Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA1+AS+LS+NS+SS+VT-MoM

Modeling, AI, and Machine Learning Applied to Interfaces

Moderators: J. Trey Diulus, NIST, **Kateryna Artyushkova**, Physical Electronics

8:20am **CA1+AS+LS+NS+SS+VT-MoM-1 Topological and Geometric Descriptors of Complex Self-assembly at Liquid Interfaces***, Aurora Clark,* University of Utah **INVITED**

Amphiphilic surfactants at liquid/liquid interfaces can form complex self-assembled architectures that underpin interfacial reactivity and transport. This has been demonstrated by surface sensitive spectroscopies and molecular dynamics simulations within the domain of liquid/liