic-scale precision, and usually involve Atomic Layer Deposition techniques, with possibly plasma assistance. Several pathways have been proposed in the literature for ASD, most commonly implying surface inhibition treatments with dedicated chemical treatments (self-assembled molecules or small molecule inhibitors for instance) to increase the nucleation delay during the subsequent ALD growth. However, the dedicated inhibition behavior eventually deteriorates when exposed to a few ALD cycles, which requires that on the one hand, nuclei formed on non-growth surfaces be removed and on the other hand, the inhibitor be systematically regenerated.

In this presentation, we will show how the insertion of an *in situ* etching step in the overall ALD process can serve as an effective corrective treatment for this purpose. The etching periodicity in conventional deposition/etching duty cycles will be investigated in details. We will show that the etching step should preferentially be carried out before the transition from the Volmer-Weber 1D island growth mode to the 2D layer by layer growth mode on non-growth surfaces, to limit plasma-induced surface defects. Moreover, the 1D island growth mode seems to coincide with the onset of degradation for the surface inhibition treatment. In this context, it will be shown that the etching periodicity is a determining parameter for the successful development of a selective bottom-up growth strategy.

3:00pm **AP1+2D+EM+PS+TF-TuA-3 Application of Etching Reaction Models to Deposition Processes***, **Nobuyuki Kuboi**,* Sony Semiconductor Solutions Corporation, Japan **INVITED**

Advanced CMOS devices require highly intricate 3D stacked structures with varying aspect ratios such as FinFETs and GAAs [1]. Understanding the process properties of plasma etching [2] and deposition [3] processes based on their mechanism and combinations has become increasingly important in addressing this challenge. Additionally, microfabrication properties should be stably suppressed within a specific range during mass production. However, the monitoring system equipped in the process chamber is limited for mass production. Therefore, we propose predictive models for plasma etching and deposition that consider the physical and chemical aspects of the plasma and surface.

First, we briefly introduce simulations for fluctuations in the SiN etching rate influenced by the chamber wall condition, critical dimensions during Si gate etching caused by $SiBr_x$ by-products dependent on open area ratios on wafer/chip/local-pattern levels, damage distribution affected by local-pattern structure, ion energy, and hydrogen concentration in the $SiO_2$ and SiN films, and selectivity during $SiO_2$-ALE [4][5][6].

We then present a modeling and simulation of the deposition process as a motif of the SiN-PECVD process using a 3D voxel method that can be associated with the previous process, such as plasma etching [7]. The model can predict film properties as well as the coverage on a large-scale pattern. Reactions among voxels are considered pseudo treatments for atomistic interactions on the surface. A statistical ensemble method involving probabilities is used to express physical and chemical phenomena such as sticking, migration, and bond formation on the deposited surface. The sticking and bond probabilities are affected by surface damage and IEADFs, respectively. Our model can successfully reproduce the experimental characteristic relationship between the morphology and film density dependent on the $SiH_4$ flow rate during the low temperature (120 ºC) SiN-PECVD process considering different gas residence times that affect surface reactions. Furthermore, we discuss the issue of modeling the ALD process.

These simulation technologies can aid in optimizing the chamber wall condition, pattern design, and etching/deposition combination process.

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4:20pm **AP1+2D+EM+PS+TF-TuA-7 Recent Advancements for Atomic Layer Advanced Manufacturing Processes: Microreactor Direct Atomic Layer Processing (µDALP™)***, **Maksym Plakhotnyuk**, A. Varga, I. Kundrata,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann,* ATLANT 3D Nanosystems; Friedrich-Alexander Universität Erlangen-Nürnberg, Denmark **INVITED**

As the demand for miniaturized and complex devices continues to grow across various industries, the need for innovative and precise atomic layer advanced manufacturing (ALAM) technologies becomes increasingly apparent[1]. Our company, utilizing proprietary Microreactor Direct Atomic Layer Processing (µDALP™), is at the forefront of pushing sALD's capabilities and broadening its application horizons. The µDALP™ process undergoes the same cyclic ALD process but only in a spatially localized area.[2] The microreactor or micronozzle confines the flows of gases used for ALD within a defined µm-scale centric area on the substrate to deposit the desired material.[3]

ATLANT 3D's recent advancements in our novel µDALP™ technology have enabled innovation within the thin film deposition field ranging from ALD material development to rapid prototyping and manufacturing. The µDALP™ process enables multiple depositions e.g., depositions with varying film thicknesses, to be deposited onto a single wafer used to calculate a given processes growth rate within only a few hours, compared to days for a traditional ALD process. In Addition, innovation of applications including optics and photonics, quantum devices, MEMS, RF electronics, emerging memory technologies, advanced packaging, and energy storage are possible and have been demonstrated using µDALP™ technology.

Discussing the improvements to the µDALP™ process, we have decreased the process resolution, increased material compatibility, and accessible morphologies. Giving one example of the recent development in morphologies, films deposited with µDALP™ have conformal coverage of gratings, microchannels, and trenches up to a depth of 25 µm using a Platinum deposition process. **Fig. 1** demonstrates how a given ALD material process (in this case, Pt) can be used with ATLANT 3D technology to deposit localized area conformal coatings of complex surfaces with an aspect ratio of 1:25. Hence demonstrating the versatility and potential of our technology for achieving inherently selective ALD for processing on complex surface morphologies.

This talk aims to shed light on how our breakthroughs in spatial ALD and µDALP™ technology contribute to the advancement of ALAM and scale-up. Fostering a deeper understanding of our technology's capabilities and exploring the possibilities it opens up for various industries.

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## Atomic Scale Processing Mini-Symposium
## Room A107-109 - Session AP2+PS+TF-TuA

### Energy Enhanced ALD

**Moderator: John F. Conley, Jr.**, Oregon State University

5:00pm **AP2+PS+TF-TuA-9 Atomic Layer Annealing with Radio Frequency Substrate Bias for Control of Grain Morphology in Gallium Nitride Thin Films***, A. Mcleod, P. Lee,* University of California, San Diego*; S. Yun, S. Ueda,* University of California, San Diego, USA*; Z. Devereaux, C. Winter,* Wayne State University*; J. Spiegelman,* RASIRC*; R. Kanjolia, M. Moinpour,* EMD Electronics, USA*; **Andrew Kummel**,* University of California, San Diego **INVITED**

Low temperature GaN deposition is critical for passivation layers on nitride power FET as low as templating and capping layers on sputtered AlN films for heat spreader. A method of performing atomic layer annealing with RF substrate bias on insulating and amorphous substrates is demonstrated for GaN deposition at 275 ℃. GaN is typically deposited by MOCVD or MBE at >600 ℃, resulting in strain upon cooling; this makes low temperature process alternatives desirable. Tris(dimethylamido) gallium (III) and hydrazine served as precursors while Ar and Kr were used for ion bombardment. Optimization of substrate bias potential is demonstrated by GI-XRD and XRR. Reference films were deposited by thermal ALD and non-substrate biased ALA processes. XPS surface and depth-profiling studies show that applied RF bias decreases film oxygen and carbon content relative to the reference films; these films also show crystallites broadening with increasing film thickness by TEM in contrast to the reference films. In summary, ALA with RF substrate bias is demonstrated as an effective method to deposit GaN thin films at a low deposition temperature on insulators.This technique has recently been expended to growth of InGaN films which applications in microLEDs.

5:40pm **AP2+PS+TF-TuA-11 Atomic Layer Annealing for sub-10 nm, Wake-up Free Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films***, **Yu-Sen Jiang**,* National Taiwan University, Taiwan*; T. Chang, S. Yi,* Taiwan Semiconductor Manufacturing Company, Taiwan*; M. Chen,* National Taiwan University, Taiwan

Conventional annealing techniques pose significant challenges in nanoscale fabrication. One prominent issue involves the heating depth, which typically exceeds the critical dimension of nanoscale devices. Consequently, conventional annealing methods introduce excessive thermal budget, resulting in performance degradation of the devices. Atomic layer annealing (ALA) is capable of adjusting the film quality at the atomic level during low-temperature (300℃) deposition without the need for any post-annealing process, which tremendously lowers the thermal budget and can tailor the film properties as required. In this report, the ALA technique was used to realize sub-10 nm wake-up free ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films with high remnant polarization and low thermal budget. The HZO thin films have also been used as gate dielectrics in junctionless transistors, demonstrating steep subthreshold swing (< 60 mV/decade) in nanoscale devices. The outcome manifests the remarkable capabilities of ALA in enabling precise engineering and fabrication of nanoscale materials and devices.

6:00pm **AP2+PS+TF-TuA-12 A System for Predicting the Area Selective Deposition of Titanium: Plasma State Diagnostics Using Electrical Simulation***, **Kyoungmi Choi**, T. Hong, H. Kim, Y. Oh,* Samsung Electronics Co., Inc., Republic of Korea

The selective deposition of thin films in specific areas is crucial for achieving the desired size and lowresistance of semiconductors. Due to differences in chemistry between molecule/surface and molecule/vapor interactions, thin films are selectively deposited on pre-patterned substrates. Although simulations have been used to predict Ti film thickness using plasma simulation and surface reaction models, the effect of selective deposition on the pattern was not studied. In this study, an electrical simulation was used to predict the selectivity of the area selective deposition process on the patterned wafer.

To identify the main factors affecting selectivity, we reviewed the plasma temperature and density. Plasma density can be indirectly inferred from the output current of the matcher. Another factor that influences selectivity is plasma temperature, specifically the electron temperature [eV]. The sheath voltage is proportional to the electron temperature. Therefore, we established an electric simulation system (Fig. 1) to estimate the sheath voltage. The CCP consists of an RF generator, a matcher, and a chamber. We identified the matcher parameters ($C_{tune}$/$C_{load}$/L) using the maximum power transmission theory, assuming that the chamber was $Z_{chamber}$(Fig 2). The model was verified using MATLAB and the sheath voltage was derived using the matcher and bottom currents. The simulations and evaluations of pressure/RF power/impedance were performed. The validity of the electrical model was confirmed by comparing the simulation and the experimental current.

To verify the simulation, Ti deposition experiments were conducted on Si/SiO wafers under 7 conditions (Table1). The simulation results for sheath voltage and the experimental results for deposition rate showed a correlation of 0.77, and the Si/SiO selectivity showed a correlation of 0.92(Fig 3).

Through the correlation result,itwasderivedasthefollowingconclusion.The correlation results between sheath voltage and the area selective deposition explains the difference in the activation energy of the Si/SiO surfaces: The Si-Si bonding energy is 3.39 eV and the Si-O bonding energy is 8.29eV (Fig 4). Since there are regions where the plasma temperature is active on Si and inert on SiO, they are selectively deposited. Therefore, a sheath voltage simulation can be used to predict the selectivity. With further development, this simulation can be applied to other deposition equipment that uses plasma, and trends in process results for other process parameters that are sensitive to plasma temperature can be inferred.

## 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

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

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 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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## Thin Film Division
## Room A105 - Session TF1-TuA
## Catalytic and Active Materials

**Moderators: Mark Losego**, Georgia Institute of Technology, **Richard Vanfleet**, Brigham Young University

2:20pm **TF1-TuA-1 MLD as a Sandbox for Photoactive Hybrid Materials***, **Ola Nilsen**,* University of Oslo, Norway **INVITED**

To an experimental chemist, the MLD approach is a desirable tool to explore chemical reactivity and to create structures that otherwise would not be possible. So, what are its limitations? And why should you use this approach? These, and other questions will be covered during this presentation where we will focus on volatilization of precursors, challenges with surface limited reactions when your material is porous, how to influence the growth during growth, and more. The MLD approach is highly effective in combining material classes that naturally do not combine. We use this approach to combine highly absorbing organic molecules with fluorides and oxides to design photoactive structures. By such manner, we have achieved complete energy transfer from the organic molecules to lanthanides without quenching. We also show drastic suppression of concentration quenching of multilayered structures of lanthanides as compared to solid solutions by confining energy migration in 2D planes. The flexibility of the MLD approach allows for exploration of exotic combinations of absorbers and emitters, but how far can you go with MLD?

3:00pm **TF1-TuA-3 Dry Pathways to Synthesize Thin Films of Covalent Organic Frameworks***, **Syed Ibrahim Gnani Peer Mohamed**, S. Nejati, M. Bavarian,* University of Nebraska - Lincoln

Covalent organic frameworks (COFs) are porous materials with potential applications in gas storage, catalysis, and electronics. However, traditional COF synthesis methods are limited by low solubility and poor processability. In contrast, oxidative chemical vapor deposition (oCVD) and oxidative Molecular Layer Deposition (oMLD) provide versatile and scalable approaches to deposit COFs on different surfaces. Porphyrins and their derivatives have attracted the attention of many researchers as precursors for COF preparation. Porphyrin and its metal complexes can serve as electrocatalysts, especially for oxygen reduction, nitrate reduction, and carbon dioxide reduction reactions. In addition, these materials have also been explored for photocatalysis, separation, optical switches, and other applications. Polymerization of porphyrins to create frameworks and networks increases the stability of these materials. Thus, preparing porphyrin-based COFs is essential for their widespread application. COFs are commonly synthesized via the solvothermal method, which involves a very long reaction time and the use of toxic organic solvents. Therefore, a dry synthetic pathway is highly desirable. Herein, we report the one-step, solvent-free synthesis of crystalline and porous porphyrin-based COFs. Both 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP) or its transition metal complex (MPOR-COF, M = $H_2$, $Cu^{2+}$, $Co^{2+}$, $Zn^{2+}$) in the presence of antimony pentachloride ($SbCl_5$), as an oxidant, polymerized. The monomer TAPP undergoes polymerization via phenazine link formation (pTAPP) in the presence of $SbCl_5$, leading to the formation of well-ordered MPOR-COFs. Here, we describe the bottom-up and dry assembly of pTAPP and its derivatives to create active materials. We also report on the control achieved over the reaction selectivity and separation performance of the thin films deposited through the oxidative vapor phase polymerization pathway and explore various strategies to control the film structure and properties. The resulting materials were characterized using various techniques such as spectroscopy, microscopy, and gas adsorption. We also investigated the effect of substrate, deposition conditions, and post-synthesis treatment on the structure and properties of the resulting COFs. Our results show that oCVD and oMLD are promising methods for synthesizing COFs with tunable properties and potential applications in various fields.

3:20pm **TF1-TuA-4 Vapor Phase Infiltration of Titanium Oxide into P3HT to Create Organic-Inorganic Hybrid Photocatalysts***, **Li Zhang**, S. Gregory, M. Losego,* Georgia Institute of Technology

Chemical doping using vapor phase infiltration (VPI) of metal halide precursors and water has been shown to dope conjugated polymers (CP). The reacted product – metal oxide clusters – remain trapped within the CP and are often thought to just act as scattering centers that lower the electronic mobility of the CP. However, in this talk we will show how these metal oxides can be used as catalytic sites for photocatalytic reactions. Metal oxides such as $TiO_x$ have been well documented for their good photocatalytic properties, with the drawback that they do not absorb in the visible region. In hybrid CP-$MO_x$ systems, the CP can act as a sensitizer absorbing light in the visible regime and then injecting the photo-excited electrons into the $MO_x$ to perform the catalysis. In this talk we will discuss our work in exploring the vapor phase infiltration of the CP poly(3-hexylthiophene-2,5-diyl) [P3HT] with $TiCl_4$ and $H_2O$ to form P3HT-$TiO_2$ hybrid photocatalysts. Specifically, we examine how these photocatalysts perform in degrading the dye methyl blue in aqueous solutions, fitting the degradation to a first-order reaction and extracting the rate constant. XPS analysis of the VPI treated P3HT confirms that the inorganic infiltrants dope the polymer, which is confirmed by electrical measurements, and leave behind $TiO_2$ clusters. Photocatalytic measurements reveal that the P3HT-$TiO_x$ hybrid material outperforms pure P3HT and pure $TiO_2$ by at least a factor of 4.5x, but only when illuminated. These results show a synergistic photosensitizing effect between the P3HT and $TiO_2$. To confirm that the electronic doping is not the sole source of enhanced photocatalytic activity, we also examined P3HT films doped with common oxidative dopants. While these doped P3HT show significantly higher electrical conductivity than the VPI treated P3HT, they had significantly lower photocatalytic activity (at least 3x lower). Dedoping of the P3HT-$TiO_2$ hybrids to reduce conductivity also did not eliminate the photocatalytic performance of these hybrids, providing further evidence that this photocatalytic effect is not simply due to higher electrical conductivity. To explore how catalytically active VPI could make the P3HT, the polymer was exposed to differing number of VPI cycles. It was found that the catalytic activity increased until 5 cycles, where the surface S:Ti ratio was 3, and then proceeded to gradually decrease for more cycles. Based on subsequent characterization, we will discuss why this design is optimal and to what extent the infiltrated $TiO_x$ species need to be near the surface of the hybrid material. We will also demonstrate how this catalyst is amongst the best performing CP-$MO_x$ photocatalysts to have been reported in the literature.

## Thin Film Division
## Room A105 - Session TF2-TuA
## Thin Films for Battery and Photovoltaic Applications

**Moderators: Richard Vanfleet**, Brigham Young University, **Matthias Young**, University of Missouri

4:40pm **TF2-TuA-8 Optimization and Structural Characterization of ITO Thin Fims for Photovoltaic Applications**, *F. Ali,* Metallurgical and Materials Engineering, The University of Alabama*; D. Li,* Electrical and Computer Engineering, Tne University of Alabama*; **Subhadra Gupta**,* Metallurgical and Materials Engineering, The University of Alabama

We have optimized the processing and annealing of sputtered indium-tin oxide (ITO) thin films for solar cell applications by DC magnetron sputtering. The effects of process parameters such as deposition power, reactive gas flow percentage, annealing temperature and time, as well as film thickness, on the sheet resistance and transmission of the ITO films was systematically studied, using a Design of Experiments. Additionally, structural characterization of the deposited films was performed using various techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), four-point probe, UV-VIS spectrometry, and atomic force microscopy (AFM). TEM analysis revealed grain boundaries, crystallinity, and d-spacing of ITO thin film. The grain size was calculated with the help of the Scherrer equation. The XRD spectra of the ITO films revealed a polycrystalline structure with preferred (222) orientation of the ITO film. The SEM image of the ITO target gives information about the morphology of the racetrack after sputtering. The topography and surface roughness were evaluated by atomic force microscopy (AFM). A sheet resistance of 10 ohms/sq. and transmission of over 90% over 400-700 nm wavelengths was achieved. Perovskite solar cells fabricated with these optimized ITO electrodes showed promising properties.

5:00pm **TF2-TuA-9 Isolating Battery Components to Understand How Processing Affects Interface Formation***, **Victoria Castagna Ferrari**[1], G. Rubloff, D. Stewart,* University of Maryland, College Park

Interfaces dominate the performance of electrochemical systems, from interphase formation to charge transfer impedances, and they require careful study to understand. We have undertaken a broadly applicable approach to isolating components of a solid-state battery (SSB) to analyze them using non-destructive electrochemical impedance spectroscopy (EIS), and systematically build up to the full device. We then apply this knowledge to the matter of spontaneous Li transfer from LiPON to $V_2O_5$ during the sputtering process, which was also seen in other electrode/electrolyte pairs but is poorly studied.

Using sputtering and *in vacuo* shadow mask exchange, we fabricated an array of 16 batteries (Si/LiPON/$LiV_2O_5$) in parallel with auxiliary devices with isolated materials and interfaces on a single 3 in Si wafer. The reproducibility of the SSBs was confirmed by electrochemical testing, and the interfaces were evaluated from EIS measurements of the auxiliary devices. Equivalent circuit models for each device were built, ensuring that the components were all physically correlated to a material property or to (non)faradaic reactions of the interface. Interface reaction dynamics were evaluated as the applied voltage was swept over the normal working range of the SSB. The parameters obtained from these auxiliary circuit models were used to build a complete and accurate electric circuit for the SSB.

To evaluate the effect of the sputtering process on the interfaces, two model systems were used offering different conditions. Ultra-thin layers (10-20 nm) of either $Li_2O$ or LiPON were sputtered on top of $V_2O_5$ using a non-reactive Ar working gas, or reactive $N_2$, respectively. EIS measurements of the models revealed the presence of an electron blocking LiPON layer, and the absence of a $Li_2O$ layer above the $V_2O_5$. Furthermore, the properties of the $Li_2O/V_2O_5$ sample were similar to the lithiated $LiV_2O_5$ previously measured. An XPS depth profile confirmed that the $V_2O_5$ was fully lithiated after sputtering $Li_2O$, while only a fractional lithiation occurred after sputtering LiPON. DC polarization measurements and spectroscopy ellipsometry showed that the interfaces have distinct optical and electronic properties that might indicate interphase formation.

This work presents a materials-agnostic platform for investigating the interfaces in a SSB using non-destructive electrochemical techniques. The auxiliary devices are created in parallel with the SSB, ensuring a 1:1 comparison. Overall, this work presents a comprehensive approach to investigate the interfaces in SSBs, including chemical and physical reactions, and provides insights into improving the interfaces of thin films in SSBs.

5:20pm **TF2-TuA-10 Towards Dual Lithium-Ion and Electronically Conductive Polymer Coatings by MLD***, **Nikhila Paranamana**[2], A. Datta, X. He, M. Young,* University of Missouri, Columbia

Lithium ion batteries (LIBs) employing solid electrolyte offer potential advantages in safety and shelf life over current LIBs made with liquid electrolyte. However, undesired reactions occur between electrode active materials and the solid electrolyte, forming interphase layers that block $Li^+$ ion transport and degrade cell performance. To prevent these interphase reactions while maintaining battery operation, protective coatings are of interest which provide both electronic conductivity and $Li^+$ ion conductivity. Recent work has demonstrated the use of molecular layer deposition (MLD) to form electrically conducting poly(3,4-ethylenedioxythiophene) (PEDOT), anion-conducting polypyrrole (PPy), and cation conducting lithicone-glycerol (LiGL). However, MLD coatings that conduct both lithium ions and electrons have proven challenging to synthesize. In this work, we report on recent efforts to form MLD films of polyhydroquinone that are cation-conductive and electronically-conductive. We employ in-situ quartz crystal microbalance (QCM) studies during MLD growth to understand the growth mechanisms, as well as ex-situ spectroscopic ellipsometry (SE), electrochemical impedance spectroscopy (EIS), and electrochemical characterization to identify the material properties. We also report early work applying these coatings to nickel rich $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NMC) cathode material to be used in solid electrolyte LIBs with the $Li_{10}GeP_2S_{12}$ (LGPS) solid electrolyte to understand how these protective coatings affect interphase layer formation in this system.

5:40pm **TF2-TuA-11 Initiated Chemical Vapor Deposition Stabilized Current Collectors for Anode-Free Lithium Metal Batteries***, **Ramsay Blake Nuwayhid**, J. Yeom, G. Waller, R. Carter, C. Love,* U.S. Naval Research Laboratory

Anode-free Li-metal batteries (AFLBs) offer a substantial enhancement in energy density over conventional graphite anodes. However, their realization is hindered by heterogeneous and irreversible Li plating/stripping from the Cu current-collector, resulting in the buildup of resistive solid-electrolyte interphase (SEI) species leading to poor cycling efficiencies. In this work, we employ initiated chemical vapor deposition (iCVD) polymeric coatings to create a stable interface between the Cu and liquid-electrolyte. The capability to deposit conformal polymer films at the nanoscale makes iCVD an attractive technique to passivate the reactive and complex Cu/liquid-electrolyte interface. We apply nanoscale coatings (5-100 nm) of poly(1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane) (pV4D4) to Cu current-collectors and evaluate their electrochemical performance in Li/Cu coin-cells. The cycling behavior reveals an overall cycling enhancement dependent on pV4D4 thickness. Moderate thicknesses (20 nm) resulted in a coulombic efficiency >90% for 100 cycles, more than double that of uncoated Cu. Through SEM and XPS analysis, it is determined that the cycling improvement is attributed to the uniform plating morphology of Li and the prevention of deleterious SEI component growth from the liquid-electrolyte. For ultrathin coatings (5 nm), a marginal improvement to bare Cu is observed and thick coatings (>100 nm) suffer from poor kinetics due to pronounced insulating effects of the dielectric pV4D4 film. Two distinct mechanisms are observed for Li plating/stripping for sufficient pV4D4 passivation; (1) moderate coatings (20 nm) function as a solid-electrolyte with Li plating beneath the layer and (2) thick coatings (>100 nm) function as a nucleation layer with Li plating on top of it. Overall, this work provides the mechanistic understanding of iCVD pV4D4 layers on Li plating/stripping and demonstrates the promising capability of iCVD to operate as stable interlayers in Li metal batteries.

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

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

## Atomic Scale Processing Mini-Symposium
## Room A107-109 - Session AP+PS+TF-WeM

### Plasma Deposition and ALD Processes for Coatings and Thin Films

**Moderators: Silvia Armini**, IMEC, Belgium, **Jessica Kachian**, Intel Corporation

8:00am **AP+PS+TF-WeM-1 Recent Progress in Analysis of the Conformality of Films by Atomic Layer Deposition***, **Riikka Puurunen**,* Aalto University, Finland **INVITED**

Conformality is a fundamental characteristic of atomic layer deposition (ALD) thin film growth technique. “Conformal” film refers to a film that covers all surfaces of a complex three-dimensional substrate with everywhere the same thickness and properties. ALD - invented independently by two groups in 1960s and 1970s - has since late 1990s been transformational in semiconductor technology. Apart from semiconductors, conformal ALD films find applications and interest in widely varied fields such as microelectromechanical systems, pharmaceutical powder processing, optical coatings, battery technologies and heterogeneous catalysts.

Conformality follows directly from the “ideal ALD” principles: growth of material through the use of repeated separate self-terminating (i.e., saturating and irreversible) gas-solid reactions of at least two compatible reactants on a solid surface. Obtaining conformality in practice is not self-evident, however. Reasons for deviation from conformality are multiple, ranging from mass transport limitations to slow reaction kinetics and various deviations from ideal ALD (e.g., by-product reactivity or a continuous chemical vapor deposition (CVD) component through reactant decomposition or insufficient purging). Incomplete conformality can also be intentional: a saturation profile inside a feature can be exposed, to enable an analysis of kinetic parameters of the reactions.

This invited talk will explore recent progress especially by the author and collaborators in understanding ALD conformality and kinetics, obtained via experiments and simulations. Experiments have been made with the recently commercialized (chipmetrics.com) silicon-based PillarHallTM lateral HAR test chips (channel height ~500 nm) and spherical mesoporous high-surface-area materials (average pore diameter ~10 nm, sphere diameter ~1 mm). Simulations are presented for 1d feature-scale models and optionally a recently developed 3d code for spheres. Two codes are available on GitHub: DReaM-ALD (diffusion-reaction model, DRM) and Machball (ballistic transport-reaction model, BTRM). Often it is assumed that diffusion during an ALD process in HAR features is by Knudsen diffusion and free molecular flow conditions prevail (Kn >>1). If so, a characteristic “fingerprint saturation profile” can be obtained, and the slope method (derived for DRM-ALD-Arts, GitHub) can be used to back-extract the lumped sticking coefficient. When diffusion is in the transition flow (Kn ~1) or continuum flow (Kn<<1), the shape of the saturation profile depends on process conditions and the slope method is not applicable.

8:40am **AP+PS+TF-WeM-3 ALD Temperature Cycling for Uniform Infilling of Macroscopic Nanoporous Solids***, **Benjamin Greenberg**, K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Uniform ALD infilling of macroscopic nanoporous solids with aspect ratio greater than $10^4$ can require precursor dose times on the order of $10^3$ seconds, at least four orders of magnitude longer than typical dose times for ALD on wafers. For ALD processes based on relatively stable precursors and straightforward chemistries, such as ALD of $Al_2O_3$ from trimethylaluminum (TMA) and $H_2O$, very long doses are generally harmless, but for some ALD processes, precursor decomposition and other side reactions are significant concerns. For example, at a deposition temperature of 180 °C, which has been chosen previously for ZnO ALD infilling to ensure rapid removal of $H_2O$ from nanopores during purging,[1] diethylzinc (DEZ) decomposition[2] and surface Zn deethylation[3] may be substantial on the ~$10^3$ s timescale.

In this work, we investigate the potential of temperature cycling as a route toward rapid yet controlled infilling of macroscopic nanoporous solids. We infill $Al_2O_3$ nanoparticle compacts of ~1.5 mm thickness and ~100 nm pore size (aspect ratio > $10^4$) with ZnO using DEZ and $H_2O$ as precursors, and we cycle the substrate temperature between ~160 °C (during $H_2O$ purges) and ~120 °C (during all other steps). DEZ infiltration is accomplished via static dosing, wherein DEZ vapor is held in the ALD chamber for >$10^3$ seconds with the pump valve closed so that, in principle, diffusion/reaction and saturation are observable as a rise (due to byproducts) and flattening of the ALD chamber pressure, respectively. The 120/160 °C cyclical-temperature process produces clear saturation signals in the pressure trace, whereas fixed-temperature processes carried out entirely at 120 or 160 °C do not, apparently due to incomplete $H_2O$ removal at 120 °C and DEZ decomposition and/or other side reactions at 160 °C. We use a variety of characterization techniques, including SEM/EDS, XRD, and electrical conductivity measurements, to assess the uniformity and purity of the ZnO infills.

1. A. Cendejas, D. Moher, and E. Thimsen, J. Vac. Sci. Technol. A **39**, 012406 (2021).
2. J. D. Ferguson, A. W. Weimer, and S. M. George, J. Vac. Sci. Technol. A **23**, 118 (2005).
3. T. Weckman and K. Laasonen, J. Phys. Chem. C **122**, 7685 (2018).

9:00am **AP+PS+TF-WeM-4 Plasmonic Plasma Process for Room Temperature Growth of High-quality Ultra-thin Dielectric Films***, **Takeshi Kitajima**, M. Miyake,* National Defense Academy, Japan*; K. Watanabe,* National defense Academy, Japan*; T. Nakano,* national defense Academy, Japan

Catalytic surface reactions utilizing gold nanoparticle plasmons have been utilized in various applications in recent years.[1] We have applied hot electrons supplied from gold nanoparticles to plasma surface reactions to use them to form high-quality ultrathin dielectric films at room temperature.[2] We focused on the mixed effect of visible light for plasmon excitation and plasma VUV emission and discovered the effect of green light excitation that promotes radical nitriding. Due to the mercury probe measurement and TEM imaging, the film grown have sperior dielectric feature and uniformity with less plasma induced damage in spite of nonuniform formation of gold nanoparticles.

In the growth sequence, Au was vapor-deposited on a $SiO_2$ / Si (100) substrate in an ultra-high vacuum chamber with an average thickness of 0.4 nm by electron beam deposition to form Au nanoparticles (C) on the surface. A 30 mTorr $N_2$-inductively coupled plasma was generated in the attached chamber, and the sample was irradiated with N radicals (R) that passed through a 30 line/inch SUS304 single mesh with the configuration shown in Fig. 1 (a) for 5 minutes. A filter and a white LED controlled the wavelength of light (L), and VUV light from $N_2$ plasma was mixed. The reaction condition consisting of the above is RLC. Figure 1 (b) shows the dielectric characteristics of the SiON film {leakage current and EOT (equivalent oxide film thickness) when 1 V is applied}. In green light suitable for Au plasmons, the hot electrons (~ 4 eV) generated by the deexcitation of plasmons enabled the bond conversion from Si-O to Si-N the ultra-thin SiON shows the same characteristics as the ideal SiON film. By mixing VUV, it is possible to increase the film thickness further and reduce leakage.

Cross-sectional TEM image of SiON film after plasmonic process is shown in Fig. 1 (c). Beneath the Au particle SiON film with wide range of uniformity is confirmed and the single crystal lattice of Si substrate is clearly identified.

From the above, it is considered that the reaction between the adsorbed N radicals and Si proceeded, and a quality SiON film was formed by superimposing the photoelectron emission from the VUV light on the hot electron injection from the gold nanoparticles by green light irradiation.

1 C. Clavero, Nat. Photonics 8, 95 (2014).

2 T. Kitajima, M. Miyake, K. Honda, and T. Nakano, J. Appl. Phys. 127, 243302 (2020).

9:20am **AP+PS+TF-WeM-5 Time Resolved Energy Diagnostics of HiPIMS Discharges With Positive Cathode Reversal***, **Zachary Jeckell**, T. Choi, M. Hossain, D. Kepelyan, N. Vishnoi,* University of Illinois at Urbana Champaign*; B. Jurczyk,* Starfire Industries*; D. Ruzic,* University of Illinois at Urbana Champaign

This work investigates the temporal evolution of a high-power impulse magnetron sputtering (HiPIMS), with a positive cathode reversal, discharge by using the Hiden ANALYTICAL PSM probe that can measure the ion energies as well as perform charge to mass (q/m) measurements. This work builds off other diagnostic work done on the chamber such as time resolved electron energy distribution functions from our time resolved Langmuir probe technique, previous work with measuring ion energy distribution functions using the SEMION probe, as well as preliminary measurements taken with the PSM probe. This work was performed on several different target materials such as Ag, Ti, ZnTe, and W. The diagnostic capabilities of the PSM allows for differentiation between the working gas and target material ions which enables us to calculate the ratio of target ions for a given condition. Previous work we have done has shown that at early stages of the positive cathode reversal there is an elevated population of metal ions and that the overall fraction of metal to working gas fraction is at its highest. Time and energy resolved mass spec data was collected on this system for a variety of conditions such as pulse lengths, pressures, and target material with the objective of developing a better understanding for the energetics at play. Additionally, by running the PSM with the filament on and a properly set repelling voltage it was possible to get a sense of the neutral energies as well. This required a deconvolution of the energy that the neutrals gain from the ionization from the filament. The goal was to use the results of those experiments to build a framework of understanding and to use that information to deposit better films, such as increasing the hardness of TiN, reducing the resistivity of N doped ZnTe, improving the crystallinity of W films or improving the optical properties of a Ag thin film.

9:40am **AP+PS+TF-WeM-6 Electron-Enhanced ALD of $TiO_2$, TiN, and TiCN at Low Temperature Using TDMAT Together with $O_2$ and $NH_3$ Reactive Background Gas***, Z. Sobell, A. Cavanagh,* ***Steven George,*** University of Colorado Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of $TiO_2$, TiN, and TiCN films at T < 70 °C.Three Ti-based films were grown using sequential exposures of tetrakis(dimethylamido) titanium (TDMAT) precursor and electrons together with a continuous reactive background gas (RBG) (Figure 1). The electrons accelerated across a grid bias of 100 V desorb surface species by electron stimulated desorption.The electrons also dissociate the RBG as they travel to the substrate.The RBGs utilized to tune the film composition were oxygen ($O_2$) for $TiO_2$ and ammonia ($NH_3$) for TiN and TiCN.

$TiO_2$ EE-ALD was performed at T < 70 °C using TDMAT together with an $O_2$ RBG at ~1 mTorr. $O_2$ is believed to be dissociated by the electron beam, creating O radicals that add oxygen to form $TiO_2$ and remove N and C from the TDMAT precursor. XPS showed no detectable C or N in the $TiO_2$ films and a slightly O-rich stoichiometry. Oxygen-rich $TiO_2$ films may be more photochemically active due to bandgap narrowing and could be useful in photocatalysis.

TiN EE-ALD was conducted at T < 70°C using TDMAT together with an $NH_3$ RBG at a pressure of ~1 mTorr. $NH_3$ is believed to be dissociated by the electron beam, liberating H and $NH_x$ radicals that facilitate Ti nitridation and C removal from the film. Electron exposures for 20 seconds led to the rapid nucleation of TiN films with purities of > 96% and ultralow resistivities of < 120 μΩ-cm. These films may be useful as diffusion barriers in backend interconnects.

Incomplete C removal resulted from shorter electron exposures during TiN EE-ALD using TDMAT with $NH_3$ RBG.This carbon residual provides a pathway for the deposition of TiCN, an important amorphous ternary nitride diffusion barrier.TiCN EE-ALD film growth and properties were explored for electron exposure lengths from 20 seconds to 0.5 seconds.Shorter electron exposures led to an increase of the C:Ti ratio from ~0.03 to ~0.33 as measured by x-ray photoelectron spectroscopy (XPS) (Figure 2).Shorter electron exposures also produced a decrease in film density from ~5.3 g/$cm^3$ to ~3.3 g/$cm^3$.In addition, shorter electron exposures yielded an increase in the film resistivity from < 120 μΩ-cm to ~2000 μΩ-cm as measured by ex situ spectroscopic ellipsometry (SE).Consequently, the enhanced diffusion barrier properties of TiCN EE-ALD films will be accompanied by higher film resistivities and lower film densities than TiN EE-ALD films.

11:00am **AP+PS+TF-WeM-10 A Non-Violent Approach to Remove SiN:H Surface Impurities (HCl) at Room Temperature***,* ***Tsung-Hsuan Yang****, T. Wang, G. Hwang,* University of Texas at Austin*; P. Ventzek, J. Zhao,* Tokyo Electron America, Inc.

Our research presents a non-violent approach to remove $H^+/Cl^-$ pairs, a common reaction byproduct, after depositing chlorosilane-type Si precursors (such as dichlorosilane, $SiH_2Cl_2$) on a SiN surface. While previous studies have suggested the use of H radicals in $NH_3$ and $CH_3NH_2$ plasma to remove Cl impurities, these methods have limitations in high-aspect-ratio structures. The recombination rate of radicals may be too fast to reach the bottom of the trench, resulting in the accumulation of Cl and possibly the formation of a salt layer that inhibits further film growth. Through first-principles calculations, we propose an alternative solution by introducing polar molecules, such as $NH_3$, $N_2H_4$, $CH_3NH_2$, and $(CH_3)_2NH$. When these polar molecules are dosed onto the surface, they can first abstract the $H^+$ from the $H^+/Cl^-$ pair to form a complex with $Cl^-$. Adjacent polar molecules then solvate the complex, forming a stable "microsolvation cluster." This cluster effectively captures $Cl^-$ while weakening the interactions between $Cl^-$ and surface amine groups, providing a pathway for HCl desorption with a lower energy barrier. Our calculations of free energy surface show that when the surface is saturated with $CH_3NH_2$ molecules, the energy barrier for HCl desorption can be significantly reduced at 300K. Based on these promising findings, we propose a novel and non-aggressive atomic layer deposition (ALD) scheme to grow SiN at low temperatures while achieving a higher growth rate.

11:20am **AP+PS+TF-WeM-11 Influence of Plasma Species on the Growth Kinetics and Properties of Epitaxial InN Films Grown by Plasma-Enhanced Atomic Layer Deposition***,* ***Jeffrey Woodward****, D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Huntington Ingalls Industries*; S. Walton,* U.S. Naval Research Laboratory*; S. Rosenberg,* Lockheed Martin Space Advanced Technology Center*; J. Hite, M. Mastro,* U.S. Naval Research Laboratory

The controlled co-delivery of reactive and energetic plasma species during plasma-enhanced atomic layer deposition (PEALD) enables the growth of epitaxial layers at significantly reduced temperatures which are prohibitive to other methods. However, this capability is challenged by the complexity which arises from the reliance on plasma-surface interactions, and it is thus necessary to understand the influence of the plasma properties on the growth kinetics and resultant film properties. Among the III-nitride binary compounds, indium nitride (InN) is particularly well-suited for the investigation of the roles of reactive and energetic plasma species, as high-quality crystalline films can be achieved using trimethylindium (TMI) and a relatively simple $N_2$/Ar plasma rather than $N_2$/Ar/$H_2$ or $NH_3$/Ar plasmas which generate greater varieties of species. This was explored in recent studies of InN PEALD on gallium nitride (GaN) using *in situ* synchrotron x-ray scattering, which revealed that the growth mode is correlated with the relative density of atomic N, while coarsening behavior is influenced by ion flux.[1]

In this work, epitaxial InN films are grown by PEALD on GaN (0001) at approximately 320 °C using TMI and $N_2$/Ar plasma within various regimes of plasma species generation in order to investigate the influence on the resultant film properties. Optical emission spectroscopy and Langmuir probe measurements are used to correlate the production of atomic N and ions with the $N_2$ and Ar gas flows into the inductively coupled plasma (ICP) source. The InN films are characterized by atomic force microscopy (AFM), x-ray reflectivity (XRR), high-resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), synchrotron grazing incidence wide-angle x-ray scattering (GIWAXS), and x-ray photoelectron spectroscopy (XPS). The films are found to exhibit wurtzite phase and sixfold rotational symmetry with a clear epitaxial relationship to the GaN. Low fluxes of atomic N are found to promote larger domains, increased crystalline order, and smoother morphology compared to films grown with high atomic N fluxes. For the high atomic N flux condition, increasing ion flux is found to promote a very rough morphology containing large cluster-like features and decreased in-plane crystalline order, but increased out-of-plane crystalline order and a reduction in mosaic twist.

[1] J. M. Woodward *et al*., J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:40am **AP+PS+TF-WeM-12 One Step Synthesis of Patterned Coatings Using Immobilized Filaments in an Atmospheric Pressure Dielectric Barrier Discharge. Effect of Gap and Power Pulsing.***, M. Brabant,* ***Annaëlle Demaude****, D. Petitjean,* Université Libre de Bruxelles, Belgium*; K. Baert, T. Hauffman,* Vrije Universiteit Brussel, Belgium*; M. Gordon,* University of California Santa Barbara*; F. Reniers,* Université Libre de Bruxelles, Belgium

Deposition of patterned coatings to generate hybrid surface properties often require a multi-step process, such as the use of masks or lithography [1]. We proposed recently a simple scalable method for the deposition of patterned coatings (morphological and chemical contrasts) [2]. As a case study, the deposition of propargyl methacrylate (PMA) based-coatings was realized, as, due to its structure (one double and one triple bond), this molecule allows very fast deposition, and can lead to hydrophobic coatings, without the need of fluorinated atoms. Moreover, we showed that, depending on the deposition conditions, one could obtain hybrid hydrophilic/hydrophobic patterns.

To test the flexibility and the limits of the method, we now investigate further this route and try to understand better the effects of the gap between the electrodes and of the pulsed/non pulsed injection of the power. The deposited coating was characterized using μ-XPS, FTIR and contact angle measurements, whereas the discharge was characterized using a high intensity camera, electrical measurements (oscilloscope and Rogowski coil), and mass spectrometry. Due to the DBD configuration, the coating exhibits two distinct areas : the spot (S) area, corresponding to the coating deposited under the filament position, and the between spot (BS) area, corresponding to the coating deposited outside the filament position.

Filaments are immobilized thanks to beads fixed to one of the dielectrics, reducing locally the gap and therefore igniting specifically the discharge at these locations. Here the gap was fixed at 2, 2.5 and 3 mm. it is shown (using a high intensity camera, and electrical measurements) that an increase in gap leads to more energetic discharges inside the filaments. As shown by XPS, this leads to a lower preservation of the precursor structure for the “S”area coating. In parallel, due to higher voltages needed to light up the discharge, surface discharges take place between the filaments leading to subsequent deposition also between the spots located under the filaments.

Pulsing the power (in the ms range) leads to more localized filaments, to a global change in the plasma behavior and to a change in the coating chemistry [3] .

References :

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[2] A. Demaude *et al*., *Advanced Science*. 2022, *9* (15), 2200237

[3] A. Demaude *et al*., *Plasma Chemistry and Plasma Processing*, submitted.

12:00pm **AP+PS+TF-WeM-13 Effect of Bias Pulsed Plasma Enhanced Atomic Layer Deposition for Void-Free $SiO_2$ Gap-Fill of High Aspect Ratio Trench Structures***, **Ye Ji Shin**, H. Kim, G. Yeom,* Sungkyunkwan University, Korea

In 3-dimentional (3D) device structures, cells are getting thinner and higher to increase the density of devices which resulted in High Aspect Ratio (HAR) structures. Gap-fill process is one of the processes that could affect the device performance of HAR trench structures. Void and seam are observed after the gap-fill process and they allow penetration of the chemical etchant used in subsequent processes, and which degrades isolation performance and increases leakage currents. To solve this issue, various processes such as thermal ALD processes with inhibitors, plasma enhanced ALD with substrate biasing, etc. have been used but, with increasing the aspect ratio of the structure, it is found to be difficult to fill the gap completely without void or seam in the trench. In this study, bias power with pulsing was introduced to PEALD processes for void and seam free $SiO_2$ gap-filling. Pulsed bias power with various pulse duty ratio from 30 to 75% were used and compared with continuous wave (CW) bias power and no bias power to identify the effect of bias pulsing. The results showed that, as the bias pulse duty ratio was decreased, void and seam were decreased and disappeared at HAR trench structures even with negative bowing. The pulse biasing with low duty ratio appeared to open the opening of the trench top while the pulse biasing with high duty ratio and CW biasing operation appeared to close the opening of the trench top possibly due to differences in combined effect of ion bombardment flux and deposition. Eventually, void-free $SiO_2$ gap-fill for HAR trench structures were obtained with bottom-up filling under the pulsed bias conditions. Detailed experimental results and analysis data will be shown in the presentation.

## 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.

References:

[1] D. Marković, J. Ašanin, T. Nunney, Ž. Radovanović, M. Radoičić, M. Mitrić, D. Mišić, M. Radetić, Fibers. Polym., 20, 2317–2325 (2019)

[2] D. Marković, H.-H. Tseng, T. Nunney, M. Radoičić, T. Ilic-Tomic, M. Radetić, Appl. Surf. Sci., 527, 146829, (2020)

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.

[1]B. Meunier, E. Martinez, O. Renault et al. *J. Appl. Phys*. **126**, 225302 (2019).

[2]B. Meunier, E. Martinez, O. Renault et al., *ACS Appl. Electron. Mater*. **3** (12), 5555–5562 (2021).

[3]O. Renault et al., *Faraday Disc*. **236**, 288-310 (2022).

[4]A. Benayad et al., *J. Phys. Chem. A* 2021, 125, 4, 1069-81.

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.

[1]Liu, Z.T., *et al*. The characterization of the optical functions of BCP and CBP thin films by spectroscopic ellipsometry. *Synthetic Materials*. 150(2):159-163. (2005)

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].

[1] M. K. Passarelli *et al.*, “The 3D OrbiSIMS—label-free metabolic imaging with subcellular lateral resolution and high mass-resolving power,” *Nat. Methods*, no. november, p. nmeth.4504, 2017, doi: 10.1038/nmeth.4504.

[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 TF1+PS-WeM

### Emerging and Advanced Materials and Processes

**Moderators: Subhadra Gupta**, University of Alabama, **April Jewell**, Jet Propulsion Laboratory

8:00am **TF1+PS-WeM-1 Modified Reactive Sputter Deposition of Titanium Nitride Thin Films via HIPIMS with Kick-Pulse**, *A. Miceli, D. Santavicca,* ***Stephen Stagon,*** University of North Florida **INVITED**

Direct current (DC) and radio frequency (RF) sputtering methods have been commonplace in industry for several decades and widely studied in the literature. Hard films of nitrides, such as titanium nitride (TiN), have been deposited using reactive DC sputtering onto cutting tools and medical devices extensively as well. For these applications, the films require excellent adhesion, high density, and high hardness. High-Power Impulse Magnetron Sputtering (HIPIMS) has emerged over the last several years as a method to produce films with increased density and mechanical properties. Process-structure-property relationships for reactive HIPIMS are not well developed. Additionally, conventional HIPIMS suffers from relatively low deposition rates, which become a challenge or barrier to adoption for applied TiN coatings that are typically greater than several microns in thickness. This work aims to look at increasing this deposition rate while maintaining the beneficial effects of HIPIMS by utilizing the short duration “kick-pulse” in the voltage/current cycle, leading to higher instantaneous deposition rates and increased adatom energy level. TiN films are deposited onto silicon (Si) wafers under varied reactive sputtering conditions, including DC, HIPIMS, and HIPIMS with kick-pulse. Structural characterizations are performed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Optical and electrical properties of the resulting films are also characterized using reflection UV-Vis spectroscopy and 4-point probe techniques. The deposition rate, morphology, and chemical composition of the films are highly affected by the processing conditions, with the kick-pulse producing significant increase in deposition rate and observed grain size. Further investigation will aim to develop a modified structural zone model to include HIPIMS with and without kick-pulse.

8:40am **TF1+PS-WeM-3 Time-Resolved ALD Reaction Heat**, ***Ashley Bielinski***, *E. Kamphaus, L. Cheng, A. Martinson,* Argonne National Laboratory **INVITED**

Atomic layer deposition (ALD) is a surface synthesis technique that consists of sequential self-limiting surface reactions between molecular precursors and a substrate.Differences in the substrate surface as well as the precursor ligands can have a significant influence on the properties of the deposited film and the formation of interfaces, even within a given material system. ALD processes are often empirically optimized with only a simplified chemical understanding of the surface reactions.While this is sufficient for some applications, emerging technologies such as area-selective ALD and site-selective ALD seek to leverage the chemical selectivity between precursor molecules, inhibitors, and the substrate surface.To better understand and direct ALD surface reactions, we must improve our fundamental understanding of the surface reaction mechanisms and energetics.

Pyroelectric calorimetry enables in situ, time-resolved measurements of the heat generated by ALD surface reactions. We present a pyroelectric calorimeter optimized to operate under standard ALD conditions with resolution down to 0.1 μJ/cm$^2$ and 50 ns.This process of ALD calorimetry was used to measure the heat generation rates from trimethylaluminum (TMA), tetrakis(dimethylamino)zirconium (TDMAZr) and water to form $Al_2O_3$ and $ZrO_2$.The aerial heat generation rates were combined with in situ spectroscopic ellipsometry and ex situ Rutherford backscattering measurements to calculate the reaction thermodynamics on a per atom basis.These results were then compared with computational first principles models as well as calculations of the standard reaction enthalpies.The total measured heat was in good agreement with the standard enthalpies, but the computational models showed greater deviation.Pyroelectric calorimetry provides a unique opportunity to validate and provide benchmarks for computational models, helping to evaluate the accuracy of proposed models and mechanisms.

The heat generation rates were also analyzed to compare reaction kinetics.For example, the water reaction occurred at significantly different speeds on the TMA and TDMAZr saturated surfaces. Due to the high time-resolution, we were able to resolve, for the first time, a multi-step reaction for TDMAZr reacting with hydroxylated $ZrO_2$. Heat generation rates provide new insight into ALD processes, helping us to untangle the thermodynamics, kinetics, and mechanisms of these heterogenous surface reactions.

9:20am **TF1+PS-WeM-5 Reducing Hysteresis in Atomic Layer Deposited $VO_2$ Thin Films**, *V. Wheeler,* ***Peter Litwin,*** *S. Bennett, M. Currie,* US Naval Research Laboratory

$VO_2$ is a phase change material that undergoes a first order crystalline phase transition at a critical temperature ($T_c$ = 68°C), resulting in significant changes in intrinsic electrical and optical properties, especially in the infrared. Optical and electrical variations associated with this phase transition are of particular interest as passive and active components of electronic and optoelectronic devices, including RF limiters, thermal regulation, and modulated signaling. Realizing this type of device often requires the integration of thin, conformal $VO_2$ films with complex, non-planar structures (like metamaterials). Thus, atomic layer deposition (ALD) is an ideal deposition method in these cases.

While ALD is useful for integrating highly uniform and stoichiometric films with dissimilar materials, the low deposition temperature results in amorphous films that do not exhibit the required phase change for device applications. Thin $VO_2$ films deposited by many methods, including ALD, typically require a post-deposition anneal to induce the crystallization necessary for large, abrupt, usable changes in properties during the phase transition. This anneal can be accomplished in many ways such as a slow traditional anneal in specific partial oxygen environments or using environmentally independent laser processes to rapidly crystallize the film. However, the microstructure and resulting phase change properties are highly dependent on the method of crystallization and can lead to deleterious effects like large hysteresis windows (> 10°C) during heating and cooling through the phase transition of these films. For optimum performance in device applications, the hysteresis needs to be reduced or even eliminated.

In this work, we will discuss developing novel processes towards achieving crystalline ALD $VO_2$ films and the impact they have on reducing hysteresis, including the introduction of nucleation layers and tailoring of plasma properties during plasma enhanced ALD. As an example, we have found that hysteresis can be reduced to a few degrees using ALD $TiO_2$ films, independent of crystallinity, phase, or thickness of the $TiO_2$ film itself, but ALD $Al_2O_3$ or $HfO_2$ buffer layers do not impact the hysteresis at all. When possible, we will discuss the possible causes and mechanisms behind hysteretic performance improvements.

9:40am **TF1+PS-WeM-6 Magnetron Sputtering Deposition and Stabilization of the Bismuth Sesquioxide ($Bi_2O_3$) High-Temperature Equilibrium Phase***, **Sandra E. Rodil**, A. Martinez, O. Depablos-Rivera,* Universidad Nacional Autónoma de Mexico

Bismuth sesquioxide ($Bi_2O_3$) exhibits a dynamic polymorphism characterized by two thermodynamically stable phases. The first is the monoclinic (α) phase, which remains stable from room temperature (RT) up to 730 °C, while the second is the defect-fluorite cubic (δ) phase, stable above 730 °C and up to the material's melting point (830 °C). Additionally, during the cooling/heating process, two metastable phases (β-tetragonal and γ-bcc) are formed, and their transformation temperature depends on factors such as the cooling rate, ambient conditions (vacuum or air), and oxygen concentration.

The production of the δ-$Bi_2O_3$ phase as a thin film date back to 1999, when it was first demonstrated using electrodeposition, followed by magnetron sputtering. The crystallographic structure of the films has been analyzed through X-ray diffraction patterns and visible Raman spectra. However, caution must be exercised when interpreting Raman spectra, as the broadband at 600 $cm^{-1}$ associated with the defect-fluorite cubic (δ) phase can also be observed in other phases. To address this issue, we critically analyzed the assignments provided in the literature for this broad Raman mode and proposed an alternative explanation consistent with its observation in all films. Our proposal attributes the 600 $cm^{-1}$ band to the presence of residual-weakly bonded [$BiO_n$] units located at the grain boundaries of the nanocrystalline films. This band is not exclusive to the defective fluorite cubic structure of $Bi_2O_3$. Interestingly, we found a similar signal in the Raman spectra of the $Bi_4O_7$ phase, which had not been reported before, suggesting possible incorrect assignments to the δ-phase. We employed a density functional approximation of the $Bi_4O_7$ molecular structure to gain further insights to calculate the Raman active bands. The theoretical estimations showed excellent agreement with experimental data, reinforcing the validity of our proposed explanation.

Finally, our investigations revealed that doping with heterovalent ions allows for stabilizing films exhibiting the δ-$Bi_2O_3$ phase within a temperature range from room temperature to 600 °C. This exciting discovery opens new possibilities for using these films as ionic conductors, potentially finding applications in various technological fields.

## 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 $VO_2$ 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 ($\sigma^2$: the mean-square relative displacements) is established. The temperature dependence of the vanadium dimers Waller factor ($\sigma_R^2$ (V-V)), as calculated from the Raman intensity, was found to follow the temperature profile of the $\sigma_{EXAFS}^2$ (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 $TiO_2$***, **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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[2] A. Herrera-Gomez, Interchannel Coupling with Valence Band Losses as the physical origin of the Shirley background in photoemission spectra (Old title: The unresolved physical origin of the Shirley background in photoemission spectra), Queretaro, 2015. http://www.qro.cinvestav.mx/%0A~aherrera/reportesInternos/unknownOriginShirley.pdf.

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.

*[1] Werner, W. , Smekal, W. , Powell, C. and Gorham, J. (2021), Simulation of Electron Spectra for Surface Analysis (SESSA) Version 2.2 User's Guide, Natl Std. Ref. Data Series (NIST NSRDS), https://doi.org/10.6028/NIST.NSRDS.100-2021.*

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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5:00pm **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.

## Magnetic Interfaces and Nanostructures Division
## Room B110-112 - Session MI+2D+TF-WeA

### Special Symposium on Coupling Phenomena in Magnetism

**Moderator: Hendrik Ohldag**, Lawrence Berkeley National Laboratory

2:20pm **MI+2D+TF-WeA-1 Coupling Spin-Orbit and Exchange Interaction in a Low-Dimensional Magnet***, **Pascal Jona Grenz**[1], M. Donath, P. Krüger,* University of Münster, Germany

Coupling exchange interaction (SOI) and spin-orbit interaction (XCI) provides the foundation for many prospective spin-based information technology applications. For example, it was suggested that the strength of SOI at a ferromagnet/heavy-metal (FM/HM) interface is decisive for the efficiency of writing magnetic bits in spin-orbit-torque MRAM devices [1].

Exploring the electronic structure is the key to access the factors underlying the coupling of SOI and XCI. We use spin- and angle- resolved inverse photoemission to study the interplay of SOI and XCI in the unoccupied electronic structure at the interface of a low-dimensional FM on a HM substrate. The prototypical FM/HM hybrid system Ni/W(110) exhibits exchange-split Ni-related states that become strongly influenced by SOI. A balanced ratio of SOI and XCI results in a magnetization- and k-dependent quenching or enhancement of the spin splitting. This remarkably large interplay of SOI reflected in the adlayer states contrasts previous studies of the occupied electronic structure of the same system, where the observations were attributed solely to either SOI or XCI [2].

Using density-functional-theory (DFT) calculations, we investigate the underlying drivers responsible for the experimentally observed coupling of SOI and XCI. We find that hybridization between adsorbate and substrate states, along with the strongly localized wave functions at the heavy W nuclei, cause the strong influence of SOI within the Ni-related exchange-split states.

[1] I.M. Miron *et al*., Nature, **476** 189 (2011)

[2] A. Nuber, PhD Thesis (University of Würzburg, Germany, 2011)

2:40pm **MI+2D+TF-WeA-2 AVS Graduate Research Awardee Talk: Temperature Dependent Magnetic and Electronic Properties of NiCo$_2$O$_4$ Thin Film Surfaces***, **Arjun Subedi**[2,3],* University of Nebraska-Lincoln*; D. Yang, C. Mellinger, X. Xu,* University of Nebraska–Lincoln*; P. Dowben,* University of Nebraska-Lincoln

Although NiCo$_2$O$_4$ thin film is shown to possess perpendicular magnetic anisotropy [1], we have observed in-plane spin polarization of NiCo$_2$O$_4$ thin film in spin polarized inverse photoemission spectroscopy (SPIPES). The unoccupied states of NiCo$_2$O$_4$, above Fermi level, were observed to have unequal density of states for spin majority and spin minority carriers in SPIPES, and the spectra obtained from the SPIPES have spectral features that can be compared to the XMCD spectra. The in-plane spin polarization of NiCo$_2$O$_4$ is found to decrease with increasing temperature, as expected.

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[1] **Falicov Student Award Finalist**

[2] **AVS Graduate Research Awardee**

[3] **Falicov Student Award Finalist**

In addition to the temperature dependent change in spin polarization, we observed that there is change in the surface electronic properties of $NiCo_2O_4$ from conducting to insulating when the temperature is increased. X-ray photoemission spectroscopy (XPS) studies show that there exist no appreciable binding energy changes of Ni $2p_{3/2}$ and Co $2p_{3/2}$ core levels with change in temperature (T) when the $NiCo_2O_4$ film exists in conducting phase. However, when the $NiCo_2O_4$ films became insulating, the core level binding energies changed reversibly with change in temperature during annealing and cooling cycles. The core level binding energy (BE) change with temperature (T) is found to closely follow a modified Arrhenius type model. The proposed model is also followed by Co $2p_{3/2}$ and Fe $2p_{3/2}$ core levels in temperature dependent XPS of insulating $CoFe_2O_4$ thin films.Our studies indicate that thermal effects and oxygen defects should play the roles in changing both magnetic and electronic properties of $NiCo_2O_4$ thin films with temperature.

[1] C. Mellinger et al., Phys. Rev. B 101, 014413 (2020).

3:00pm **MI+2D+TF-WeA-3 Antiferromagnetic Real-Space Configuration Probed by Dichroism in Scattered X-Ray Beams with Orbital Angular Momentum***, **Sophie Morley**, M. McCarter, A. U. Saleheen, A. Singh,* Lawrence Berkeley Lab*; R. Tumbleson,* University of California Santa Cruz*; J. Woods,* Argonne National Laboratory*; A. Tremsin,* UC Berkeley*; A. Scholl,* Lawrence Berkeley Lab*; L. de Long, J. Hastings,* University of Kentucky*; S. Roy,* Lawrence Berkeley Lab **INVITED**

X-ray beams with orbital angular momentum (OAM) are a promising tool for x-ray characterization

techniques. Beams with OAM have an azimuthally varying phase, and new material properties can

potentially be probed by utilizing this unique phase structure. Here, we show how OAM beams are

created through resonant diffraction from an artificial antiferromagnet with a topological defect. The

scattered OAM beams have circular dichroism whose sign is coupled to the phase of the beam [1]. Using

magnetic scattering calculations, we show that this dichroism is related to the real-space configuration

of the antiferromagnetic ground state. Thermal cycling of the artificial antiferromagnet can change the

ground state, as indicated by the changing dichroism. These results exemplify the potential of OAM

beams to probe matter in a way that is inaccessible using currently available x-ray techniques.

[1] M. R. McCarter et al., Phys. Rev. B 107, L060407 (2023)

5:00pm **MI+2D+TF-WeA-9 Spin-dependent Hybridization of Image-potential States with Tl States in Tl/Ag(111)***, **Sven Schemmelmann**[1],* Universität Münster, Germany*; P. Härtl,* Universität Würzburg, Germany*; P. Krüger,* Universität Münster, Germany*; M. Bode,* Universität Würzburg, Germany*; M. Donath,* Universität Münster, Germany

The $BiAg_2$ and $PbAg_2$ surface alloys exhibit giant Rashba splittings [1-4]. The related $TlAg_2$ surface alloy is expected to show states with smaller but still large Rashba splittings due to the lower atomic number of Tl. However, this alloy forms only small patches with long-range structural order [5]. For higher coverages of Tl on Ag(111), a smooth and stable wetting layer forms with a moiré superstructure due to the lattice mismatch between Tl and Ag. We present a study of the unoccupied electronic structure of this superstructure by spin- and angle-resolved inverse photoemission. The experimental results are accompanied by DFT calculations. We observe surface states and an image-potential resonance located several Å in front of the surface. Surprisingly, one surface state exhibits almost no Rashba splitting even though it is located around the Tl atoms. This result is explained by the orbital symmetry of the respective state. For the image resonance, we find hybridization with a downward dispersing Tl state leading to spin-dependent spectral intensities that vary strongly close to the hybridization point. This observation, both in experiment and bandstructure calculations, is supported by charge distribution calculations showing an expeditious change from the image resonance to the Tl-induced surface state depending on $k_{||}$.

[1] C. R. Ast *et al.*, Phys. Rev. Lett. **98**, 186807 (2007)

[2] G. Bihlmayer, S. Blügel, and E. V. Chulkov, Phys. Rev. B **75**, 195414 (2007)

[3] S. Wissing *et al.*, Phys. Rev. Lett. **113**, 116402 (2014)

[4] L. El-Kareh *et al.*, New J. Phys. **16**, 045017 (2014)

[5] P. Härtl, S. Schemmelmann, P. Krüger, M. Donath, and M. Bode, submitted to Phys. Rev. B

5:20pm **MI+2D+TF-WeA-10 Distinct Tamm and Shockley Surface States on Re(0001) Mixed by Spin-Orbit Interaction – A Photoemission Study***, **Marcel Holtmann**, P. Krüger,* University of Münster, Germany*; K. Miyamoto, T. Okuda,* HiSOR, Japan*; P. Grenz,* University of Münster, Germany*; K. Shimada,* HiSOR, Germany*; M. Donath,* University of Münster, Germany

Tamm and Shockley states, these two paradigmatic concepts are used to describe surface states not only in electronic systems but also in photonic and phononic crystals. The Re(0001) surface was found to host both types of electronic surface states in neighboring, but qualitatively different gaps [1]. Interestingly, spin-orbit interaction generates a double W-shaped energy vs $\mathbf{k}_{||}$dispersion by mixing both types of states and lifting their spin degeneracy. We employ a combination of spin- and angle-resolved photoemission, tight-binding model calculations, and density functional theory that accounts for the photoemission process to establish reliable criteria for distinguishing between the two types of surface states. Our approach leads to a coherent understanding of the mechanism of spin-orbit interaction in such a situation.

From a detailed investigation of the Re(0001) surface along the ΓM and ΓK high-symmetry directions [2], we obtain Rashba parameters of 0.32 and 0.34 eVÅ along the two respective directions. This indicates a slight warping of the surface state. Regarding the aforementioned state's spin polarization: at variance with theoretical predictions for a perfect hcp(0001) of rhenium [3], we do not find any out-of-plane spin polarization. This is attributed to monatomic steps of a real Re(0001) surface with alternating terminations, leading on average to an effective sixfold surface symmetry and vanishing net out-of-plane spin polarization.

[1] M. Holtmann *et al.,* Phys. Rev. B **105**, L241412 (2022)

[2] M. Holtmann *et al.,* Phys. Rev. B **107**, 165420 (2023)

[3] A. Urru and A. Dal Corso, Surf. Sci. **686**, 22 (2019)

5:40pm **MI+2D+TF-WeA-11 Coupling between Spin Order and Orbital Order in 2D-Superlattice Perovskite Film***, **Bin Hu**,* University of Tennessee Knoxville **INVITED**

The coupling between spin order and orbital order presents a fundamental request to develop advanced multifunctional materials. 2D-superlattice perovskite films, known as solution-processing semiconductors, possess strong orbital order within non-degenerate Rashba band structures under the concurrent influence of spin-orbital coupling and symmetry breaking. This provides a fundamental condition to dynamically couple spin order and orbital order through multiferroic interface design. Here, we combine ferroelectric 2D-suparelattice perovskite (4,4-$DFPD_2PbI_4$) film and ferromagnetic cobalt (Co) film to form multiferroic perovskite/Co interface. By using this multiferroic interface design, we found that the circularly polarized orbitals with right and left handedness (**s**$^+$ and **s**$^-$) in Rashba band structures can selectively interact with spin-up and spin-down spin dipoles on the Co surface, leading to a mutually selectivity between spin order and orbital order. Particularly, this selective interaction between spin order and orbital order can enable spin-switchable phenomena towards developing emerging functionalities in these solution-processing hybrid metal halide perovskites. When the ferromagnetic spins on the Co surface are altered between positive and negative magnetic field directions (+**B** and -**B**), the circularly polarized luminescence (CPL) in 2D-superlattice perovskite can be switched between **s**$^+$ and **s**$^-$polarizations, leading to spin-switchable phenomena at room temperature. More interestingly, our polarized neutron reflectometry (PNR) studies found that circularly polarized photoexcitation generates a static magnetization within 2D-superalttice perovskite film prepared on the Co surface. This presents an optically induced magnetization phenomenon. Essentially, this optically induced magnetization reveals a long-range coupling between the spin order on the Co surface and the orbital order within Rashba band structures in 2D-

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[1] **Falicov Student Award Finalist**

superlattice perovskite film. This presentation will discuss the fundamental coupling between spin order and orbital order through Rashba band structures in 2D-superlattice perovskite film.

## Thin Film Division
## Room A105 - Session TF+QS-WeA

### Thin Films for Space and Electronic Applications

**Moderators: John Hennessy**, Jet Propulsion Laboratory, **Richard Vanfleet**, Brigham Young University

2:20pm **TF+QS-WeA-1 From Space Thrusters to Exoplanets Research*, Christine Charles*,** *R. Boswell, M. Davoodianidalik, J. Machacek, D. Tsifakis, M. Shadwell, H. Punzmann,* Australian National University, Australia*; K. Takahashi,* Tohoku University, Japan*; J. Lecomte, N. Suas-David, L. Rutkowski, E. Dudas, A. Benidar,* Université de Rennes, France*; S. Kassi,* Université de Grenoble-Alpes, France*; R. Georges,* Université de Rennes, France*; N. Smith, P. Tesch,* Oregon Physics **INVITED**

Thousands of nano and micro-satellites are expected to be launched over the next decade, many in constellations, and rideshare opportunities are increasing. The Space Plasma, Power and Propulsion (SP3) laboratory works on a range of projects dealing with fundamental physics in astrophysical plasmas (infrared spectroscopy of exoplanet atmosphere) as well as physics and engineering challenges related to space propulsion systems (geometric and plasma nozzles, the “Bogong” Naphthalene cold gas thrusters). The scalability in geometry and power of radiofrequency plasma devices has allowed the development of a range of electrodeless thrusters such as the low pressure (~1 mTorr) Helicon thruster and the higher pressure (~1 Torr) Pocket Rocket thruster. These have yet to be flown but have surprisingly been wonderful training platforms and opened doors to new areas of research. Expanding nearly collisionless plasmas (i.e. Helicon thrusters) can be used to investigate out-of-equilibrium thermodynamics via polytropic index studies both in the laboratory and in space. Expanding collisional plasmas (i.e. Pocket Rocket thruster) can be used to investigate plasma fluid flows in nozzle. As an example, the development of the Pocket Rocket thruster into a laminar nozzle capable of producing high vibrational temperatures for molecular gases, “Platypus”, was carried out for implementation onto the SMAUG exoplanet research apparatus (Spectroscopy of Molecules Accelerated in Uniform Gas flows) which produces non-LTE (Local Thermodynamic Equilibrium) spectra of various molecules characterised using cavity ringdown spectroscopy yielding successful acquisition of absorption spectra in the infrared using naphthalene/argon plasmas. Naphthalene is also our propellant of choice for the cost-effective green and safe “Bogong” thruster, co-developed by Boswell Technologies and SP3, fully space qualified and deployed in Low Earth Orbit on the 4th of January 2023 by a Space X Falcon 9 rocket (Transporter-6 Mission, 300 kg Skykraft satellite stack).Similar radiofrequency plasma technologies are used for our various thruster concepts and for our focused ion beam (FIB) studies using the Hyperion source developed by Oregon Physics. The use of such FIB applies to materials characterisation, forensic studies and bio-medical applications. SP3 is collaborating with Oregon Physics to develop an $O_3^-$ negative ion source. It is interesting that the mature ion gridded thruster technology (in operation on many commercial satellites including the deep space Bepi Colombo spacecraft on its way to Mercury) share technical similarities with focused ion beam sources.

3:00pm **TF+QS-WeA-3 Photodegradation of Self-Immolating Polymers as a Potential Solution to Optical Scattering*, Alexandra Stapley*,** *S. McFarland, J. Vawdrey, K. Mitchell, W. Paxton, D. Allred,* Brigham Young University

Starshades and other optical devices that are sensitive to scattered light require dust mitigation techniques to provide low-scatter surfaces and edges. Poly(olefine) sulfones have been shown to photodegrade with the assistance of a photobase generator when exposed to deep UV light (254 nm) and heat (120°C). These may be applicable in minimizing dust on optical surfaces for space applications. Their behavior in vacuum was not investigated, however. We synthesized Poly(2-methyl 1-pentene) sulfone (PMPS) and Poly(1-hexene) sulfone (PHS) with and without a photobase generator. We studied the photodegradation (172 nm or 254 nm) of thin films in vacuum. Spectroscopic ellipsometry was used to quantify film thickness over time. The PMPS film with photobase generator fully degraded when exposed to 172 nm light in vacuum. A significant finding was that heat was not required to produce this result. PMPS film degradation without the photobase generator was slower and incomplete. The results of our PHS studies are also promising. This study shows that a PMPS film could potentially be used to protect optical surfaces until their deployment in space.

3:20pm **TF+QS-WeA-4 Enhancement of the Bifacial Absorber of Silver Antimony Sulfur Selenide Photovoltaic Devices*, Sanghyun Lee,*** University of Kentucky*; M. McInerney,* Rose-Hulman Institute of Technology

Silver Antimony Sulfur Selenide, $AgSb(S_xSe_{1-x})_3$ thin-film solar cells have promising properties such as tunable bandgap (0.7 - 1.9 eV), good doping concentration ($10^{16}$ $cm^{-3}$), and high absorption coefficient (>$10^4$ $cm^{-1}$). The efficiency of $AgSb(S_xSe_{1-x})_3$ thin-films with x=0.53, 0.58, and 0.61 has been studied with >2.77 %. Since Antimony Sulfur Selenide, $Sb(S_xSe_{1-x})_3$thin-films have shown good optical and electronic properties as an absorber layer, further optimization of thin-film absorber layers could be achieved by utilizing both $Sb(S_xSe_{1-x})_3$ and $AgSb(S_xSe_{1-x})_3$ thin-films for bifacial devices. Furthermore, substituting Ag in $Sb(S_xSe_{1-x})_3$ thin-films tends to increase the bandgap of the absorber layer by lowering the valence band based on studies of other thin-film absorber layers (CIGS, CZTSSe).

In this contribution, we have theoretically studied bifacial photovoltaic devices by combining thin-film absorbers of $AgSb(S_xSe_{1-x})_3$, $Sb(S_xSe_{1-x})_3$, and the combination of $AgSb(S_xSe_{1-x})_3$ and $Sb(S_xSe_{1-x})_3$ thin-films from the electronic band structure perspective. To fully utilize the promising properties of both $Sb_2(S_xSe_{1-x})_3$ and $AgSb(S_xSe_{1-x})_3$ films, we investigated different compositions and concentrations of Sulfur and Selenium with proposed empirical equations for electron affinity and bandgap energy through modeling and simulations.

Four different structures of thin-film absorbers have been studied above Molybdenum metal thin-films. For both $AgSb(S_xSe_{1-x})_3$ and $Sb(S_xSe_{1-x})_3$ thin-films, the electron affinity and bandgap energy increase as Sulfur (x) composition increases. However, the increased bandgap is not directly translated into improved solar cells efficiency due to the alignment of thin-film electronic structures. The best efficiency was achieved with 2 um $AgSb(S_{0.4}Se_{0.6})_3$ thin-film devices(18.4 %) at sulfur concentration, x = 0.4. However, once we combine two $AgSb(S_xSe_{1-x})_3$ and $Sb(S_xSe_{1-x})_3$ thin-films while keeping a total thickness, 2 um (1 um/1 um), an interface between $AgSb(S_{0.4}Se_{0.6})_3$/ $Sb_2(S_{0.4}Se_{0.6})_3$ and Molybdenum metal thin-films is preferably formed due to reduced effective Schottky hole barrier. If we assume the same amount of defect states at the interface, the improved effective Schottky hole barrier is 128 mV due to the favorable band alignment, which is approximate 4.3 times better than a $AgSb(S_{0.4}Se_{0.6})_3$ thin-film structure. With a bi-layer $AgSb(S_{0.4}Se_{0.6})_3/Sb_2(S_{0.4}Se_{0.6})_3$ -thin-film absorber, we studied various doping concentrations impact on device efficiency based on the modified electronic band structure of each thin-film. The doping concentration of $AgSb(S_{0.4}Se_{0.6})_3$ thin-film mainly increases the photogenerated current while $Sb_2(S_{0.4}Se_{0.6})_3$ -thin-film improves open circuit voltage.

4:20pm **TF+QS-WeA-7 Atomic Scale Processing and Surface Engineering to Maximize Microdevice Performance for Remote Sensing and Imaging Applications*, Frank Greer,*** Jet Propulsion Laboratory (NASA/JPL) **INVITED**

Future UV, X-ray, infrared, and sub-millimeter telescopes and spectrometers have the potential to revolutionize our understanding of the formation and habitability of the modern universe, Earth, and other planetary bodies.[1-4] Star formation, dark energy, and the composition of the intergalactic medium are only some of the key scientific topics that can be addressed by UV astronomy and astrophysics. Sub-millimeter astronomy can probe the fine structure of the cosmic microwave background, giving glimpses into the early universe immediately following the Big Bang.[5] Remote observation in the infrared is critically important for the understanding of many aspects of Earth Science and Exoplanet atmospheres.

Unfortunately, harnessing the full potential of these missions is often constrained by performance of the available detectors and optical elements (the eyes of the instruments) that make the measurements and take the images. The limitations of these key components are frequently due to non-idealities in the materials and interfaces that are imbedded in or form these devices. Thus, the state-of-the art in materials science, thin films, and semiconductor processing can limit what we can know and learn because it constrains what we can "see". To improve our ability to "see" (by making new types of observations or observations with greater sensitivity), effort is required to improve the specialized materials that impact space-based instruments.

While bulk materials are important, many of the critical challenges in materials science for space applications occur at the nanoscale. Nanoscale coatings deposited by techniques such as atomic layer deposition (ALD) can be used in a variety of ways, including, but not limited to: anti-reflective coatings for UV detectors, passivation layers for infrared detectors, wiring layers in superconducting circuits, or superconducting sensing elements.Nanoscale surface engineering through atomic scale processes can substantially improve the optoelectronic properties of III-V sensors and optical elements such waveguides, especially in shorter wavelength ranges where surface roughness is particularly important.

This presentation will detail the fundamental materials science, surface engineering, and ALD/ALE approaches we have used in the fabrication of a variety of devices in multiple different wavelength ranges, demonstrating the boost in performance that is obtained with atomic level precision at key steps in the fabrication process.

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5:00pm **TF+QS-WeA-9 Advances in Plasma-Based Atomic Layer Processing of AlF$_3$ for the Passivation of FUV Mirrors***, **Virginia Wheeler**, D. Boris,* US Naval Research Laboratory*; L. Rodriguez de Marcos, J. del Hoyo,* NASA Goddard Space Flight Center*; N. Nepal, A. Lang, M. Sales, S. Walton,* US Naval Research Laboratory*; E. Wollack, M. Quijada,* NASA Goddard Space Flight Center

Efficient ultraviolet mirrors are essential components for UV astronomy. While aluminum mirrors with fluoride-based passivation layers are commonly used in this application space due to their proven stability and reliability, the optical performance is still insufficient for systems where several reflections are required. In previous work, we demonstrated the feasibility of a new, room temperature plasma process based on electron beam-generated plasma in a benign SF$_6$ environment to simultaneously remove the native oxide and form an AlF3 layer with tunable thickness [1]. This process has been used to demonstrate Al-mirrors with high FUV reflectivity (R≈90% at λ=121nm), large area uniformity of the fluoride coating layer, low coating-induced polarization aberration, and improved durability. Plasma-enhanced atomic layer deposition (PEALD) is a known low temperature, highly conformal coating process which has previously been shown to produce AlF3 films [2], though little has been reported on their performance in FUV applications. In this work, we focus on optimizing PEALD AlF3 films and compare both the materials properties as well as the FUV performance with those produced through self-fluorination electron beam generated plasma process.

PEALD AlF3 films were deposited using trimethylaluminum and SF$_6$ plasma precursors in a Veeco Fiji G2 reactor equipped with a turbo pump and substrate biasing. This reactor has also been customized to include a similar planar electron beam generated plasma if required to etch the native oxide from substrates prior to deposition of AlF3 films. ALD windows were optimized using an *in situ* ellipsometer to monitor the growth rate directly on Al substrates and supplemented with post-deposition x-ray photoelectron spectroscopy and atomic force microscopy to elucidate process-structure-property relationships. Plasma diagnostics, including optical emission spectroscopy and Langmuir probe measurements, were also conducted on the reactor to correlate plasma properties, such as fluence and ion energy, to resulting film properties. Initial plasma characterization showed that there was high atomic fluorine present at the substrate surface using a 1:1 Ar/SF6 plasma at 10mTorr but that this concentration was slightly reduced from that measured within the remote ICP plasma. Additionally, it was found that the fluorine density within the plasma increases linearly with SF6 flow fraction and RF power but only subtle differences were seen with increasing pressure. The influence of these parameters on the AlF3/Al interface and FUV performance will also be discussed.

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5:20pm **TF+QS-WeA-10 Thin Film Processes for UV Detector Technologies for Next Generation NASA Missions***, **Robin Rodríguez**, A. Jewell, J. Hennessy, M. Hoenk, T. Jones, S. Nikzad,* Jet Propulsion Laboratory (NASA/JPL)

Galileo was the first deep space mission to fly a silicon charge-coupled device (CCD) for imaging; since then, silicon-based photodetectors have been used for imaging and/or spectroscopy on nearly every NASA mission. JPL's Advanced Detectors and Nanomaterials Group utilizes thin-film processing and nanoscale interface engineering methods to fabricate advanced detector technologies with improved stability and sensitivity. Our research is largely focused on the use of molecular beam epitaxy (MBE) for band structure engineering and passivation of silicon-based photodetectors. Developments in recent years has been geared toward wafer-scale processing as well as improving the space worthiness of MBE-passivated detectors. We also use atomic layer deposition (ALD) processes to engineer new coatings for advanced optics or detectors, including the customization of detector response over a broad wavelength range. The performance objectives for our technologies are defined to meet the objectives of a variety of NASA research programs with the ultimate goal of flight instrument and mission infusion. This presentation will provide an overview of recent advances in detector optimization for ultraviolet (UV) imaging and spectroscopy applications. Copyright 2023. All Rights Reserved.

5:40pm **TF+QS-WeA-11 Commercializing Nanowire LEDs***, **David Laleyan**, B. Le, G. Frolov,* NS Nanotech Canada*; M. Stevenson, S. Coe-Sullivan,* NS Nanotech

MicroLED display technology consists of many carefully arranged microscopic light-emitting diodes (LEDs) to directly create color pixels. MicroLED displays thus have the potential brightness, efficiency, and response time of inorganic LEDs, but suffer from the high cost of epitaxy, as well as the challenges of creating red, green, and blue emitters on a single material and substrate. Furthermore, conventional approaches of growing planar LEDs and then etching them into micron-scale devices cause a fundamental loss of efficiency, especially for the smallest devices. In this regard, nanowire-based LEDs for microLED applications have been of great interest and a topic of extensive research for over a decade. This is due to their unique ability to maintain high efficiencies as the LED size becomes quite small, even into the sub-micron regime, contrary to conventional thin-film LEDs. Another valuable benefit is the ability to form photonic crystal arrangements, such that the formation of a photonic bandgap leads to highly directional and narrow bandwidth emission. Most recently, reports have shown nanowire LEDs in the green with >25% external quantum efficiency (EQE) and red with >8% EQE, competitive with the best direct green and InGaN red LEDs ever fabricated – despite being sub-micron in size.

These structures were obtained by molecular beam epitaxy (MBE) using a selective area epitaxy (SAE) technique, where nanostructures can be controllably grown on a thin-film template. Novel development and engineering efforts are required for such nanowire LEDs to become commercially viable. This work presents a pathway towards the wafer-scale production of nanowire LEDs for displays. This talk will explain how breakthrough academic research can be made manufacturable by studying run-to-run variability, understanding the process windows, targeting yield-limiting steps, and ensuring process scalability. Focusing on the reproducibility and uniformity of nanowire growth by SAE is the first critical step toward the large-scale deployment of these highly efficient LED that are perfectly suited for the next generation of microLED displays.

## 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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2. M R. Keenan, G. F. Trindade, A. Pirkl, C. L. Newell, K. Ayzikov, J. Zhang, L. Matjacic, H. Arlinghaus, A. Eyres, R. Havelund, J. Bunch, A. P. Gould, A. Makarov and Ian S. Gilmore, in preparation.
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

[1]R. Sandenbergh, M. Biermann, and T. von Moltke, ‘Surface Analytical Characterization of Chromium Passivation on Tinplate’, in *Passivation of Metals and Semiconductors, and Properties of Thin Oxide Layers*, P. Marcus and V. Maurice, Eds., Amsterdam: Elsevier Science, 2006, pp. 143–148. doi: 10.1016/B978-044452224-5/50024-X.

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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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## Electronic Materials and Photonics Division
## Room B116 - Session EM+TF-ThM

### Wide- and Ultra-Wide Band Gap Materials and Devices

**Moderators: Erica Douglas**, Sandia National Laboratories, **Seth King**, University of Wisconsin - La Crosse, **Daniel Pennachio**, Naval Research Laboratory

8:00am **EM+TF-ThM-1 $Ga_2O_3$ and AlN for Power and RF Electronics***, **Grace Xing**,* Cornell University **INVITED**

It's of little surprise that there has been a consistent drive toward the use of wider bandgap materials for power and RF electronics. After all, the wider the bandgap, the greater the breakdown field, opening the door to making devices with a higher breakdown voltage for the same material thickness. Furthermore, the saturation velocity of mobile carriers in ultra-scaled devices tends to be about 1-2 x $10^7$ cm/s in most semiconductors.

However, nature is not always that generous. Typically, a move to a wider bandgap is accompanied by more challenging doping, point defect control, ohmic contacts, quality junctions, along with difficulty in making high-quality native substrates. $Ga_2O_3$ and AlN are among the promising contenders, given their large bandgaps, availability of large-size bulk substrates (>2 inches), and heterojunctions.But both lack p-type.AlN possesses high thermal conductivity – slightly worse than that of copper but $Ga_2O_3$ has a low thermal conductivity – worse than that of sapphire.

Given all these promises and obstacles, is it possible to harvest all the benefits in AlN and $Ga_2O_3$ and demonstrate devices that are superior to those made from SiC and GaN?I will reflect on our efforts in seeking answers to these questions in the past many years researching on power and RF devices with a focus on $Ga_2O_3$ and AlN [1-6].

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8:40am **EM+TF-ThM-3 Deep UV Photoluminescence Mapping of Gallium Oxide***, **Matthew McCluskey**,* Washington State University

Photoluminescence (PL) spectroscopy is an important method to characterize dopants and defects in gallium oxide. Features in the PL spectrum include the intrinsic UV band, blue and green bands that involve donor-acceptor pairs, and red emission due to $Cr^{3+}$ impurities. PL mapping with excitation wavelengths as short as 266 nm reveals the spatial distribution of these features with submicron resolution. In Czochralski-grown β-$Ga_2O_3$:Fe, the $Cr^{3+}$ emission intensity shows striations that are attributed due to inhomogeneities during growth. In addition to defects in the bulk, PL microscopy has revealed several specific defects on the surface. Some of these localized centers are very bright UV emitters. Raman scans of these bright emitters revealed hydrocarbon peaks, which may point toward the origin of the light emission. Samples damaged by high-intensity laser pulses show significant changes in the intensity and energy of the intrinsic UV band.

9:00am **EM+TF-ThM-4 Spatially Resolved Polymorph Conversion in $Ga_2O_3$***, U. Bektas, P. Chekhonin, R. Heller, R. Hübner, M. Liedke, N. Klingner, **Gregor Hlawacek**,* Helmholtz Zentrum Dresden-Rossendorf, Germany

Monoclinic galliumoxide (β-$Ga_2O_3$) is a promising wideband gap semiconductor with a bandgap of 4.7 eV and a high breakdown voltage. However, the existence of several metastable polymorphs and the immature fabrication technology limits its applications. The research is based on the recent observation that β-$Ga_2O_3$ can reliable be converted into γ-$Ga_2O_3$ using high energy ion beams [1,2]. It could also be shown that the resulting γ-$Ga_2O_3$ layer exhibits an exceptional tolerance towards high fluence ion beam irradiation [3].

Here, we use focused ion beam (FIB) induced processing to convert β-$Ga_2O_3$ into γ-$Ga_2O_3$ in a spatially controlled way. We employ focused Ne ions from a helium ion microscope (HIM) and liquid metal alloy ion sources (LMAIS) based FIB with Co, Si, and In to induce the polymorph conversion. Electron backscatter diffraction (EBSD), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are used to confirm, in a spatially resolved way, the successful polymorph conversion. From the obtained EBSD data the orientation relationship between the irradiated and unirradiated material is resolved. Broadbeam irradiated reference samples have been used to corroborate these results with channeling Rutherford backscattering spectrometry (c-RBS), X-ray diffraction (XRD) and Doppler broadening variable energy positron annihilation spectroscopy (DB-VEPAS) results. The obtained crystal structure and defect distribution data supports the model suggested for the conversion mechanism [3].

This research is supported by the tax funds on the basis of the budget passed by the Saxonian state parliament in Germany and the COST Action CA19140 FIT4NANO https://www.fit4nano.eu/.

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9:20am **EM+TF-ThM-5 Low-Temperature Epitaxy and in-situ Doping of Ultrawide Bandgap $Ga_2O_3$ Films via Hollow-Cathode Plasma-ALD***, S. Ilhom, A. Mohammad, N. Ibrahimli, J. Grasso, B. Willis,* University of Connecticut*; A. Okyay,* OkyayTech Inc*; **Necmi Biyikli**,* University of Connecticut

Wide and ultrawide bandgap (WBG/UWBG) semiconductors make the backbone of high-power high-frequency electronics, used in electric vehicles, 5G and beyond wireless communication systems, and smart power grids. Gallium oxide (Ga2O3) is an emerging UWBG semiconductor showing superior material properties particularly ideal for harsh environments (high temperature, high-energy radiation, corrosion) applications. Reducing the growth and doping process temperatures for $Ga_2O_3$would potentially enable a wider integration platform towards post-CMOS integration and flexible electronics.

Herein, we report on the low-temperature as-grown crystalline *β*-$Ga_2O_3$films on Si, glass, and sapphire via hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD). The films were deposited using triethylgallium (TEG) and Ar/$O_2$plasma as metal precursor and oxygen co-reactant, respectively. Additionally, we have employed *in situ* atomic layer doping to n-type dope $Ga_2O_3$ films where tris-dimethylaminosilane

(TDMAS) and tetrakis-dimethylaminotin(IV) (TDMASn) were utilized as the dopant precursors. Growth experiments have been performed at 240 °C under 50 W rf-plasma power. The doping process was carried out via both supercycle (ABC-type ALD-cycle) and co-dosing methods. Additionally, eachunit ALD-cycle was followed by an *in-situ* Ar-plasma annealing treatment, which consisted of Ar-plasma exposure for 20 seconds at 250 W rf-power. Both *in-situ* and *ex-situ* ellipsometry were employed to measure the thickness and optical properties of the $Ga_2O_3$samples. X-ray diffraction (XRD) of the sample on sapphire revealed epitaxial $Ga_2O_3$films with monoclinic *b*-phase, while GIXRD analyses of the samples grown on Si and glass displayed *b*-phase polycrystalline films. HR-STEM imaging and EDX elemental analysis confirmed the epitaxial relationship of the films grown on sapphire substrates and displayed successful incorporation of dopant elements. Preliminary electrical conductivity measurements showed highly resistive samples. Therefore, *ex-situ* thermal annealing studies are carried out to explore dopant activation processes. Further studies from our XPS characterizations will provide additional insight about the chemical bonding states of the dopant species. A significant effort will be devoted for the comparison of Si and Sn-doping strategies and potential suggestions will be provided to overcome the challenges in achieving device quality undoped and doped $Ga_2O_3$layers at low processing temperatures.

9:40am **EM+TF-ThM-6 Growth of Metastable $Ga_2O_3$ Epitaxial Films Using Metalorganic Chemical Vapor Deposition and Halide Vapor Phase Epitaxy***, **Jingyu Tang**, K. Jiang, M. Weiler, M. Moneck, R. Davis, L. Porter,* Carnegie Mellon University

Gallium oxide ($Ga_2O_3$) is an ultra-wide bandgap semiconductor of interest for electronics that can operate in extreme conditions, such as high power, high temperature and radiation exposure. β-$Ga_2O_3$ is thermodynamically stable at atmospheric conditions up to its melting point and is the phase produced in melt-grown, single-crystal substrates.However, epitaxial films of metastable polymorphs of $Ga_2O_3$ are also of interest because they possess unique properties – such as piezoelectricity, ferroelectricity, or ferromagnetism – that could lead to new types of heterostructure devices.We report here the growth and characterization of both mixed-phase and phase-pure epitaxial films of each of the metastable polymorphs: κ(ε) and γ using metalorganic chemical vapor deposition (MOCVD); and α, κ and γ using halide vapor phase epitaxy (HVPE). The effect of variables, such as substrate temperature, will be reported, as will the use of different substrates / orientations to produce phase-pure epitaxial films of α-, κ-, and γ-$Ga_2O_3$ in the same grown runs.The microstructure, composition, and morphology of the films and film/substrate interfaces were characterized using x-ray diffraction (XRD) θ-2ωscans, rocking curves, and ϕ scans; scanning electron microscopy (SEM); and high-resolution cross-section transmission electron microscopy (TEM) with energy dispersive x-ray (EDX) analysis.

11:00am **EM+TF-ThM-10 AlGaN/GaN HEMTs with Submicron Gates for High-Frequency Operation in Harsh Space Environments***, **Isabel Harrysson Rodrigues**, M. Rais-Zadeh,* Jet Propulsion Laboratory, California Institute of Technology

Indium aluminum nitride/gallium nitride high electron mobility transistors (AlGaN/GaN HEMTs) offer excellent properties such as high electron mobility and wide bandgap, making them ideal for high-frequency and high-power applications, in harsh environments. The wide band gap of the AlGaN/GaN heterostructure infers inherent radiation tolerance compared to traditional Si microelectronics. Owing to the advantageous two-dimensional electron gas, AlGaN/GaN HEMTs can provide increased sensitivity, fast response time, and low noise levels while withstanding extreme temperatures, radiation, and vibrations found in space. Its robustness and reliability make it ideal for long-term missions, ensuring accurate and uninterrupted sensing and detection in difficult space conditions. DC operation has been achieved for AlGaN/GaN HEMTs with various larger gate dimensions. Separate studies have shown successful operation of AlGaN/GaN HEMTs at high temperatures reaching 1000°C. However, in achieving high-frequency operation, the device geometry must be size-optimized from large-area to scaled gate lengths in the submicron regime. RF analysis at both room temperature and high temperature is a necessary next step to determine the merits of these devices for extreme environment applications where these devices have advantages over other semiconductor technologies. In this work, the performance of AlGaN/GaN HEMTs are optimized by reducing the gate length toward high-frequency operation in harsh space environments, with specific applications in on-board rover communications and for in situ readout of sensor data. The geometry schemes were chosen during the design phase, and the microfabrication process, metallization, and passivation materials were carefully evaluated. These results are promising for further testing, e.g., radiation tolerance, high temperatures, and monolithic circuit Integration. The presented devices have an advantage over traditional heterogeneous integration strategies for GaN devices which requires silicon ASICs that, without cooling, cannot operate in high-temperature environments.

11:20am **EM+TF-ThM-11 Selected-Area P-Type Doping of GaN Using Focused-Ion Beams***, **Sam Frisone**,* University of Michigan*; M. Titze, A. Katzenmeyer,* Sandia National Lab*; B. Li,* Yale University*; A. Flores,* Sandia National Lab*; Y. Wang,* Los Alamos National Laboratory*; R. Goldman,* University of Michigan*; E. Biejelec,* Sandia National Lab*; J. Han,* Yale University

Due to their potential for high breakdown voltage and low on-resistance, GaN-based electronic devices are promising for high-power and high-frequency electronics. Vertical GaN p-i-n devices are expected to offer improved thermal management and reduced leakage current in comparison to their lateral counterparts; however, typical etching and regrowth processes introduce interfacial impurities that limit control of dopant profiles. Thus, a strategy for both vertical and lateral dopant selectivity, without the need for etching and regrowth, is essential for the development of high-quality vertical GaN devices. Here, we report on Mg doping using a liquid-metal ion source (LMIS) in a mass-selecting focused-ion-beam (FIB) column. For these studies, an unintentionally doped (UID) 3.6µm GaN layer is grown by metalorganic chemical vapor deposition on n-type GaN. In preparation for FIB implantation, the UID GaN layer was patterned with an array of Au/Ti markers. Checkerboard patterns consisting of alternating 70x70 and 50x50µm squares, with and without Mg FIB implantation, were prepared using a Mg-doped AuSi eutectic as the LMIS. The ion energies were set to 70keV, resulting in a most probable ion implantation depth of 70nm; seven ion fluences ranging from $10^{12}$-$10^{15}$ $cm^{-2}$, corresponding to Mg concentrations of $10^{16}$-$10^{19}$ $cm^{-3}$, were used. To examine the activation of Mg dopants in GaN, we compare the pristine and implanted regions before and after rapid-thermal processing (RTP). A distinct checkerboard pattern is observed in secondary electron (SE) images, with reduced SE image intensities in the implanted regions compared to the pristine regions. Following removal of the Au/Ti markers and 30 seconds of RTP at 1100°C, the checkerboard pattern is reduced in the vicinity of the four lowest ion fluences. For all regions, cathodoluminescence (CL) spectroscopy reveals GaN near-band edge (NBE) emissions at 3.4eV. The intensity of NBE emission is highest in the pristine regions, especially those in the vicinity of the two lowest ion fluences. Furthermore, in pristine regions adjacent to the two lowest ion fluences we observe CL emissions at 2.85eV and 2.2eV. As discussed in [1], we attribute these emissions to impurity-related donor-acceptor pairs and yellow luminescence, respectively. The reduced SE image intensity and limited CL emission in the vicinity of the highest ion fluences suggest incomplete Mg dopant activation. The influence of additional RTP on the dopant activation will be discussed. [1] 10.1016/j.nanoen.2022.107689

11:40am **EM+TF-ThM-12 Epitaxial Growth and Characterization of High ScN Fraction ScAlN on NbN and SiC***, **Matthew Hardy**, S. Katzer, A. Lang, E. Jin, N. Nepal, B. Downey, V. Gokhale, V. Wheeler,* U.S. Naval Research Laboratory

ScAlN thin films have attracted significant attention due to their factor of five increase in piezoresponse over AlN for $Sc_{0.43}Al_{0.57}N$. Integration of metallic epitaxial NbN with ScAlN using molecular beam epitaxy (MBE) enables a pathway towards a highly conductive lower electrode while preserving high crystal quality even in relatively thin ScAlN films suitable for use at or above X-band frequencies. Maintaining phase-pure and high crystal quality $Sc_xAl_{1-x}N$ at high *x* is critical to improve resonator bandwidth and reduce insertion loss.

In this work, we show the importance of the ScAlN nucleation layer to the final crystal quality and anomalously oriented grain (AOG) density of MBE-grown ScAlN films on SiC and NbN/SiC. Starting the ScAlN growth with a $Sc_{0.32}Al_{0.68}N$ layer can suppress the rock-salt ScAlN material at the nucleation interface, as seen by reflection high-energy electron diffraction (RHEED) and transmission electron diffraction (TEM). Nucleation using a linear composition grade from $Sc_{0.32}Al_{0.68}N$ to $Sc_{0.40}Al_{0.60}N$ over 100 nm leads to further improvements in the RHEED pattern, including a narrowing of the spots early in the growth, as well as elimination of remaining ring-like character in the final RHEED pattern after an additional 40 nm of growth, resulting in an X-ray diffraction (XRD) FWHM as low as 1.22° for ScAlN films grown on SiC. TEM shows near elimination of cubic grains that otherwise form in the initial layers of the $Sc_{0.40}Al_{0.60}N$. The grade thickness can be reduced to 25 nm (with the remaining 125 nm $Sc_{0.40}Al_{0.60}N$) without degrading the XRD FWHM or RHEED pattern, increasing the average ScN fraction from 0.373 to 0.393. Finally, a 500-nm-total-thickness sample (100 nm $Sc_{0.32}Al_{0.68}N \rightarrow Sc_{0.40}Al_{0.60}N$, 400 nm $Sc_{0.40}Al_{0.60}N$) was grown to show the impact of defect annihilation in thicker films, resulting in a reduction of XRD FWHM to 0.89°. The improved layer initiation shows that more gradual changes in surface energy and strain reduces the nucleation of undesirable cubic grains, and may point to a general strategy for elimination of anomalous grains in high ScN fraction ScAlN.

Employing a similar growth approach and using a novel two-step AlN interlayer enables integration of ScAlN on an NbN epitaxial metal lower electrode. Growth conditions to first encapsulate the NbN layer, and then provide a smooth surface for ScAlN nucleation are critical to minimize degradation in XRD FWHM or AOG density. ScAlN on NbN structures enable characterization of the ScAlN dielectric constant and electromechanical coupling coefficient ($k_t^2$). A dielectric constant of 25 and $k_t^2$ of 27% was extracted for $Sc_{0.32}Al_{0.68}N$ from a $Sc_{0.32}Al_{0.68}N$/AlN/NbN/SiC sample.

12:00pm **EM+TF-ThM-13 Novel Graphene and SiC Epitaxy to Enable Film Transfer**, ***Daniel Pennachio***, *J. Hajzus, A. Lang,* US Naval Research Laboratory; *R. Stroud,* Former employee of US Naval Research Laboratory; *R. Myers-Ward,* US Naval Research Laboratory

Remote epitaxy (RE) is a promising technique for epitaxial film transfer that utilizes graphene as a release layer [1]. Graphene grown on SiC(0001) substrates through Si sublimation or through propane chemical vapor deposition (CVD) is an ideal platform for remote epitaxy of wide bandgap (WBG) semiconductors as there is no need for a graphene transfer step, mitigating contamination or defects that can complicate the remote epitaxy process. In addition, the graphene/SiC materials system is compatible with commercially-viable WBG semiconductor growth and processing, making it a suitable choice for scalable future development. A challenge to utilizing SiC is that CVD growth is typically conducted using high-temperature hydrogen-based chemistries that could damage or remove graphene. This study investigates the effect of alternative low-$H_2$ CVD growth conditions on SiC/graphene/SiC(0001) remote epitaxy that may reduce damage to the graphene barrier. In addition, graphene preparation and associated surface morphology is varied to explore its effect on SiC epilayer formation.

For this work, the effects of Ar:$H_2$ process gas flow ratio, growth precursor C/Si ratio, and growth temperature on hot-wall CVD SiC RE crystalline quality were investigated. Both semi-insulating nominally on-axis 6H-SiC(0001) and n-type 4° off-axis 4H-SiC(0001) substrates were used to produce different surface morphologies and graphene layer numbers. Nomarski optical microscopy, scanning electron microscopy, and atomic force microscopy found CVD deposition at 1620°C with Ar/$H_2$ ratios <20/5 slm, and C/Si ratios <1.55 to have the smoothest surface morphology and fewest polytype inclusions. Substrates with offcuts <0.1° from SiC(0001) exhibited lower epilayer macrostep density but showed evidence of polytype impurities and 3D growth at C/Si ratios > 1.0. RE on EG/4H-SiC(0001) substrates with a 4° off-cut from SiC[0001] had a wider parameter range resulting in single-crystalline growth compared to growth on the nominally on-axis substrates despite growth of >1 monolayer EG on these substrates. This study found smooth, single-crystalline polytype-pure SiC(0001) epilayers on EG substrates could be grown using predominantly Ar carrier gas, with $H_2$ concentrations as low as ~2%. Through this study, optimal SiC RE growth conditions are suggested for a balance of EG survivability and SiC film morphology.

[1] Kim, Y., Cruz, S., Lee, K. et al. Nature 544, 340–343 (2017).

## Magnetic Interfaces and Nanostructures Division
## Room B110-112 - Session MI+2D+TF-ThM

### 2D Magnetism and Superconductivity

**Moderators: Markus Donath**, Muenster University, Germany, **Valeria Lauter**, Oak Ridge National Laboratory

8:00am **MI+2D+TF-ThM-1 Heterostructures for Tunneling and Point-Contact Spectroscopy of Two-Dimensional Superconductors**, ***Benjamin Hunt***, *Q. Cao,* Carnegie Mellon University; *E. Telford, C. Dean,* Columbia University **INVITED**

Tunneling spectroscopy is an indispensable experimental tool of modern condensed matter physics. Vertical planar tunneling, which uses a fixed-width tunnel barrier, offers advantages over other spectroscopic tools such as scanning tunneling microscopy (STM). One such advantage is the ability to tunnel in reorientable and very large (≥40 T) magnetic fields at dilution refrigerator temperatures (≤30 mK), a capability that has application in, for example, determining the order parameter symmetry of novel two-dimensional (2D) superconductors. We demonstrate a novel vertical planar tunneling architecture for van der Waals heterostructures based on via contacts, namely, metallic contacts embedded into through-holes in hexagonal boron nitride (hBN). This via-based architecture overcomes limitations of other planar tunneling designs and produces high-quality, ultra-clean tunneling structures from a variety of 2D materials. The physical area of our via-based tunnel contacts is limited only by nanofabrication techniques, and we demonstrate a crossover from diffusive to point contacts in the small-contact-area limit by studying the spectrum of a 2D superconductor, $NbSe_2$. We show that our tunneling technique may enable highly-sought measurements of newly-discovered 2D superconductors such as monolayer 1T'-$WTe_2$, rhombohedral trilayer graphene, twisted trilayer graphene, and twisted bilayer BSCCO.

8:40am **MI+2D+TF-ThM-3 Ghost States and Topography Inversion in 2D Materials**, ***Mina Yoon***, Oak Ridge National Laboratory, USA **INVITED**

In this talk, I will discuss the challenges associated with characterizing the surface structures of single-atom thick materials, such as graphene and boron nitride, on metallic substrates or the surface of bulk systems, including quantum topological Kagome systems, using scanning tunneling microscopy (STM). The understanding of fundamental properties of two-dimensional (2D) materials and surface properties depends critically on the presence of "ghost" states, which arise due to different decay lengths in the wave function of the underlying layers and surfaces.

The existence of these ghost states, in conjunction with long-lived substrate states or underlying layers, plays a crucial role in interpreting and understanding the surface properties of 2D materials. These ghost states can originate from various sources, such as the bulk or the substrate, and can even arise from the boundary on the opposite side. The appearance of ghost states due to different decay lengths leads to unexpected results in surface structure measurements, including the intriguing phenomenon of topography inversion. Topography inversion refers to the counterintuitive result where the observed topography in STM images is opposite to the expected atomic geometry, as discussed in our recent study [1,2]. This inversion occurs as a consequence of the pervasive substrate states overshadowing the intrinsic states of the 2D materials. As a result, the measurement of the intrinsic properties of 2D materials becomes complicated, with the ghost and substrate states dominating the observed topography. To address these challenges, we employ a combination of first-principles density functional theory calculations and analytical modeling. Through our investigations, we demonstrate the critical role played by these ubiquitous substrate and ghost states in the observed topography inversion in STM images. By unraveling the influence of these states on STM measurements, we provide crucial insights for the accurate interpretation of STM topographies of atomically thin materials.

Our findings not only shed light on the phenomenon of topography inversion, but also contribute to the further development of 2D materials in (opto)electronic and quantum applications. Understanding and characterizing the ghost and substrate states is essential to unlock the full potential of 2D materials and enable their use in various technological advancements.

[1] “Spatially resolved on-dimensional boundary states in graphene-hexagonal boron nitride planar heterostructures”, J. Park et al., Nat.Com. 5, 5403 (2014).

[2] “Topography inversion in scanning tunneling microscopy of single-atom-thick materials from penetrating substrate states”, C. Park and M. Yoon, Sci. Reports 12, 7321 (2022).

11:00am **MI+2D+TF-ThM-10 Spatially-Resolved Photoemission Studies of Magnetic Weyl Semimetals**, *S. Sreedhar,* University of California, Davis; *M. Staab, R. Prater,* University of California at Davis; *A. Rossi,* Italian Institute of Technology, Italy; *V. Ivanov,* Lawrence Berkeley Lab; *Z. Shen,* University of California at Davis; *G. Conti,* Lawrence Berkeley Lab; *V. Taufour, S. Savrasov,* University of California at Davis; *S. Nemsak,* Lawrence Berkeley Lab; ***Inna Vishik***, University of California-Davis **INVITED**

$Co_3Sn_2S_2$ is a magnetic Weyl semimetal below its Curie temperature ($T_c$) of 177K. I will discuss spatial and temperature-dependent angle-resolved photoemission spectroscopy (ARPES) and x-ray photoelectron spectroscopy (XPS) studies in this system.Across $T_c$, we observe signatures of a topological phase transition, but also observe changes in bulk bands which are inconsistent with a simple lifting of exchange interactions, suggesting enhanced electronic correlations in the regime without long-range magnetic order.I will also discuss spatial-dependent ARPES and XPS data which quantify the characteristic differences between Sn- and S-terminated surfaces, with relevance for interpreting surface-dominated phenomena.

11:40am **MI+2D+TF-ThM-12 High-Temperature Superconductor FeSe Films Enabled Through Temperature and Flux Ratio Control***, **Maria Hilse**, H. Yi, C. Chang, N. Samarth,* The Pennsylvania State University*; R. Engel-Herbert,* Paul-Drude-Institut für Festkörperelektronik, Germany

FeSe, a bulk superconductor with a $T_C$ of 9 K has attracted a high level of attention since a skyrocketing boost in TC was reported for a single unit cell (UC) layer of FeSe grown on SrTiO3(001) by molecular beam epitaxy (MBE) to as high as 100 K. FeSe-SrTiO3 heterostructures have since been fabricated by many groups but the record TC proved difficult to reproduce and thus the mechanism behind it remains concealed. After extensive work in the past, the field appears to agree on certain key "ingredients" in the heterostructure sample preparation that are believed essential for the boost in TC. Those are; 1. an ultra-clean substrate surface of a double $TiO_{22}$ termination realized by a chemical and thermal *ex-situ* and/or thermal *in-situ* substrate preparation; 2. ultra-thin – one UC thickness – limit of FeSe; 3. a high number of Se vacancies in the FeSe film ensured through post-growth annealing steps in ultra-high vacuum (UHV) for several hours; 4. followed by a capping layer growth protecting FeSe against oxidation during *ex-situ* characterization.

We present our findings on FeSe thin film growth by MBE and present a roadmap for high-$T_C$ – 222 % higher than the reported bulk value in *ex-situ* transport measurements – circumventing above mentioned steps 1, 2, and 3 by simple *in-situ* Se/Fe flux ratio and temperature control during FeSe growth. FeSe films of 20-UC-thickness grown at varying temperatures and Se/Fe flux ratios and the structural and morphological properties of the obtained uncapped FeSe films were analyzed. The morphology of the films showed a sensitive dependence on the growth temperature and flux ratio spanning from perfectly smooth and continuous films with atomic terraces at 450 °C growth temperature and a low flux ratio of 2.5 to exclusively disconnected island growth of large height but smooth top surfaces at lower temperatures and/or higher flux ratios. Surprisingly, the tetragonal P4/nmm crystal structure of beta-FeSe was maintained for all investigated films and the *in-situ* observed diffraction pattern in reflection high energy diffraction also maintained the streaky pattern characteristic for smooth FeSe films even for the samples with the most pronounced island growth resulting in a root mean square atomic force microscopy roughness of more than 18 nm. Smaller flux ratios than 2.5 resulted in mixed – beta-FeSe/elemental Fe – phase samples. FeSe films grown under optimized conditions at 450 °C and a flux ratio of 2.5 (but without any post-growth UHV anneal) and capped with the commonly used FeTe (300 °C) and elemental Te (room temperature) layers yielded superconducting onset temperatures of about 30 K and a TC of 20 K.

12:00pm **MI+2D+TF-ThM-13 Unraveling Picosecond Dynamic Material Processes on the Mesoscale by X-Ray Microscopy***, **Thomas Feggeler**,* University of California, Berkeley*; J. Lill, D. Guenzing, R. Meckenstock, D. Spoddig, B. Zingsem,* University of Duisburg-Essen, Germany*; M. Efremova,* Eindhoven University of Technology, Netherlands*; S. Pile, T. Schaffers,* Johannes Kepler University, Austria*; S. Wintz,* Max Planck Institute for Intelligent Systems, Germany*; M. Weigand,* Helmholtz Center Berlin, Germany*; A. Ney,* Johannes Kepler University, Austria*; M. Farle, H. Wende, K. Ollefs,* University of Duisburg-Essen, Germany*; D. Shapiro,* Lawrence Berkeley National Laboratory*; R. Falcone,* University of California, Berkeley*; H. Ohldag,* Lawrence Berkeley National Laboratory

Dynamic processes govern a multitude of phenomena in physical, chemical and material sciences. Time- and spatially resolved element-specific monitoring of such processes is crucial in the understanding of phenomena like magnetization dynamics, battery charging and discharging, and phase transitions of several kinds. Time-Resolved Scanning Transmission X-ray Microscopy (TR-STXM) [1] is a versatile tool fulfilling these demands on the mesoscopic scale, offering element-specific observations with sub 50 nm spatial resolution and picosecond time sampling. By introducing a phased-locked-loop excitation synchronization scheme, TR-STXM also allows to sample dynamics originating from continuous wave excitations. This presentation introduces the TR-STXM technique and its principle of operation, and the setup developed at the Advanced Light Source at Lawrence Berkeley National Laboratory. The presentation is complemented by examples of dynamic magnetic measurements, which allow for local monitoring of magnetization dynamics in fields such as spintronics, magnonics, biomedical and energy related applications. Here we demonstrate TR-STXM results on Py/Co microstructures [2], Py stripe ensembles [3] and magnetite nanoparticle chains inside magnetotactic bacteria *Magnetospirillum Magnetotacticum* [4,5], showcasing localized uniform and non-uniform resonant magnetic responses, supplemented by micromagnetic simulations in good agreement.

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[1] T. Feggeler, A. Levitan, et al. J. Electron Spectrosc. Relat. Phenom. 2023. **267**: 147381.

[2] T. Feggeler, R. Meckenstock, et al. *Sci. Rep.*2022, **12**:18724.

[3] S. Pile, T. Feggeler, et al. *Appl. Phys. Lett.* 2020, **116**(7): 072401.

[4] T. Feggeler, R. Meckenstock, et al. *Phys. Rev. Res.* 2021, **3**(3): 033036.

[5] T. Feggeler, J. Lill, et al. *New J. Phys.* 2023, **25**(4): 043010.

## Surface Science Division
## Room D136 - Session SS2+AS+TF-ThM

### Thin Film Surface Chemistry

**Moderators: Eric Altman**, Yale University, **Zdenek Jakub**, CEITEC

11:00am **SS2+AS+TF-ThM-10 Ultrafast Exciton Dynamics of Phthalocyanine Films with Different Molecular Orientations***, **Hui Ung Hwang**, S. Kim, J. Kim,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea

Organic semiconductors (OSCs) have enormous potential in advanced optoelectronic devices, such as organic light-emitting diodes and organic solar cells. To achieve higher performance and functional versatility for these applications, a deeper understanding of the generation and relaxation mechanism of photoexcited excitons in molecular films is essential. In this study, we investigate the ultrafast dynamics of excitons in planar-shape molecules of phthalocyanines (Pc), which can adopt a lying-down or standing-up orientation depending on the substrate used, as shown in Fig. 1.[1] The distinct ionization-energy difference of more than 0.5 eV measured by photoelectron spectroscopy confirms that the Pc thin film on HOPG substrate grows in the lying-down direction and the Pc on ITO grows in the standing-up direction. Exciton energy and population from the molecules with these two different orientations are measured by time-resolved two-photon photoemission (tr-2PPE) with time resolution of 85 fs.In this measurement, we first pump a singlet exciton population in the Pc with a femtosecond pulse and probe its evolution as a function of delay time with an ultraviolet pulse. Singlet excitons have a variety of relaxation pathways, including diffusion between molecules, intersystem crossing to triplet states, and dissociation at the interface with metals. The tr-2PPE experiments show that the exciton relaxtion in Pc molecules with the standing-up geometry is dominated by exciton diffusionin the direction perpendicular to the substrate, resulting in relatively slow exciton relaxation. However, for Pc molecules in the lying-down geometry, the excitons undergo faster transfer to the metal interface due to aligned π-orbital overlap with neighboring molecules toward the substrate. These results imply that OSCs exhibit different exciton relaxtion dynamics depending on their orientation and suggest that for planar molecules like Pc, the lying-down geometry is more favorable for exciton transfer and dissociation to the metal interface.

11:20am **SS2+AS+TF-ThM-11 Understanding the Surface Chemistry of Oxide Thin Films by Isotope Labeling***, **Yingge Du**,* Pacific Northwest National Laboratory **INVITED**

Isotopic engineering is developing into a key approach to study the nucleation, diffusion, phase transition, and reaction of materials at an atomic level to reveal transport pathways, kinetics, and working/failure mechanisms of functional materials and devices. Understanding these phenomena leads to deeper insights into relevant physical processes, such as the transport and intercalation of ions in energy conversion and storage devices, and the role of active sites and supports during heterogeneous catalytic reactions. Likewise, isotopic engineering is being pursued as a means of modifying functionality to enable future technological applications. In this talk, I will present our work employing isotope labeling (e.g., $^{18}O$ and $^{2}H$) during complex oxide thin films' (e.g., $WO_3$, $SrFeO_{2.5}$, and $La_{1-x}Sr_xFeO_3$) synthesis and post-growth processing to track the distribution and redistribution of the isotope tracers. Isotope-resolved analysis techniques with high spatial resolution, such as time-of-flight secondary ion mass spectrometry and atom probe tomography, facilitate the accurate quantification of isotopic placement and concentration in well-defined heterostructures with precisely positioned, isotope-enriched layers. These studies allow us to better understand the growth mechanisms, surface chemistry, and elemental diffusion under working and extreme conditions.

12:00pm **SS2+AS+TF-ThM-13 Interaction of Self-Assembled Monolayers with Atomic Oxygen During Area-Selective Atomic Layer Deposition***, **Silvia Armini**,* IMEC Belgium*; A. Brady Boyd,* School of Physical Sciences, Dublin City University, Ireland

Utilising self-assembled monolayers (SAMs) to achieve area-selective atomic layer deposition (AS-ALD) as an approach to bottom-up nanofabrication has recently gained significant attention from the nanoelectronics industry.

With the continued downscaling of feature sizes, top-down processing can no longer reach the challenging demands of the industry which requires conformal coating of high aspect ratio vias and a reduction in misalignment errors in multi-layered devices. In this work we attempt to imitate the effects of the ALD oxidation pulse experienced by the SAMs during the AS-ALD process by exposing two SAMs of different chain lengths and different functional groups, (3-trimethoxysilylpropyl)diethylenetriamine (DETA) and octadecyltrimethoxysilane (OTMS), to numerous controlled in-vacuo atomic oxygen exposures with subsequent characterisation by X-ray photoelectron spectroscopy (XPS). We monitor the sequential removal of the deposited monolayers with each successive atomic oxygen exposure for both SAMs. The etch rate is observed to be distinct for the different SAMs, the amino-terminated short chain DETA SAM reveals a linear etch rate while the longer chain OTMS SAM reveals an exponential etch rate. The results presented provide some insights into what characteristics are important for choosing the correct SAM for AS-ALD applications.

### Thin Film Division
### Room A105 - Session TF-ThM

### Creating Organic-Inorganic Hybrid Materials

**Moderators: Devika Choudhury**, ASM, **Robin Rodriguez**, Jet Propulsion Laboratory

8:00am **TF-ThM-1 Functional Ceramic Heterostructures via Vapor and Liquid Phase Infiltration of Polymer Templates***, **Diana Berman**,* University of North Texas **INVITED**

Robust and efficient process for synthesis of various composition inorganic coatings with controlled nanoporosity and structure is highly desirable for design of efficient catalytic, purification, and detection systems. Recently, infiltration of a nanoporous polymer template with inorganic precursors using sequential infiltration synthesis with inorganic vapor precursors followed by oxidative annealing was proposed as a new and efficient approach to create porous inorganic structures with tunable porosity and composition. The major limitations of the original water-based thermal sequential infiltration synthesis, though, are the thickness of the patterned structure being limited by vapor penetration depth of the precursors into the polymer template and the resulting material selection being restricted by the availability of high vapor pressure precursors. Here, we propose a swelling-based modification to the polymer infiltration process that allows to overcome these limitations. We summarize the basics of the multi-step infiltration approach, the structure and properties of the resulting materials, and their functional potential for practical applications. We report ultra-high accessibility of the pores when porous films are prepared via the polymer swelling-based infiltration synthesis (SBI). Using a quartz crystal microbalance (QCM) technique, we demonstrate increased solvent absorbing capabilities of highly porous ceramic films as a result of high interconnectivity of the pores in such structures. Our results show that the approach can be been extended toward preparing conformal coatings, freestanding membranes, and powders consisting of metal or metal oxide nanoparticles embedded in a porous oxide matrix.

8:40am **TF-ThM-3 Effect of Polymer Templates on Nanoporous Inorganic Coatings Synthesized by Polymer Infiltration***, **Khalil Omotosho**, D. Berman,* University of North Texas

Polymer templates infiltration synthesis of all-inorganic metal oxide architectures provides control over their thickness, porosity, and composition**.** In this study, we provide insights into the synthesis of nanoporous zinc oxide films as a model system via infiltration of polymers such as polymer of intrinsic microporosity (PIM-1) and representative of the block-copolymers family (polystyrene-polyvinyl pyridine block copolymer) that have different mechanisms of interaction with metal oxide precursors. We investigated the polymer infiltration process with both gas (diethyl zinc, DEZ, and water vapors) and solution (zinc acetylacetonate, Zn(acac)2, dissolved in ethanol) phase precursors. We systematically studied the effect of polymer template and the form of the metal oxide precursors on the properties of synthesized metal oxide thin coatings using the quartz crystal microbalance (QCM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses. Our study prove that the infiltration of polymer templates can be efficiently achieved using both gas phase and solution phase precursors. Furthermore, we show that the crystallinity of the synthesized ZnO films is mainly affected by the state of the precursor (gas or solution phase) and is independent of the polymer template type. In turn, the polymer type affects the surface termination of ZnO films. In addition, our findings demonstrate that the surface of porous ZnO coatings synthesized with BCP (here PS-P4VP) is more accessible than the surface of ZnO synthesized with PIM; however, despite the lower surface accessibility for ethanol molecules, ZnO synthesized via infiltration of PIM-1 with solution-phase precursors demonstrates the largest change in resistivity upon its exposure to ethanol vapor at room temperature.

9:00am **TF-ThM-4 Alkylation of Esters by Ticl$_4$ Vapor Phase Infiltration (VPI) and the Resulting Chemical and Thermophysical Properties of the Hybrid Materials***, **Shuaib Balogun**,* Georgia Institute of Technology, USA*; S. Yim,* Georgia Institute of Technology*; B. Jean, T. Yom,* Georgia Institute of Technology, USA*; A. Steiner,* Sandia National Laboratories*; M. Losego,* Georgia Institute of Technology, USA

Vapor phase infiltration (VPI) is a post-processing modification technique used to imbue inorganic materials into polymers to create organic-inorganic hybrid materials with new properties. In VPI, inorganic material can become entrapped by reaction with the polymer functional group, by reacting with a co-reactant or by physical entrapment due to loss of volatility. While several VPI precursor-polymer chemistries have been explored and their chemical mechanisms have been noted, a lack of chemical intuition remains for fully understanding the chemical mechanisms that govern VPI processes. This study seeks to continue to build this knowledge by examining the chemical reaction mechanisms that occur during $TiCl_4$ infiltration into esters namely PMMA and PLA. In this research, the poly-methyl methacrylate / $TiO_x$and poly-lactic acid / $TiO_x$ hybrid materials are prepared using VPI. The chemical states of the atoms in the polymerspre &post infiltration are studied using x-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared (FTIR) spectroscopy. The chemical mechanism of infiltration appears to occur via an acid catalyzed SN2-alkylation reaction. As infiltration occurs in PMMA, there is an increase loss of methyl groups in the PMMA ester, whereas, in PLA there is an observed cleavage of the main chain at the methoxy bond, resulting in degradation of the polymer. The kinetics of this reaction and consequently the $TiCl_4$ infiltration increases with both VPI process temperature and $TiCl_4$ exposure time. Interestingly, the resulting hybrid materials offer new properties due to the reaction with $TiCl_4$. Increased titanium loading leads to up to 100% chemical stability in PMMA. Additionally, films infiltrated with up to 6% Ti have a 50 % and 70 % reduction in coefficients of thermal expansion (CTE) below and above $T_g$ respectively. CTE continually reduces with increased titanium loading. In this talk, we will discuss how these chemical and physical changes could be used for various applications.

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9:20am **TF-ThM-5 Free and Simple Simulations of Vapor-Phase Infiltration Process Kinetics Using Google Colab**, ***Mark Losego***, Georgia Institute of Technology

Vapor-phase infiltration (VPI) is a post-polymerization chemical modification technique that exposes organic polymers to gas-phase inorganic precursors that sorb and become entrapped within the polymer to create organic-inorganic hybrid materials. The process kinetics for VPI are a complicated convolution of sorption, non-Fickian diffusion, and reaction processes. We recently introduced a reaction-diffusion model to capture many of the VPI process kinetics phenomena, and recent experimental work has demonstrated the validity of this model's process predictions. This talk will introduce our publication of this model on Google Colab, a free, web-based environment for running Python codes without any need for installing or configuring a Python platform on your personal computer. This web-based platform makes it free and simple for anyone to now run our reaction-diffusion VPI process simulation model. This talk will include how to access and run these simulations, defining the important model variables as well as how they relate to physical process parameters. Example simulations will be run and then compared to experimental data we and others have published to demonstrate how this reaction-diffusion model can be used to interpret and help predict VPI process phenomena.

9:40am **TF-ThM-6 High-Throughput Molecular Layer Deposition for the Discovery of Organic-Inorganic EUV Photoresists**, ***Duncan Reece***, University of Washington, UK; *E. Crum*, University of Washington; *Y. Choe*, University of Washington, Republic of Korea; *D. Bergsman*, University of Washington

Continued progress in information and communication technologies requires sustained innovations in memory and storage devices' architecture and production processes. However, scaling technology to sub-5nm features may require Extreme Ultraviolet (EUV) sources, which necessitates new photoresist materials that are highly adsorbing of EUV while meeting the formal requirements of a photoresist. Such materials must also be environmentally conscious and abundantly available. One potential solution is a hybrid inorganic-organic thin film produced through molecular layer deposition (MLD), the organic equivalent of atomic layer deposition. However, the discovery process for new MLD materials is typically slow and needs improvement.

Here, we present a high-throughput multi-chamber MLD reactor that can quickly screen hybrid MLD processes for their EUV compatibility. In the reactor, films are deposited with one shared inorganic reactant and six independent counter-reactants in parallel, simultaneously producing multiple potential resist materials. In this work, inorganic reactants consisted of highly and non-highly EUV absorbing metals, like diethyl zinc, trimethylaluminum, and tin(IV) t-butoxide, while the organic counter-reactants included ethylene glycol, 1,2,4-trihydroxybenzene, 1,5-hexadiene-3,4-diol, 2-butyne-1,4-diol, cis-2-butene, and 2-methylenepropane-1,3-diol. The resulting films were tested for solvent, developer, and etchant stability before and after exposure to deep UV, electron beam, or X-rays. Promising resists were further characterized and could be used for patterning. Results showed that the inorganic and organic linkers exhibited a range of stabilities and light sensitivities, which could be used to optimize the performance of thin film EUV resists. In addition, this method provides a much faster screening process for potential photoresist materials in a scalable system, allowing for the continued improvement of processor efficiency and progress.

11:00am **TF-ThM-10 Understanding the Physicochemical Properties and Structural Evolution of Sequential Infiltration Synthesis Derived Indium Oxyhydroxide Clusters for $CO_2$ Absorption**, ***Thabiso Kunene***, *A. Martinson*, Argonne National Laboratory

Sequential infiltration synthesis (SIS) is a versatile route to hybrid organic-inorganic materials. While SIS is inspired ALD and often utilizes the same precursors and tools, SIS requires infiltration of these vapor phase precursors into a polymer film that includes reversible or irreversible interactions with polymer functional groups. In a second step, the infiltration of an oxygen source (e.g. $H_2O$) affords reaction to form an inorganic oxyhydroxide that may be chemisorbed at the functional site or physically trapped within the polymer matrix. However, the atomic structure of the first few-atom clusters and the evolution of local coordination environment remain unresolved. Therefore, a more fundamental and detailed understanding of the growth mechanism and structural evolution of indium clusters during SIS is necessary to inform the synthetic design of target clusters for various applications. This talk will discuss the experimental and theoretical efforts to elucidate the growth and structure of indium oxyhydroxide clusters from trimethyl indium (TMIn) during SIS in PMMA polymers. FTIR, UV-vis and DFT calculations suggest the existence of octahedrally coordinated $[In]^{3+}$ species where water ligands complete the coordination sphere. The spectroscopic observations also indicate that the weak adducts formed between trimethyl indium precursor and the Lewis basic carbonyl and ester groups in PMMA are central to the oxyhydroxide growth pathways during SIS. Considering the traditional, solution phase organometallic properties and chemistry of trimethyl indium, we demonstrate a link between solution phase organometallic synthesis and the vapor phase SIS process. DFT calculations and In K-edge EXAFS with PDF analysis suggest the formation of dimeric indium oxyhydroxide species in the very first SIS cycle which is driven by the hydrolysis pathways of TMIn. The talk will also present refined SIS process conditions in which nucleation is only feasible in the first SIS cycle, in order to favor only indium oxyhydroxide cluster growth in subsequent cycles. Furthermore, the nature of SIS-derived $InO_xH_y(H_2O)_z$ clusters as a function size (i.e., SIS cycle number) is examined by vibrational and UV-vis absorption signatures and compared to simulated spectra from DFT simulations. The SIS grown indium oxyhydroxide in PMMA presents opportunities to improve the $CO_2$ absorption capacity and gas selectivity of inexpensive polymers. The SIS-grown clusters provide a platform for use as a model system to study indium (oxy)hydroxide surface reactivity towards environmentally important transformations such as $CO_2$ capture and conversion.

11:20am **TF-ThM-11 Optimizing Aluminum Oxyhydroxide Vapor Phase Infiltration for the Vapor Phase Mordanting of Natural Dyes to Polyester Fabrics**, *M. Losego*, ***Nicole McClelland***, *E. McGuinness*, Georgia Institute of Technology

Industrial textile dyeing and finishing processes are a significant environmental concern producing large quantities of wastewater that require significant treatment to remove unused synthetic chemicals. Polyester fabrics in particular utilize high temperatures and chemical carrier agents in their dyeing processes. In this work, we present a method for attaching natural dye materials derived from madder root to polyethylene terephthalate fabrics via the introduction of aluminum oxyhydroxides through vapor phase infiltration. Vapor phase infiltration (VPI) is an emerging polymer modification technique that exposes a polymer to metalorganic precursors that diffuse into the polymer and become entrapped as inorganic clusters. The resulting hybrids have unique properties of both organic and inorganic materials. The VPI process has found significant use in modifying the properties of textile materials including their mechanical and optical properties. In this study, we examine the use of VPI to act as a mordant for natural dye adsorption and how the inorganic loading can be optimized for both dyeability and mechanical performance. Specifically we examine VPI of trimethylaluminum (TMA) into polyethylene terephthalate (PET) fabrics. Inorganic loading is controlled by varying the dose pressure of TMA (moles of TMA) and fabric mass (moles of carbonyl functional group) during VPI and quantified using thermogravimetric analysis (TGA). The resulting hybrid AlOx-PET fabrics have various inorganic loadings from 1 wt% aluminum oxyhydroxide to >20 wt%. The hybrid fabrics were then dyed with alizarin (derived from madder root) and the dye absorbance was quantified with UV-Vis spectroscopy. At low inorganic loadings the strength of color varied with inorganic content, but a steady-state absorbance was reached at around 1.8 wt% inorganic loading. At these low inorganic loadings, hybrid fabrics maintain key mechanical behaviors such as stiffness (as measured by drape) which is seen to increase significantly with additional inorganic loading. This change in texture was quantified using the Cusick drape test to determine shear and bending stiffness changes as a result of higher inorganic loading. By exploring dye saturation curves for different inorganic loadings, kinetics information was gathered to further optimize this dyeing process for industrialization. Overall, using VPI as a vapor phase mordanting process to fix natural dyes to PET fabrics illustrates the impact that even small quantities of the vapor deposited inorganic can have on approving dyeability, highlighting the practical use of these fabrics in the field of textile sustainability.

11:40am **TF-ThM-12 Tuning the Thermal Stability of Vapor Phase Infiltrated Polyacrylonitrile Fabrics**, ***Téa Cook***, *B. Jean*, *E. McGuinness*, *A. Gonzalez*, *M. Losego*, Georgia Institute of Technology

VPI creates hybrid organic-inorganic materials by infiltrating polymers with vapor phase metalorganic precursors that sorb and permeate into the bulk of the polymer. Polyacrylonitrile (PAN) is a polymer previously unexplored in VPI. PAN is used in textiles and filtration, but one of its most common applications is as a precursor to carbon fiber. The metalorganic precursor trimethyl aluminum (TMA) has been shown to form a reversible adduct with the nitrile functional group, which is found on the backbone of PAN polymer chains. The VPI process has been shown to alter numerous properties of materials and, specifically, to reduce the thermal stability of hybrid materials. This work will discuss the role of VPI in modifying the thermal properties of infiltrated PAN fabrics as a function of VPI processing conditions such as exposure time, desorption time, and processing temperature. To explore the effects of inorganic loading on the thermal properties of this system, PAN is infiltrated with TMA and co-reacted with water vapor under varied processing conditions to tune the inorganic in each hybrid PAN/$AlO_x$ fabric. PAN infiltrates with high quantities of inorganic loading that can be tuned from 1% to 17% inorganic by weight, as measured by thermogravimetric analysis (TGA). TGA is further used to study the thermal degradation profile of the hybrid PAN/$AlO_x$, and the kinetics of degradation via the Flynn-Wall-Ozawa analysis method. Through this analysis, the thermal stability of the PAN fabric is shown to decrease after infiltration. The temperatures of the first degradation event in the hybrid fabrics are about 100°C lower than the temperatures of the first degradation event of neat PAN fabric. The activation energy to degrade a PAN/$AlO_x$ hybrid of 7.5 wt % alumina is 67% of that required to degrade a PAN/$AlO_x$ hybrid of 15 wt % alumina. While infiltration reduces the activation energies of each degradation event relative to neat PAN, the change in activation energy varies with loading, suggesting that the thermal stability of hybrid PAN fabrics can be tuned by altering VPI processing conditions which may prove advantageous in the energy-intensive carbon fiber manufacturing process. Overall, this work explores a new VPI system: infiltration of TMA into PAN. Additionally, this work explores the vapor phase modification of PAN fabrics and how processing conditions can be used to tune the inorganic loading of $AlO_x$/PAN hybrid fabrics and their thermal stability.

## Manufacturing Science and Technology Group
## Room C120-122 - Session MS+AP+AS+TF-ThA

### Machine Learning for Microelectronics Manufacturing Process Control

**Moderator: Tina Kaarsberg**, U.S. Department of Energy, Advanced Manufacturing Office

2:20pm **MS+AP+AS+TF-ThA-1 Human-Machine Collaboration for Improving Semiconductor Process Development***, **Keren Kanarik**,* LAM Research **INVITED**

Although chips have been designed by computers for decades, the processes used to manufacture those chips are mostly developed manually – a costly endeavor using highly trained process engineers searching for a combination of tool parameters that produces an acceptable result on the silicon wafer. To assess whether AI could be beneficial in accelerating process engineering innovation and reducing costs, humans and machine algorithms were benchmarked on a virtual high aspect ratio plasma etch process [Kanarik, et al. Nature 616, 707–711 (2023)]. This talk will review results and take a behind-the-scenes look at the study, which showed a “human first, computer last” approach could reach process engineering targets dramatically faster and at half the cost compared to today's approach. While human expertise and domain knowledge are essential for the foreseeable future, the results point us to a path to foundationally change the way processes are developed for manufacturing chips.

3:00pm **MS+AP+AS+TF-ThA-3 Machine Learning-based Atomic Layer Deposition***, **Kanad Basu**,* University of Texas at Dallas **INVITED**

Atomic Layer Deposition (ALD) is dependent on a host of process parameters. These independent parameters can be set to a particular value to create customized recipes for growing films. Although they are considered to significantly influence the ALD process, existing research does not provide a methodology to quantify the impact of these parameters on growth rate and final thickness of a film. Moreover, process parameter-based thickness estimation is a resource- and time-intensive approach, requiring numerous experiments. To address these challenges, we propose a machine learning (ML)-aware strategy that generates "feature importance maps" to determine the most critical process parameters. In our study, we utilize a Veeco® Fiji Gen2 ALD system to grow a CeO2 film. Specifically, our study is associated with 78 process parameters, which include chuck temperatures, chamber temperatures, line temperatures, precursor temperatures, gas flow rates, among others. Our approach utilizes a random forest classifier, which is identifies the top-10 features (parameters) that affect ALD processes. The proposed approach furnishes promising results of up to 99% thickness prediction accuracy using the deduced top-10 features. These results are subsequently validated using in-situ spectroscopic ellipsometry, thereby advocating its effectiveness in generating the feature importance maps. We posit that only these ten features can be utilized to monitor and control ALD processes. Furthermore, in this analysis, we demonstrate the robustness of our solution, which is independent of the type of ALD process considered - standard ALD process or temperature-dependent Temperature-Time-Thickness (TTT) ALD processes. Moreover, by monitoring just ten of the 78 process parameters, the proposed approach has implications of reduced data dimensionality (up to 87.2% reduction in feature space).

3:40pm **MS+AP+AS+TF-ThA-5 Rapid Optimization of Gap-Fill Recipes Using Machine Learning***, **Sebastian Naranjo**, L. Medina de Oliveira, M. Chopra,* Sandbox Semiconductor

Creating and optimizing deposition recipes for nanostructured devices is costly and time-consuming. A major source of defects and device performance degradation is the formation of interior voids. These voids can have a number of causes, including non-uniform deposition rates along the substrate surface due to imperfect seeding and/or mass transport and reaction kinetics factors, as well as critical dimension variations in the initial profile due to imperfections in preceding processing steps. For example, during electroplating, the substrate surface is seeded before material deposition is set to fill the gap. Non-conformal seedings can cause the deposited material to accumulate at different rates and lead to localized voids. Void defects can also occur in highly conformal processes such as atomic layer deposition or chemical vapor deposition due to critical dimension variations such as bowing or tapering in the pre-deposition profile. Current methods for optimizing process performance rely largely on trial and error. Here we present a cost-effective and systematic computational approach to optimize recipe conditions using Sandbox Studio AI, which employs a combination of feature scale modeling and machine learning to rapidly predict process outcomes for a given electroplating system using a minimal number of experiments. In this approach, we first use critical dimension information about the fill height and void defects from a set of experiments to calibrate a feature scale model. We then use the calibrated model to predict critical dimension outcomes for thousands of possible process parameter combinations. These predictions are used to maximize process window stability and provide recipe recommendations that minimize the formation of voids even in the presence of seeding or initial profile imperfections. The showcased approach demonstrates how computational modeling can be used to accelerate learning cycles, improve process quality, and reduce development costs.

## Thin Film Division
## Room A105 - Session TF-ThA

### Organic and Polymeric Materials

**Moderators: Mark Losego**, Georgia Institute of Technology, **Matthias Young**, University of Missouri

2:20pm **TF-ThA-1 Chemical, Biological, and Topological Control Using Chemical Vapor Deposition Polymerization***, **Joerg Lahann**,* University of Michigan, Ann Arbor **INVITED**

Chemical vapor deposition (CVD) polymerization is a highly effective method for producing conformal, defect-free, and precisely adjustable organic thin films. CVD is particularly advantageous for barrier coatings due to its ability to eliminate the environmental, health, and safety risks associated with solvents, while also providing a wide range of post-polymerization modification options. In this presentation, I will discuss the use of poly-p-xylylene (PPX) and its functional derivatives for modifying the chemical and biological properties of surfaces.

Beyond film deposition, anisotropic liquids, such as liquid crystalline (LC) phases, offer an intriguing possibility for templating materials due to their unique long-range alignment and elastic properties. By combining the benefits of CVD with LCs, we were able to synthesize end-attached nanofiber arrays supported by a solid surface using LC-templated CVD polymerization. Upon rinsing the LC template with organic solvents, we observed that the alignment of the resulting nanofibers correlated with the molecular ordering of the LC template. For example, when a nematic LC film with homeotropic (vertical) anchoring to the substrate was used, the resulting nanofibers were straight, whereas a cholesteric LC film induced helical nanofibers. We further manipulated the morphology of the nanofibers to form enantiomerically pure nanohelices by using a precursor with a chiral center.

T.M. Hafshejani, X. Zhong, J. Kim & J. Lahann, Chemical and Topological Control of Surfaces using Functional Parylene Coatings. *Organic Materials* **2023**, (in press).

X. Zhong, R. Jordan, J.-R. Chen, J.E. Raymond, J. Lahann, Mechanistic studies into the area-selectivity of chemical vapor deposition polymerization, *ACS Applied Materials and Interfaces* **2023** (in press).

D. Varadharajan, K. Nayani, C. Zippel, E. Spuling, K.C. Cheng, S. Sarangarajan, S. Roh, J. Kim, V. Trouillet, S. Bräse, N.L. Abbott, J. Lahann, Surfaces decorated with enantiomorphically pure polymer nanohelices via hierarchical chirality transfer across multiple length scales, *Advanced Materials* **2022**, 34, 2108386.

K.C.K. Cheng, M.A. Bedolla-Pantoja, Y.-K. Kim, J.V. Gregory, F. Xie, A. de France, C. Hussal, K. Sun, N.L. Abbott, J. Lahann,Templated Nanofiber Synthesis via Chemical Vapor Polymerization into Liquid Crystalline Films, *Science* **2018**, 362, 804–808.

3:00pm **TF-ThA-3 On the Mechanism of Oxidative Molecular Layer Deposition***, **Matthias Young**, Q. Wyatt, K. Brathwaite, M. Mehregan, M. Ardiansyah, N. Paranamana, K. Brorsen,* University of Missouri

Oxidative molecular layer deposition (oMLD) was first reported in 2014 to form poly(3,4 ethylenedioxythiophene) (PEDOT) thin films using sequential gas-phase exposures of ethylenedioxythiophene (EDOT) monomers and an $MoCl_5$ chemical oxidant. In the last few years, the number of oMLD polymer chemistries has expanded to include at least four additional monomers, with successful demonstrations using at least three different chemical oxidants. These advances have laid the foundation for oMLD to potentially access a large library of polymers and copolymers with molecular-level precision of thickness and composition. However, within this broad landscape it has been unclear which polymer chemistries will and will not be accessible by oMLD. Here, we report on work to establish fundamental insights into the oMLD growth mechanism to guide further oMLD research. We examine oMLD growth using EDOT, pyrrole (Py), paraphenylenediamine (PDA), thiophene (Thi), and furan (Fu) monomers. We specifically identify (a) the importance of surface monomer-oxidant complexes that lead to self-limiting oMLD surface reactions and (b) the necessity for a two-electron chemical oxidant in these reactions, which must have sufficient oxidation strength to oxidize both a surface and a gas-phase monomer to enable oMLD growth. The mechanistic insight from these studies provides a conceptual framework to predict which oMLD chemistries are accessible using current known oxidants and identify opportunities to develop new chemical oxidants to access a broader range of oMLD chemistries.We report on studies testing the limits of these mechanistic principles by examining oMLD of various monomers and oxidants, as well as oMLD of copolymers. Interestingly, we also identify that molecularly assembled copolymer structures formed by oMLD provide improved electrochemical properties over the corresponding isolated homopolymers. The insights from these studies (1) help establish a roadmap for promising future directions in oMLD research, (2) provide a pathway to address previously intractable questions regarding the molecular origins of polymer properties, and (3) provide an opportunity to control and optimize polymer structure and properties for electrochemical applications including energy storage, water desalination, and sensors.

3:20pm **TF-ThA-4 Adsorbed Polymer Crystals in Icvd: Prevention and Control***, **Simon Shindler**, R. Yang,* Cornell University

Initiated chemical vapor deposition (iCVD) is a technique used to fabricate polymer thin films from the vapor phase. For most applications, films produced in iCVD are practically defect free. However, as the technique is used more often in precision applications like membrane synthesis and even at an industrial scale, quality control and defect prevention will become critical. In this study, we address an important knowledge gap in iCVD by investigating defect formation, a topic that has received little attention to date. We show for the first time that polymer chains which accumulate in the reactor during normal operation can cause defects by forming aggregates on the sample surface. To study these defects in a controlled environment, we mimic the conditions under which they form. Nucleation and growth of defects are measured using optical microscopy over a range of temperatures and in the presence and absence of adsorbed monomer to better understand what drives aggregation. With this understanding we propose a method by which aggregates (and by extension, defects) can be prevented without restricting the domain of potential deposition conditions or stage temperatures used. Our investigation provides a better understanding of the factors driving polymer aggregation in iCVD, which may lead to further improvements in the deposition process.

3:40pm **TF-ThA-5 Area-Selective Initiated Chemical Vapor Deposition (AS-iCVD) for Non-Lithographic Patterning of Polymer Thin Films***, **Junjie Zhao**[1],* Zhejiang University, China

Patterning of polymer thin films is key to device fabrication and surface engineering. Developing non-photolithographic strategies such as area selective deposition (ASD) could bypass the need for complex optical systems and provide versatile routes for producing polymeric nanostructures. While previous attempts to achieve area selectivity for condensation polymerization and ring-opening metathesispolymerization have been reported, strategies are yet to be explored for initiated chemical vapor deposition (iCVD) which involves free radical polymerization. In this talk, we will present a plasma surface treatment method to enable area-selective initiated chemical vapor deposition (AS-iCVD) for poly(1,3,5-Trivinyl-1,3,5-trimethylcyclotrisiloxane) ($pV_3D_3$). Using HBr/Ar and $O_2$ plasma, we were able convert Cu regions to high oxidation states, creating radical inhibitors in the non-growth area for iCVD. Our plasma surface treatment resulted in a nucleation delay of ca. 30 min, and enabled a deposition selectivity of ca. 90% on $SiO_2$ surface. We will discusshow plasma processing time affects the composision of surface Cu species and the resulting area selectivity for iCVD $pV_3D_3$.We will also show the application of our AS-iCVD process to pre-patterned Cu/$SiO_2$ substrates as a demonstration for self-aligned polymer patterning.

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[1] **TFD Paul Holloway Award Winner**

## Thin Film Division
## Room Oregon Ballroom 203-204 - Session TF-ThP
## Thin Film Poster Session

**TF-ThP-2 High Heat Resistant $Y_2O_3$ Film on Quartz Prepared by Ion-Assisted Deposition***, **Naoto Kihara**, S. Ogawa, K. Kawahara, R. Hayashi, T. Ogawa,* AGC Inc., Japan*; M. Tanimura, H. Okada, M. Ishikawa,* Tsubasa Science Corporation, Japan

Background

Along with the miniaturization of semiconductor devices, equipment using plasma processes such as dry etcher is required to have high plasma durability and low particle generation. Yttrium oxide ($Y_2O_3$) is used as a passivation film on the surface of the parts which are equipped in the chamber. In recent years, $Y_2O_3$ films with high heat resistance are required to etch low-volatility or difficult-to-etch materials and developed for new plasma processes. In this study, we focused on the difference of thermal expansion between quartz substrate and $Y_2O_3$ film, then report that $Y_2O_3$ film with high heat resistance of 500°C was obtained introducing intermediate layer $Y_2O_3$-$SiO_2$

Experiment

In this study, $Y_2O_3$ and $Y_2O_3$-$SiO_2$ films were deposited on quartz substrate using the ion-assisted deposition method (IAD). The $Y_2O_3$-$SiO_2$ film which is the intermediate layer was formed by two-source co-evaporation of $Y_2O_3$ and $SiO_2$. Plasma resistance was evaluated by measuring the etched depth of the film using a profilometer after etching with $CF_4$ plasma. For heat resistance, the presence or absence of cracks was evaluated using an optical microscope after annealing in atmospheric environment. In addition, crystallinity and morphology were confirmed by X-ray diffraction measurement (XRD) and scanning electron microscopy (SEM), respectively.

Results and Discussion

On the basis of the XRD analysis results, the obtained $Y_2O_3$ film crystal structure was a cubic crystal with the (222) orientation as the main peak. In addition, a uniform surface morphology without voids and pores was obtained from surface and cross-sectional SEM observation. The etching rate was 0.009 µm/hr, which was 1/100 of quartz. Moreover, in the heat resistance test results, there were no cracks at 400 °C, and cracks occurred at 500 °C. In the quartz/$Y_2O_3$-$SiO_2$/$Y_2O_3$ stacked film intended to improve heat resistance, there were no cracks at 500 °C, but cracks occurred at 600 °C. Thus, by introducing the intermediate layer, Y2O3 stacked film having heat resistance at 500 °C was obtained. The reason for the improvement on heat resistance is presumed that the thermal expansion coefficient of $Y_2O_3$-$SiO_2$ has an intermediate value between quartz (0.5 ppm/°C) and $Y_2O_3$ (7 ppm/°C), which reduces thermal strain and stress. The detailed mechanism is under analysis.

**TF-ThP-3 Improvement of Transparency and Electrical Conductivity of Ti-Doped ZnO Thin Films***, **Naoya Utsu**, I. Takano,* Kogakuin University, Japan

In recent years, transparent conductive films have been used for touch panels, liquid crystal displays, solar cell electrodes, and other applications. Currently, indium tin oxide (ITO) or other oxide semiconductors are the mainstream materials that combine transparency and electrical conductivity. On the other hand, indium (In) is a rare metal with limited the production area, which limits its stable supply and causes significant price fluctuations. In this study, we focused on zinc oxide (ZnO) with sufficient resources and improved the transparency and electrical conductivity of ZnO by doping titanium (Ti).

The sample substrate was a slid glass with 15 x 10 mm in a size that ultrasonically cleaned with ethanol for 10 minutes. The oxide thin films were deposited by reactive sputtering using the multi-process coating system (BC5146, ULVAC Corp.). The deposition conditions were Zn sputtering input power of 20 W with an Ar gas flow rate of 20 sccm and an $O_2$ gas flow rate of 5 sccm to obtain a film thickness of 50 nm. At the same time, Ti was doped from 0 to 40 % with calculating from the Ti sputtering rate. For example, in the case of 10 % in the Ti doping, the sputtering rate of Zn is 0.085 nm/s (RF input power 20 W) and that of Ti is 0.0094 nm/s (DC input power 53 W).

For optical properties, transmittance was measured using a UV-visible spectrophotometer (UV-2550, Shimadzu Corp.). For electrical characteristics, the electrical conductivity was calculated from the resistance value of the deposited sample using a four-point probe (RG-5, NPS Corp.) with a pin spacing of 1.0 mm. Crystal structure analysis was performed by X-ray diffraction (SmartLab, Rigaku Co., Ltd.) at an X-ray incidence angle of 0.4 degrees.

The optimum condition for the transmittance and electrical conductivity was obtained at ZnO doped with Ti of 30 %. The transmittance and electrical conductivity of the film were 95.2 % and 739 S/m, respectively.

**TF-ThP-4 Improving Compositional Analysis of Copolymer Thin Films Using a Simple Density Correction***, **Simon Shindler**, R. Yang,* Cornell University

When synthesizing copolymer thin films, accurate measurements of the polymer composition are essential to understanding and optimizing material properties. Determining the composition of thin films synthesized from the solution phase (e.g. spin coating, or spin casting) is straight forward, since researchers generally know the composition of the polymer before fabricating the film. In polymer vapor deposition of copolymers, the characterization of composition relies instead on techniques like Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS). While helpful in some applications, chain re-orientation at the polymer-air interface and adventitious carbon often bias XPS data – making it an unreliable tool for standalone film compositional measurement. FTIR transmission spectra are more commonly used to determine composition by comparing peak areas associated with known chemical functionality. This technique uses the Beer-Lambert law to relate composition to absorption and pathlength (film thickness). To obtain composition from this method, it is necessary to measure film thickness (generally using ellipsometry) and assume that all films being analyzed have equal density. For certain chemistries, copolymerization changes the polymer packing, causing density to vary significantly with composition. When uncorrected, the assumption of constant density leads to large errors and non-physical compositions. In the process of collecting film thickness from spectroscopic ellipsometry, the refractive index of the film is also measured. Because the density and refractive index are related through the Lorentz-Lorenz equation, film density is easily estimated. By applying a density correction, we demonstrate significant improvements to the measurement of composition from FTIR at essentially zero cost. Density correction improves the accuracy of compositional analysis using data that is already collected in many labs, making it a simple and cost effective improvement to existing methods.

**TF-ThP-5 Theoretical Prediction of Trisilylamine (TSA) Adsorption and Decomposition on Hydrogen-rich Silicon Nitride***, **Tsung-Hsuan Yang**, T. Wang, G. Hwang,* University of Texas at Austin*; P. Ventzek, J. Zhao,* Tokyo Electron America, Inc.

The reactions of trisilylamine (TSA) precursor on silicon nitride (SiN) thin film in atomic layer deposition (ALD) process was investigated by density functional theory (DFT). A N-rich, H-terminated surface model was used to simulate the surface after $NH_3$ plasma treatment. Two reaction mechanisms were proposed depending on the abundance of excess hydrogens on the surface: (1) TSA reactions with primary amine ($-NH_2$) and (2) TSA reactions with hydrogenated primary amine ($-NH_3$). The source of excess hydrogen originates from the H radical from the $NH_3$ plasma which can survive on the SiN surface by being captured by the surface amine groups. Results show that in the first mechanism, the rate-determining step for TSA chemisorption is the TSA-adduct formation step which requires overcoming an energy barrier of 0.67eV predicted by climbing-image nudged elastic band (CI-NEB) method (*i.e.,* $TSA(g) + -NH_2 \rightarrow -NH-SiH_3 + (SiH_3)_2NH(g)$). In the second mechanism, the rate-determining step is the hydrogen transfer step with a much lower energy barrier of 0.34eV (*i.e.,* $TSA(g) + -NH_3 \rightarrow \bullet SiH_3(g) + (SiH_3)_2NH(g) + -NH_2$).

**TF-ThP-6 Effects of Surface Morphology on the Phase Coexistence and Evolution in $Li_xCoO_2$ Films Studied by PEEM***, **Elena Salagre**,* Dpto Fisica Materia Condensada, Universidad Autónoma de Madrid, Spain*; E. Fuller,* Sandia National Laboratories*; M. González-Barrio, A. Mascaraque,* Dpto Física de Materiales, Universidad Complutense de Madrid, Spain*; T. Mentes, A. Locatelli,* Elettra-Sincrotrone Trieste, Italy*; I. Takeuchi,* Materials Science and Engineering, Univ. Of Maryland*; A. Talin,* Sandia National Laboratories*; P. Segovia, E. Garcia Michel,* Dpto Física Materia Condensada, Universidad Autónoma de Madrid, IFIMAC, Spain

The cathode material $Li_xCoO_2$ (LCO) and related intercalation oxides are widely used in lithium-ion batteries and are now being investigated for applications in catalysis and neuromorphic computing[1][2][3], leading to great interest in their surface properties and mechanisms. The ability of LCO to change its composition from stoichiometric $LiCoO_2$ to $Li_xCoO_2$ is the key feature for most technological applications. This process changes its atomic and electronic structures. Oriented islands and epitaxial thin films of $Li_xCoO_2$ grown on $SrTiO_3$ (STO) have been studied at the Nanospectroscopy beamline of the Elettra storage ring using photoemission electron microscopy (PEEM) and low energy electron microscopy (LEEM)[4].

Different surface morphologies have been studied during Li deintercalation, including the phase coexistence regime. Stoichiometric LCO islands and films were delithiated in situ under UHV conditions by preferential Ne$^+$ sputtering followed by thermal treatment. Surface crystallinity and morphology were maintained throughout the experiments. The effects of delithiation on island size, distribution and the surrounding substrate and wetting layer were characterized. A shift in the valence band position towards the Fermi energy marks the IMT and is accompanied by a change in the surface conduction, observed as changes in the charge shift of the PEEM spectra. This has allowed us to relate the Li content to the metallization and therefore emergence and propagation of the IMT.

The spatial resolution of PEEM provides further and more detailed information on phase formation and evolution, as well as nucleation points and domain sizes. We were able to isolate the contribution of the different phases formed in the $0.5<x<1$ region.

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**TF-ThP-7 Sorption-Vapor Synthesis of Zr-MOF, UiO-66-NH$_2$, Sponge Composites***, **Jimmy Nguyen**, G. Parsons,* North Carolina State University

Metal-organic frameworks (MOFs) are materials of interest for their high surface area and chemical tuneability. MOF-Fabric, fiber, and sponge composites have been an area of research enhancing materials for applications like catalysis, separation, sensors, and energy storage. In comparison to other support matrices, sponges have greater molecular transport through their macroporous structure. The majority of current approaches for creating MOF-sponge/foam composites require multiple lengthy and resource consuming steps. These approaches often rely on either support pretreatment followed by MOF synthesis or support formation around premade MOF powder. The pretreatment method adds an additional hazardous step using high temperatures or heated acidic solutions. The support formation method requires more uncommon instruments like a high-pressure homogenizer and/or freeze-dryer. Here, a straight forward method for *in-situ* synthesis of a MOF film onto as-received commercially available sponges is reported. Sorption-vapor synthesis first involves the sponge absorbing precursor solution followed by a vapor-driven MOF nucleation and growth phase. The vapor phase exposure serves multiple roles including increasing the mobility of reactants to connect together, promoting crystalline behavior, and creating desired defects in the framework under specific conditions. This sorption-vapor synthesis technique enables the formation of plant fiber sponge@UiO-66-NH$_2$ composites retaining significant mechanical integrity capable of withstanding compressions. Through exploring different solvent systems, acidic vapors, and metal precursors, the conditions that maintain the most structural integrity was discovered. The conditions using a dimethyl formamide, ethanol, and water solvent system, acetic acid and water modulating vapor, and ZrCl$_4$ led to a crystalline MOF composite with a BET surface area of 114 ± 17 m$^2$/g.The composite formed via sorption-vapor synthesis was found to be capable of catalyzing the hydrolysis of an organophosphate, dimethyl paraoxon, with a preliminary study exhibiting a half-life of < 20 mins. This work presents insight into a simple vapor driven mechanism for UiO-66-NH$_2$ film growth onto an as-received, commercial sponge.

**TF-ThP-8 Coating the Insides of Capillaries with a Flow-Through Atomic Layer Deposition (ALD) Reactor***, **Jacob Crossman**, J. Pinder, D. Patel,* Brigham Young University*; D. Bell,* RESTEK*; M. Linford,* Brigham Young University

Atomic layer deposition (ALD) is a process by which single or partial atomic or molecular layers are applied sequentially to a substrate. ALD often relies on a series of self-limiting half-reactions, where the number of these reactions applied to a surface is used to control the thickness of a deposited film to atomic dimensions. Ideally, ALD layers are consistent and conformal, which makes it an increasingly useful technique for semiconductor manufacturing. Traditionally, ALD is performed in a vacuum chamber that introduces and pumps away the precursors of the half-reactions. This approach is often effective on planar surfaces. However, it is not a viable method for coating high aspect ratio materials like the interior walls of capillary columns that are 5 meters or longer. To resolve this limitation, we developed a flow-through, atmospheric pressure (AP) ALD reactor that relies on flowing nitrogen rather than diffusion in a vacuum to present a precursor to the substrate surface. Thin film growth with this reactor was confirmed with spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), chromatography, and transmission electron microscopy (TEM). Indeed, our AP-ALD reactor includes two witness chambers containing planar silicon 'witness shards' placed before and after the capillary. The operation of this reactor was demonstrated with the well-known trimethylaluminum-water reaction. Reasonable ALD growth of Al$_2$O$_3$ was confirmed by SE of witness shards and TEM of sections of a coated capillary. Little difference in film thickness was observed between witness shards in the two witness chambers and in the capillary itself. A chemical engineering analysis of our system suggested that a ca. 10-fold excess of reagent was present in the capillary, which explains the nearly uniform film growth at both ends of the capillary and in the witness chambers.

**TF-ThP-9 Surface studies and molecular beam epitaxy of Kagome Antiferromagnetic Mn$_3$GaN grown on MgO (001)***, **Ali Abbas**, A. Smith, A. Shrestha,* Ohio University

There have been very few studies of antiperovskite structure Mn$_3$GaN in general although it was seen in molecular beam epitaxial growth as a second-phase precipitate when growing MnGaN [1]. And so, we grow thin films of Mn$_3$GaN on MgO (001) substrates using rf N–Plasma MBE. In this abstract, we will discuss the growth recipe and surface study of Mn$_3$GaN. To take advantage of noncollinear antiferromagnetic thin films in spintronics applications, it is important to study their spin structures using local probes like spin polarized scanning tunnelling microscopy. Initially we start with room temperature scanning tunneling microscopy of MBE–grown Mn$_3$GaN surfaces and later will progress toward variable low temperature spin–polarized scanning tunnelling microscopy. In our work, Mn$_3$GaN is deposited at 250 ± 10°C with a Mn: Ga: N flux ratio of 3:1:1. We keep the Ga:N ratio fixed using an RF plasma nitrogen source. The sample surface is continuously monitored throughout the growth using reflection high energy electron diffraction. During growth, the RHEED pattern was observed to be highly streaky, indicating an atomically smooth surface. In addition, we observed half-order fractional streaks (2x pattern) in the [100] direction. The calculated *in–plane* lattice constant based on RHEED is 3.89 ± 0.06 Å. This value is very close to the theoretical lattice constant *a* of Mn$_3$GaN (3.898 Å) [3] and with the *in–plane* experimental value for sample growth by sputtering (3.896 Å); and in that work, the authors also observed a 2x pattern [2]. We also measure the *out–of–plane* lattice constant using X–ray diffraction. For the major 002 peak, the value calculated is 3.84 ± 0.06 Å which also agrees well with the theoretical value (3.898 Å) [3] and with the experimental reported *c* value (3.881 Å) [2]. Rutherford backscattering confirms a stoichiometry of 3:1:1.

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**TF-ThP-10 Improved Interface of Mo/Si Bilayers by Magnetron Sputtering***, **Chao-Te Lee**, W. Chen, H. Chen,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

The periodic Mo/Si bilayers were deposited on Si substrate by RF magnetron sputtering with cooling system.The effects of substrate temperature on the surface roughness and interface of Mo/Si bilayers were investigated by atomic force microscopy (AFM), and high resolution transmission electron microscopy (HRTEM), The AFM measurements showed the Mo/Si bilayers to have a uniform morphology with a very low surface roughness value under 0.2 nm. It was found that the Mo-on-Si and Si-on-Mo interfaces of Mo/Si bilayers were clearly observed by HRTEM in sputtering without using cooling system. The thickness of Mo-on-Si interface was almost 0.45 nm in the Mo/Si bilayers. However, the thickness of the Si-on-Mo interface was increased with increasing layers of Mo/Si bilayers. It was increased from 0.9 to 1.36 nm. After using cooling system in sputtering, the temperature was 15 °C, the Mo-on-Si and Si-on-Mo interfaces were all under 0.1 nm.The improved interface of Mo/Si bilayer was attributed the interdiffusion of Mo/Si bilayer was been improved in sputtering by cooling system.

**TF-ThP-11 Optical Emission Spectroscopy Analysis of Self-limiting AlN Growth Process during Low-Temperature Plasma-Assisted ALD***, **Narmin Ibrahimli**, R. Sultana, I. Saidjafarzoda,* University of Connecticut*; M. Kilinc,* University at Buffalo*; A. Okyay,* OkyayTech*; N. Biyikli,* University of Connecticut

This research aims to present the potential and advantages of implementing optical emission spectroscopy (OES) as a non-invasive technique to investigate and optimize the plasma-assisted atomic layer deposition (ALD) process for AlN thin films. OES enables the identification of species present in the plasma and analysis of the light emitted, rendering it as a crucial tool for evaluating the reactant species delivered to the surface and for gaining unique insights into the surface reaction products and possible mechanisms of the deposition process. The incorporation of time-resolved OES measurements allows for the determination of optimal precursor dosing and plasma exposure times necessary for saturating half-reactions, thereby enhancing the efficiency of the ALD process. Additionally, the versatility of time-resolved OES as a process monitoring tool for plasma-assisted ALD processes on production equipment provides the capability for real-time detection of process faults and monitoring of reactor wall conditions.

AlN thin films were deposited by employing trimethylaluminum (TMA) in combination with various nitrogen plasmas (N2/H2/Ar). The growth experiments were carried out in a hollow-cathode plasma-ALD reactor at 200 °C and 100 W RF plasma power. The light emission during the plasma half-cycle is coupled into a multimode fiber through one of the optical access ports via a collimating lens which feeds a compact spectrometer unit spanning from 300 to 1000 nm with a wavelength resolution of ~2 nm. The spectral data obtained from the AlN deposition procedure was assessed by examining the emission spectrum within the initial few milliseconds of a plasma half-cycle that followed a TMA dose, and contrasting it with the emission spectrum observed towards the end of the same half-cycle, when the plasma had become adequately saturated. The differences in the emission spectra are due to the reactions initiated by plasma species with precursor fragments adsorbed at the surface. At the end of the plasma step, when the surface reactions have saturated, the emission spectrum recorded during the ALD cycle resembles that of a steady-state plasma. The results indicate that time-resolved OES measurements can help determine optimal precursor dosing and plasma exposure times to enhance the efficiency of the ALD process. Future work involves a more detailed investigation of surface ligand-exchange reactions, plasma-surface interactions, and formed reaction byproducts in real-time to gain a deeper insight into the ALD process.

**TF-ThP-12 Oblique Angle Deposition on Porous Polymer Films***, S. Bacheller, N. Welchert, **Malancha Gupta**,* University of Southern California

Our group has developed a modified initiated chemical vapor deposition (iCVD) process in which frozen monomer is first captured on a cooled substrate, then polymerization occurs via a free radical polymerization mechanism, and finally the excess monomer is sublimated resulting in a porous polymer film. This talk will discuss applying oblique angle deposition to this modified iCVD process. We will demonstrate that delivering the monomer through an extension at an oblique angle results in porous films with three morphological regions: region 1 consists of porous polymer pillars, region 2 consists of densified pillars, and region 3 consists of dendritic structures. We will discuss the role of the substrate temperature, the extension angle, and the monomer deposition time on the growth process.

**TF-ThP-13 Fabrication and Characterizations of Aluminum Doped Cadmium Oxide (CdO:Al) Thin Film using Sol-Gel Spin-Coating Method***, M. Syed, **Krastin Harvey**,* LeMoyne Owen College*; M. Syeda, J. Sultana,* University of Memphis

Aluminum-doped cadmium oxide (CdO:Al) thin films are deposited on silica substrates by the sol–gel spin-coating method as a function of spin coater's rpm (revolution per minute). Cadmium acetate dihydrate and Aluminum nitrate have been taken as the precursor material and a source of Al-dopant respectively. CdO:Al thin films are characterized by x-ray diffraction (XRD), Fourier Transform Infrared (FT/IR), Field emission scanning electron microscopy (FE-SEM) and SEM-EDX. XRD result indicates the highest crystallinity at 6000 rpm with a crystallite size of 31.845 nm, cubic phase formation, and strain of ~1.6 X10-2. FE-SEM/SEM/EDX shows the well-faceted homogeneous surface structure at 6000 rpm having the average particle size of 130.05 nm. FT/IR confirms the presence of CdO:Al in the film with the peak position shifting to higher wavenumbers.

Keywords: Cadmium oxide, Thin Film, SEM, Crystallinity, Sol–gel process

**TF-ThP-14 Structural and Electronic Impact on Various Substrates of $TiO_2$ Thin Film Using Sol-Gel Spin Coating Method***, **Moniruzzaman Syed**, T. Crosby, M. Frierson, J. Muhammad,* LeMoyne Owen College*; M. Syeda, J. Sultana, M. Azim,* University of Memphis, USA

Titanium dioxide ($TiO_2$) thin film has been deposited on glass and silica substrates by using Sol-Gel spin coating method. The effect of annealing temperature on the structure, surface morphology, optical and electrical properties of these films are characterized by Raman, XRD, FT/IR, UVvis and four-point-probes measurements. XRD confirms the anatase phase of $TiO_2$. Maximum crystal sizes are found to be ~31 nm on silica and ~23 nm on glass substrates at 500°C respectively. Electrical resistivity decreased with increasing annealing temperature having the higher value on glass substrates observed.

**TF-ThP-15 Thin Film Transformations with Spinodal Mechanisms***, **Rahul Basu**,* JNTU, India

The topic of nucleation and growth in thin films traditionally has relied on the free energy barrier concept. In the present approach the growth of secondary phases is examined using a Moving Boundary analysis with heat transfer balances. The coupling of other components is not neglected. The possibility of spinodal breakup occurs within a miscibility gap and involves additional terms in the diffusion equation. These 4th order terms are modeled appropriately and included in the dominant Fickian diffusion model. The thin film approximation is used with a perturbation expansion.

Although the spinodal model required two or more component alloys in a miscibility gap, the differential equations do not exclude a general one component model. It is shown that the onset of a nucleation regime is predictable from the MBP heat transfer analysis without the explicit use of Free Energy variables.

**TF-ThP-16 Optical Coating with High Hardness for MIR Optics Deposited by HIPIMS Deposition Technique***, **Bo-Huei Liao**,* Taiwan Instrument Research Institutes, Taiwan

In this research, silicon nitride and silicon oxynitride multilayers are deposited by high power impulse magnetron sputtering. In order to increase the adhesion of theAR coating, plasma treatments in a rf discharge of Ar and $O_2$ are used to activate and clean the Ge substrate. Besides, $Al_2O_3$ films are also deposited as the adhesion layer before the multilayers AR coating. The average transmittance from 3000 to 5000 nm was larger than 93.2%.The Mohs hardness scale was also larger than 8.

**TF-ThP-17 Thermal Atomic Layer Deposition of Er2O3 Films from a Volatile, Thermally Stable Enaminolate Precursor***, **Chamod Dharmadasa**, C. Winter, N. Jayakodiarachchi,* Wayne State University*; P. Evans, R. Liu,* University of Wisconsin - Madison

Lanthanide oxide films have many applications in optics, catalysis, and semiconductor devices. $Er_2O_3$ films have useful properties that arise from its high dielectric constant, a large band gap energy, high refractive index, and thermodynamic stability at high temperatures. These properties have led to the investigation of $Er_2O_3$ films for possible inclusion in CMOS devices, antireflective and protective coatings on solar cells, and passivation layers for III-V semiconductors. $Er_2O_3$ films have been grown by many techniques, including PVD, CVD, and ALD. ALD is an important technique, since it gives Angstrom-level thickness control and can afford 100% conformal coverage in high aspect ratio features. ALD precursors reported to date for $Er_2O_3$ films have problems that include low reactivity toward water as a co-reactant, oxidation of substrates when ozone is used as the co-reactant, and variable thermal stabilities. Recently, we described a series of volatile and thermally stable lanthanide(III) complexes that contain enaminolate ligands.[1] We report here detailed synthetic studies of the $Er(L^1)_3$ precursor complex, its ALD precursor properties, and its use in the ALD of $Er_2O_3$ films using water as the co-reactant. Depending upon the reaction conditions during precursor synthesis the compounds $Er(L^1)_3$, $Er(L^1)_3(L^1H)$, or $K[Er(L^1)_4]$ can be isolated. The reaction conditions can be selected to provide high yields of $Er(L^1)_3$. The volatility and thermal stability characteristics of $Er(L^1)_3$ are favorable for use as precursors for $Er_2O_3$ and other rare-earth oxides. An ALD window in the growth of $Er_2O_3$ films using $Er(L^1)_3$ with water as the co-reactant was observed from 150 to 250 °C, with a growth rate of 0.25 Å/cycle. The films were characterized by electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and atomic force microscopy. Advantages of $Er(L^1)_3$ include its simple synthesis, good volatility and high thermal stability, and high reactivity with water to afford $Er_2O_3$ films. This class of new ALD precursors has the potential to enable more widespread use of the favorable properties of rare-earth oxide compounds and can be expanded to multi-component complex oxides containing rare earths.

**TF-ThP-18 Highly Sensitive and Stable pH Sensor Electrodes of TiN Fabricated using HiPIMS with Kick***, **Lucas Mougeot**, S. Stagon, J. Aceros,* University of North Florida

Titanium nitride deposition-sputtered sensors have been shown to function as sensitive pH sensors. The electrical conductivity and inertness of TiN advocates for this functionality. Literature has shown results only for DC-sputtered TiN pH sensors, however. This research identifies and analyzes the differences between DC-sputtered TiN sensors and those fabricated with HiPIMS and HiPIMS with Kick. The methods differ in their power source. Note that DC-sputtering involves a DC power signal. HiPIMS stands for High Power Impulse Magnetron Sputtering and uses a square wave power signal. HiPIMS with Kick also requires a square wave, but involves a short pulse before relaxing to the equilibrium voltage. For all sputtering methods, the power input to the titanium target averages at 250W. Additionally, the initial chamber pressures are all 10^-6 torr. Some settings differ to achieve consistent deposition rates between the techniques, such as the working pressure (3-5 mtorr). To create the sensors, TiN is deposited onto a ceramic screen-printed electrode (with gold metallic ink). There are four leads: active, counter, reference, and signal. The active and signal leads connect to the active electrode. The counter and reference leads connect to their own respective electrodes. TiN is deposited onto the active electrode. The reference electrode is composed of Ag/AgCl. In aqueous environments, a potential difference forms between the active and reference electrodes. This voltage is used to determine the pH of the solution. To compare the sensors, measured properties include sensitivity, hysteresis, response time, and drift. To measure sensitivity, the Nernst equation is employed to determine the linear relationship between voltage and pH. The slope of this graph directly relates with sensitivity, with steeper slopes denoting higher sensitivity (and vice versa). To measure hysteresis, the sensor measures a sequence of pH buffer solutions in time-contained steps (i.e. a pH sequence 4, 7, 10, 7, 4 limited to 240 seconds each). The voltage difference that exists between a first-stage measurement and a second-stage measurement of the same solution denotes hysteresis. For measuring response time and drift, the sensor is placed into a solution for a duration of time. Response time is the duration that exists between the initial exposure to the solution and the point when the output is first within 0.1 pH of the true value. Drift is longitudinal. Measured over the course of hours, drift is the output decay rate from the sensor's initial steady state. The Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) are used characterize the TiN depositions. The SEM characterizes the topographic features of the depositions. The AFM characterizes the film thickness.

**TF-ThP-19 Temperature Dependent Thermal Conductivity Measurements of Thin Oxide Films Via Steady State Thermoreflectance***, J. Gaskins, D. Olson, T. Bates, P. Hopkins,* Laser Thermal*; **Ron Fisher**,* Laser Thermal, USA

Continued dimensional scaling of materials in integrated circuits have resulted in major challenge in power dissipation and thermal management. These characteristic length scale reductions at all tiers of devices lead to temperature increases which accelerates the degradation of performance and reliability of very large scale integration. As technology nodes push to the <5 nm length scale, these thermal problems become more pronounced due to metal interconnect scaling resulting in reduced thermal conductivities, interfacial thermal resistances, and novel ultra-low-k amorphous dielectric layers that have intrinsically low thermal conductivities. Accurate understanding of these thermal properties will help guide the upcoming generations of interconnect and transistor technologies. Using Steady State Thermoreflectance in Fiber Optics (SSTR-F), we measure the thermal conductivity of a series of oxide thin films on silicon wafers. Prior to SSTR-F measurement, we coat the samples with a thin (~80 nm) film of Al to serve as an opto-thermal transducer. In practice, due to the steady state nature of the SSTR-F measurements, we are minimally sensitive to the thermal mass of the Al (heat capacity and thickness) as compared to TDTR or FDTR, which is a typical major source of uncertainty in TDTR and FDTR. We report on the thermal conductivity of oxide films with thicknesses of 98, 229, 287, 431, and 867 nm. For the thinnest three samples, SSTR-F measures the thermal resistance of the oxide layer in addition to the ITR at each adjacent oxide layer interface (Al/oxide and oxide/Si). Thus, we measure the thermal conductivity by fitting the thermal resistance of this thickness skew as a function of thickness and fit a series thermal resistor model to these data to determine the thermal conductivity of these amorphous oxide films. This approach yields a the thermal conductivity of 0.96 +/- 0.04 W/m/K. For the thickest two oxide samples, the thermal resistance is dominated by that of the oxide, and thus we report on direct measurements of the thermal conductivity of these films by dividing the thickness of the films by the measured thermal resistance and also come to a thermal conductivity of 0.96 +/- 0.04 W/m/K. The uncertainties in our measured values are calculated from spot to spot variation and propagation of uncertainty in the assumed parameters in our analysis. These SSTR-measured values agree well with prior measurements of the thermal conductivity of amorphous thin film dielectrics on silicon using TDTR that have been reported previously.

**TF-ThP-20 Investigation on Atomic Layer Deposition Assisted Growth of Metal Organic Frameworksfilms and Their Sensing Performance***, **Zhe Zhao**,* Fudan University, China

Weak interactions, non-uniformity and powdery assemblies limited the wide application of metal organic frameworks (MOFs) in devices[1, 2]. We report a new strategy for area-selective assembly of MOF particles to prepare a thin film with the assistance of atomic layer deposition (ALD)[3-5].The mechanism of this strategy is utilizing ALD pretreatment to induce the growth ofhydroxy double salt (HDS) nanosheets on substrates, and the HDS nanosheets are then chemicallyconverted into a MOF structure[6]. Self-assembled hierarchically porous MOF films such as ZIF-67 (Co), ZIF-8 (Zn), Ni-MOF (Ni), PCN-333 (Fe), MIL-53 (Fe), etc. were formed on both flat and complex three-dimensional (3D) substrates at a combination of gas and liquid fabrication approaches, and can be precisely patterned by photolithography[7-10]. We demonstrate that the MOF film obtained possesses excellent electrochemical activity and can be applied in biosensor for ultra-high sensitivity and a low limit of detectiontowards glucose, lactic acid and dopamine[5-7]. This strategy is promising to prepare MOF film-based on-chip devices with advanced functions.

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**TF-ThP-21 Vapor Phase Infiltration of Metal-Organic Framework for Electrocatalysis***, **Fan Yang**, M. Cao, H. ren, R. Chen,* Huazhong University of Science and Technology, China

Abstract: Metal-organic frameworks (MOFs) with well-defined structures and uniformly arranged tunable pore sizes, large surface area attract lots of attentions for a wide range of application including catalysis, sensing and etc. Intrinsic MOFs, however, often suffers from low conductivity, reactivity, selectivity and etc. Vapor phase infiltration (VPI), as a gas-phase method modified from atomic layer deposition, assures an accurately infiltrated deposition of materials into porous materials like MOFs, due to the self-limiting characteristic. In our work, VPI were applied for MOFs as post-modification at organic ligands and metal nodes, respectively. Due to the modification accuracy both in position and amount altering the MOFs coordination environment, excellent electrochemical $CO_2$ reduction reactivity of modified MOFs were obtained, showing promising reactivity and selectivity, comparing to pristine MOFs. The VPI strategy gives great implications for the precise and accurate construction of MOFs coordination environment.

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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).

[1] M. A. Moreno *et al. JVST B,* vol. 36, MAY 2018.

[2] A. Priebe *et al. ULTRAMICROSCOPY,* vol. 173, pp. 10-13, FEB 2017.

[3] A. G. De Carvalho *et al. Biointerphases,* vol. 15, 2020.

[4] C. Uwizeye *et al. PNAS.* **Vol 118**, e2025252118, 2021.

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)

1. X. Yao et al., Energy Environ. Sci., 2023, DOI: 10.1039/D2EE04006A.
2. S. Marchesini et al., ACS Appl. Mater. Interfaces, 14(2022)52779-52793.

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.

References:

[1] A. Chandrasekaran, R.W.E. van de Kruijs, J.M. Sturm, A.A. Zameshin and F. Bijkerk, ACS Applied Materials & Interfaces **11**, 46311 (2019)

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.

## Electronic Materials and Photonics Division
## Room B116 - Session EM1+TF-FrM

### Advanced Patterning and Fabrication for Device Scaling

**Moderators: Stephen McDonnell**, University of Virginia, **Michelle Paquette**, University of Missouri-Kansas City

8:20am **EM1+TF-FrM-1 Thin Film Challenges and Opportunities in a 3D-Evolving Memory Landscape***, **Johan Swerts**,* imec, Belgium **INVITED**

Device architectures used in SRAM memory transitioned in the past decade from the historical 2D planar transistor to FINFET. The next innovation revealed for the 3nm node is a 3D stacked gate-all-around architecture in combination with a backside power delivery network. For further scaling, stacking nmos and pmos, the so-called complementary-FET (CFET) design, is envisaged to happen in 2030. New metallization schemes to tackle the RC challenge as device dimensions of the interconnects shrink, such as Cu replacements materials in a direct metal etch integration scheme. A broad variety of complementary deposition techniques and introduction of new materials will be needed to enable the above-mentioned novelties.

A similar trend towards stacking functional cells can be observed in various memories, such as the emerging memories that aim to bridge the gap between DRAM and NAND, thereby enabling fast data storage and retreival for real-time processing in connected devices at low cost. These memories are based on phase change, filamentary, magnetic, or ferroelectric mechanisms and often use multi-element materials. They have been extensively explored in 2D capacitor or transistor based devices, but for further density scaling 3D device designs are needed where a conformal deposition technique such as ALD is required. Cell scaling challenges also hold for the traditional DRAM which lead to exploring 3DDRAM integration routes. One viable pathway for scaling implies the replacement of the typical Si-channel based transistor by a deposited semiconductor oxide channel. Ultimate 3DDRAM implementation would require a conformal deposition of that channel.

This presentation reviews key thin film opportunities and challenges, including but not limited to ALD, in a 3D-evolving memory landscape.

9:00am **EM1+TF-FrM-3 Patterning Challenges in the Era of Vertical Scaling***, **Luciana Meli**,* IBM Research Division, Albany, NY **INVITED**

With the end of conventional device scaling, achieving higher compute power has relied on a combination of design and integration innovations, and material breakthroughs to keep up with scaling demands. While traditional dimensional scaling will only continue for the back end of the line, controlling pattern variability and placement remains a critical challenge from a lithography perspective.

Looking ahead, vertical scaling paths will be essential to enhance performance in traditional analog computing and to scale up qubits in quantum computing. This talk will focus on key patterning challenges associated with these vertical scaling pathways, including stacked FETs and chiplet-based architectures, and address opportunities for innovation.

9:40am **EM1+TF-FrM-5 Plasma Etch Challenges and Innovations to Enable sub-26nm Pitch L/S Patterning with High-NA EUV***, **Nafees Kabir**,* Intel Corporation

Extreme ultraviolet (EUV) lithography has been a game changer for the semiconductor industry, enabling tight pitches of 36-40 nm for the 7nm logic technology node. Employing an extremely short 13.5nm wavelength, EUV lithography has surpassed 193i by improving resolution and thus the ability to print tighter features, as well as replacing the complex and expensive multiple-step patterning of 193i with single-patterning. However, despite achieving single-exposure 28nm pitch for the 5nm logic technology node, the current scanner is approaching its resolution limit.

As we prepare to embrace another litho evolution, **high-NA EUV lithography technology**is projected to enable 2nm and beyond logic technology nodes without requiring complex multi-step patterning. The key enabler to improve resolution is the numerical aperture (NA) of the lens. Hence, moving from current **0.33NA to 0.55NA** has the ultimate capability to enable 8nm resolution and patterning 16nm pitch with single-exposure. With this change in NA, the depth-of-focus (DOF) is reduced and pushes us towards the use of **thinner resists** (~20-25nm FT).

This brings us to a new process territory, not only for litho, but also for plasma etch. Need for etch innovation is at a premium to work hand-in-hand to enable pattern transfer of critical features in beyond-2nm logic nodes to further advance Moore's Law.

In this work, we will share some early innovative plasma etch techniques to demonstrate patterning of basic elements like lines/spaces, contact holes etc. and novel process integration schemes involving Chemically Amplified Resists (CAR) to enable more complex structures with high fidelity.

10:00am **EM1+TF-FrM-6 Area-Selective Deposition with Carborane and Aromatic Self-Assembled Monolayer Blocking Layers***, **Michelle Paquette**, R. Bale,* University of Missouri-Kansas City*; B. Garland,* Lehigh University*; S. King,* Intel Corporation*; A. Molder, N. Oyler, S. Pinnepalli,* University of Missouri-Kansas City*; N. Strandwitz, V. Vemuri,* Lehigh University*; T. Vo,* University of Missouri-Kansas City

Area-selective deposition (ASD) is an important strategy in improving the fidelity of and/or reducing the complexity of current multi-pattern pitch-division processes. Dielectric on dielectric (DoD) deposition is of interest for fully self-aligned via flow; however known DoD processes are limited in terms of materials, selectivities, and processing ranges. A common strategy for achieving ASD is to use a blocking layer on the non-growth surface (e.g., a metal) to be able to deposit a target material selectively on the desired surface (e.g., a dielectric). The most well-established blocking layers are self-assembled monolayers (SAMs) based on long alkyl chains, such as dodecanethiol. While these have demonstrated extremely promising results, they do present limitations such as restricted processing windows (e.g., temperature), a typical requirement for solution-phase processing, long exposure times (e.g., 12–48 h), limited stability (temperature, time, chemical), and presence of defects (e.g., pinholes) resulting from disorder or alkyl chain distortions. We investigate two alternative classes of SAMs as blocking layers on metal: carborane thiols and aromatic thiols. Both classes possess several appealing features including the capacity for well-ordered packing (based on 3D symmetry and Van der Waals packing for carboranes and pi-stacking for aromatics), vapor phase deposition, and—importantly—cross-linking through a variety of mechanisms including heat, plasma, and radiation (e.g., UV, e-beam), thus potentially enabling fewer defects, greater stability (leading to wider/more flexible processing windows and/or higher selectivity), as well as the possibility of additional top-down patterning. We investigate the influence of SAM formation (substrate, derivative, deposition conditions, post-deposition treatment) on their resulting composition and structure as well as their blocking capability toward a selection of atomic layer deposition chemistries.

## Plasma Science and Technology Division
## Room A107-109 - Session PS+NS-FrM

### Advanced Patterning and Plasma-Engineered Materials

**Moderator: Angelique Raley**, TEL US

8:20am **PS+NS-FrM-1 EUV Lithography Patterning towards Devices Nano Scaling***, **Danilo De Simone**,* IMEC, Belgium **INVITED**

Nowadays, the device scaling driven by the Moore's law is continuing by the deployment of the 0.33NA extreme ultraviolet lithography (EUVL) in high volume manufacturing further driven by the need to improve cycle time and cost. To further simplify and improve EUV patterning reducing cost and enable 2nm technology and below, high NA EUV lithography (0.55NA) is under development. At the same time, as the nanoscale is pushed further down, the stochastic nature of the patterning process and the thinning down of the films become the major patterning roadblocks. To enable the high NA technology, new knobs and faster learning cycles on patterning process development are needed to improve the process window. This presentation will show the latest development on EUV patterning materials and their challenges and provide an insight status of overcoming these obstacles towards the devices scaling at nanometric level.

9:00am **PS+NS-FrM-3 Break Healing and LER Mitigation for Low Dose EUV Exposure***, **Rémi Vallat**, P. Bézard, B. Chowrira,* IMEC, Belgium*; A. Fathzadeh, W. Halim,* KU Leuven, Belgium*; F. Lazzarino, K. Ronse,* IMEC, Belgium

Challenges introduced with High NA EUV lithography will be defectivity management with ultra-thin resists while using low EUV dose[1]. Reducing the density of bridges and breaks is thus a major point of focus for its introduction[2]. Ultra-thin resists, at low EUV dose, may come with high bridge/ break density (positive/ negative-tone resist, respectively). In the case of bridges, a descum step is traditionally introduced, which creates breaks instead (in ultra-thin resists) and further reduces the resist budget for underlayer patterning. Therefore, recovering breaks is a strategic capability for defect reduction.

The proposed way to recover breaks is to use non-conformal PECVD deposition on top of spin-on-glass (SoG). Since, the resist budget is going to be ultra-thin, the underlayer beneath will also have to be ultra-thin, leading to its failing as an hard-mask (break creation) during transfer into an amorphous carbon layer. Depositing extra Silicon-based polymers on top of the ultra-thin underlayer addresses that issue, by increasing the hard-mask etch budget. However, the polymer must be deposited on SoG, selectively to amorphous carbon to prevent the formation of an etch-blocking layer. This approach is presented in figure 1.

The selectivity of deposition is successfully developed, and results are shown in figure 2. The underlayer budget is clearly increased using PECVD. Also, the reduction in break density is demonstrated in figure 3 using a radical ion etching and/or quasi-atomic layer etch into aC, designed to maximize the break density in order to easily observe any improvement brought by the PECVD. The line-edge roughness is improved as well, due to the reduced contribution of breaks.

[1] L. Meli et al,*Proc. SPIE* 11609, 116090P (2021)

[2] P. De Bisschop, *J. Micro/Nanolithogr. MEMS MOEMS* 16, 041013 (2017)

9:20am **PS+NS-FrM-4 Carbon Resist Microlens Etching in DF-CCP $CF_4$ Plasmas: Comparison between Modeling and Experiments***, P. Ducluzaux,* Univ. Grenoble Alpes, CNRS, LTM / STMicroelectronics, France*; D. Ristoiu,* STMicroelectronics, France*; G. Cunge, **Emilie Despiau-Pujo**,* Univ. Grenoble Alpes, CNRS, LTM, France

Over the past decade, the development of image sensors used in smartphones has focused on reducing pixel size to improve photography resolution. Microlenses are a key component of these sensors, as they focus the incident light on the photodiode, enhancing the sensor's quantum efficiency. However, the manufacture of resist microlenses requires an etching step in low-pressure fluorocarbon plasmas, in which complex chemico-physical reactions can lead to a final 3D shape that is difficult to control.

In this paper, we propose to investigate numerically the influence of tunable operating conditions (RF power, pressure, etc.) on the etching of carbon resist microlenses in CF4 plasmas, to better understand the link between process parameters, plasma properties and the final microlens shape. Using a 2D hybrid model (Hybrid Plasma Equipment Model), we simulate the CF4 plasma gas-phase in a dual-frequency capacitively coupled plasma reactor. We then use the plasma properties obtained from this simulation (densities, fluxes, and energies of charged and neutral species) as entry parameters for an etching profile model (Monte Carlo feature profile module). First, we investigate numerically and experimentally (ellipsometry, TOF-SIMS) the impact of pressure (30-200 mT) and RF powers (100-1500 W) on the etch rate and on the cross-sectional structure (chemical composition, reactive layer thickness) of resist blanket wafers. Then, we analyze the impact of these parameters on the etching of spherical resist microlenses, comparing the simulated 3D final shape with experimental profiles (AFM, SEM) obtained in an industrial reactor.

Our results show that the low-frequency (13.56 MHz) power increases the F penetration in the resist due to an increase in the ion energy, while the high-frequency (40 MHz) power increases the etch rate due to an increase in the ion flux. The impact of operating conditions on the microlens profiles will be discussed in details during the presentation and provide insights into the chemico-physical mechanisms involved in carbon resist etching.

9:40am **PS+NS-FrM-5 Investigations of Surface Reaction Mechanisms in Euv Induced Hydrogen Plasmas***, **Tugba Piskin**,* University of Michigan*; V. Volynets, S. Nam, H. Lee,* Samsung Electronics Co., Inc., Republic of Korea*; M. Kushner,* University of Michigan

The deployment of extreme ultraviolet lithography (EUVL) is enabling a few nm critical sizes in microelectronic processing.In one implementation, the EUV photon beams are produced by ablating and ionizing tin droplets with a pulsed laser.The ionized tin species emit photons with 13.5 nm wavelength—where these photons are collected by reflective optics and transferred to the scanner unit.The collector mirror is exposed to the tin plasma, which potentially results in a decrease in reflectivity and lifetime.Pumping $H_2$ through the EUV chamber can help resolve this problem as an in-situ cleaning technique of deposited tin on the mirror. The hydrogen slows down fast tin radicals by reacting with them in the gas phase and etching. Photoionization of the $H_2$ by the EUV produces a plasma which etches the deposited tin on the mirror by producing stannane.

EUV photons with 92 eV energy are capable of photo-dissociating and ionizing hydrogen gas while producing energetic electrons and H atoms. Ions, energetic electrons, and photons in turn produce secondary electron emission from surfaces, the latter of which can also produce energetic electrons.In this work, we computationally investigate the etch rate of tin and the redeposition of stannane in a generic EUV lithography tool by the EUV produced hydrogen plasma using a modified version of the Hybrid Plasma Equipment Model (HPEM).The consequences of secondary electron emission from the surfaces by electrons and photons will be discussed.The fluxes of hydrogen radicals and ions to the collector mirror are the most significant factor for the in-situ cleaning. The energy and angular distributions and fluxes to the collector mirror of hydrogen radicals and ions for pressures of a few to hundreds of Torr and hundreds of Watts EUV power will be discussed.

Work supported by Samsung Electronics and the US National Science Foundation.

10:00am **PS+NS-FrM-6 Area Selective Processing Based on Physisorption to Improve Functions of Extreme Ultraviolet Resist***, **Van Long Nguyen**, N. Maldonado, G. Denbeaux, C. Vallee,* SUNY Polytechnic Institute, Albany

In semiconductor manufacturing, ~10 nm critical dimensions are already in production by using EUV lithography [1]. The smaller critical dimensions require better line edge/width roughness (LER/LWR) or local critical dimension uniformity (LCDU) of EUV resists to ensure the quality of patterning features, as well as device performance. Furthermore, ultrathin EUV resists (20- to 40-nm) are currently utilized to minimize the risk of pattern collapse, which however results in poor etching selectivity to underlying layers for post-lithographic pattern transfer. Recently, employing area selective deposition as a post-treatment method on the EUV resist patterns has been reported as a promising strategy to improve the function of EUV resists [2]. In this research, we tried to improve the local roughness and thickness of the EUV resist by developing an area selective (AS) processing including both deposition and infiltration based on the physisorption mechanism, instead of the conventional chemisorption mechanism. We achieved AS physisorption based on the difference in Van der Waals interactions of surfaces/bulks with a specific gas molecule. The interaction of physisorbed molecules with samples is calculated based on a classical model. $SO_2$ gas was chosen based on the theoretical calculation to test its selective physisorption capability to the Sn-based resist versus $SiO_2$. After $SO_2$ exposure, we observed a significant thickness increase in the case of Sn-based resist (Figure S1a) but not in the $SiO_2$ (Figure S1b), as shown in the supplemental document. The observed thickness increase suggested $SO_2$ could both selectively physisorbed onto the surface and into the bulk of the resist due to its porosity. These selective physisorbed molecules onto the surface and into the bulk of the resist are then converted to chemisorbed molecules by a dissociation process using energetic Ar plasma to complete a cycle of AS deposition and AS infiltration, respectively. Ellipsometry, angle-resolved X-ray photoelectron spectroscopy, and atomic force microscopy are employed as key techniques to characterize changes during and after the AS processing. This work is funded by Semiconductor Research Corporation (SRC).

[1] https://irds.ieee.org/editions/2022/executive-summary for International Roadmap for Devices and Systems (IRDS), 2022 Edition.

[2] Nye, Rachel A., et al. "Enhancing Performance and Function of Polymethacrylate Extreme Ultraviolet Resists Using Area-Selective Deposition." Chemistry of Materials 35.5 (2023): 2016-2026.

10:40am **PS+NS-FrM-8 Recent Advances in $Ga_2O_3$ Material Development at AFRL***, S. Mou, T. Asel, A. Neal, Y. Kim, **Brenton Noesges**, A. Charnas, J. Li, T. Back, K. Burzynski, B. Newton, A. Green, J. Blevins,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA **INVITED**

$Ga_2O_3$ has been of interest due to its critical electric field (8 MV/cm)[1], its ability for native substrates to be grown from the melt, and the ability to controllably dope thin films of $Ga_2O_3$ via growth methods such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD). All of these properties make $Ga_2O_3$ an attractive candidate for high power electronic applications and the ability to grow substrates from the melt make it economically feasible in this space when compared to other materials such as GaN and SiC. The Air Force Research Lab (AFRL) has invested into substrate development with Northrup Grumman Synoptics to provide a domestic source of substrates. Czochralski grown (010) Fe and Mg doped $Ga_2O_3$ has been demonstrated up to 2 inch wafers by Northrup Grumman Synoptics and challenges in surface polishing have been overcome by using a 2 step process that removes subsurface damage and produces a surface that is ready for epitaxial growth. AFRL's in house research on epitaxial films via plasma assisted MBE has identified sources of unintentional doping during the growth of $Ga_2O_3$. It was demonstrated that both the oxidation of the Si doping source material and the quartz bulb used to provide the oxygen plasma during growth were contributing significant amounts of Si in the grown films. By adjusting the plasma power to reduce the etching of the quartz plasma bulb we were able to demonstrate epitaxial films with unintentional doping levels <1 × $10^{16}$ $cm^{-3}$. Control of the intentional Si doping was achieved in collaboration with Cornell University by modifying the Si doping source to include a "showerhead" to reduce the effect of the oxidation of the Si source material[2, allowing control from 8 × $10^{16}$ $cm^{-3}$ to 1 × $10^{19}$ $cm^{-3}$. Additional thin film development was done in collaboration with Agnitron on MOCVD grown $Ga_2O_3$ films. High purity $Ga_2O_3$ films were demonstrated using trimethylgallium as the source for gallium during the growth. The MOCVD grown films' mobility and carrier concentration were measured via temperature dependent Hall Effect at AFRL and exhibited a record electron mobility of 23,400 $cm^2$/Vs at 32 K, with a low acceptor concentration of 2 × $10^{13}$ $cm^{-3}$, further demonstrating the purity of the films grown via this method[3]. These results demonstrate the investment that AFRL has in $Ga_2O_3$ and present the contributions that AFRL has made to the development to $Ga_2O_3$ material system.

[1] M. Higashiwaki et al. Appl. Phys. Lett. **100,** 013504 (2012).

[2] J.P. McCandless et al. Appl. Phys. Lett. **121,** 072108 (2022).

[3] G. Seryogin et al. Appl. Phys. Lett. **117**, 262101 (2020).

11:20am **PS+NS-FrM-10 Reverse Lift-Off Process to Avoid Sidewall Artifacts Resulting from Dry Etching "Challenging" Materials**, *D. Lishan,* Plasma-Therm, LLC*; V. Genova,* Cornell University*; S. Norris,* Axoft*; K. Dorsey,* Physical Sciences, Inc.*; **Sabrina Rosa-Ortiz,*** Plasma-Therm LLC

This work explores a process to avoid sidewall redeposition issues when dry etching materials that do not readily form volatile and desorbing etching byproducts under common operating temperatures. Common dry patterning approaches for these challenging thin films use methods relying on physical mechanisms (i.e., sputtering with accelerated ions) and often result in material being redeposited on the sidewalls of the masking material. Upon removing the mask, the resputtered sidewall material remains and forms features projecting above the material. These features, sometimes referred to as rabbit or dog ears, fences, and veils, may fall over, break and cause particles, or penetrate over layers. We present an etching approach that avoids these issues. Materials such as Pt, Au, Ni, $LiNbO_3$, Cu, Ni, Fe, Mn, Co, Mn, PZT, ScAlN, and perovskites fall in the category of "challenging" to etch materials and impact applications such as MRAM, PiezoMEMS, quantum devices and photonics.

Lift-off patterning requires line-of-sight deposition which is typically an evaporative process that constrains thermal budgets and materials that can be deposited. We discuss a technique derived from this well-known additive method of patterning thin metal layers but using a subtractive approach. In this "reverse -lift" off approach, a layered structure with an undercut in a sacrificial layer is also used. Following etching, the material that was sputter etched and redeposited on sidewalls is removed along with the sacrificial layer. Unwanted redeposition is avoided with the proper choice of sacrificial layer material, mask, and undercut structured or with familiar lift-off resist patterning (LOR). Importantly, the dry etching can be done in common parallel plate RIE and ICP configurations and does not require an ion gun source, thus making the method more accessible.

Results demonstrate physically etching a difficult material without the consequences of resputtered material. Pt was used as a test vehicle with film thicknesses up to 200 nm. Positive results were obtained with LOR patterning, with $SiO_2$ as the mask with a Si sacrificial layer, and with a Cr sacrificial layer. Both IBE and ICP configurations were used with similar results showing that the expected feature dimensions were maintained without the profile changes typically observed with tilt and rotation IBE. Modeling considered feature spacing, resputter distribution (cosine ejection), and incident ion angles to better understand the limits and dimensions of the lift-off structure. This work offers a process technique that can solve the issue of dog ears when plasma etching low or nonvolatile materials.

11:40am **PS+NS-FrM-11 Control of Ge/Si Core/Shell Nanoparticles Growth In Pulsed Nonthermal Plasmas***, **Yifan Gui**, J. Polito, M. Kushner,* University of Michigan

Core/Shell nanoparticles(CSNPs) are a type of nanomaterial that has the characteristic structure of a core and an outer shell composed of distinct materials. CSNPs have received increasing attention over the past decade due to their tunable optical properties and wide applicability in the biomedicine, semiconductor and catalyst fields. The major challenges in synthesizing CSNPs with consistent specifications lie in the variation of size uniformity, core and shell purity as a result of diverse operating conditions. While continuous-wave nonthermal plasma approaches for synthesis of CSNPs have enabled crystalline growth at low reactor temperatures, pulsing the plasma could give an edge in CSNPs production by addressing these issues. Both computational and experimental prior works have demonstrated the capability of pulsed nonthermal plasma in synthesizing nanoparticles with improved size uniformity[1,2].

The aim of this work is to computationally investigate the consequences of pulsed power nonthermal plasmas on size uniformity and core/shell purity of Si/Ge CSNPs using the Hybrid Plasma Equipment Model (HPEM) coupled with DTS Dust Transport Simulation Module (DTS). The test system is an inductively coupled plasma (ICP) having two plasma sources intended to enhance CSNP size uniformity while utilizing separate core and shell synthesis zones for better core/shell purity control. CSNPs are produced under operating conditions of a few Torr, 10 W of ICP power with pulse period of 50 µs, with Ar/$GeH_4$ and Ar/$SiH_{-4}$ gas mixtures flowing from top and middle inlets. The consequences of process parameters such as pulse period, duty cycle and ICP power, and the corresponding impacts on CSNP properties will be discussed and compared to CSNP properties resulting from continuous-wave operation.

Work supported by Army Research Office MURI Grant W911NF-18-1-0240, the National Science Foundation (PHY-2009219), and the Department of Energy Office of Fusion Energy Science (No.DE-SC0020232).

[1] S. J. Lanham, et al. Journal of Applied Physics **132,** 073301 (2022)

[2] J. Schwan, B. Wagner, et al. J. Phys. D: Appl. Phys. **55**, 094002 (2022)

## 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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2. Journal of Membrane Science, 2015, 475, 39–46
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4. ACS Appl. Mater. Interfaces, 2017, 9, 16669–16678
5. Separation and Purification Technology, 2023, 312, 123377
6. Journal of Materials Chemistry A, 2019, 7, 8107-8116
7. Sensors and Actuators B: Chemical, 2021, 344, 130302

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.

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

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 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.

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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 C̊ 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 »360$m^2/g_{comp}$. 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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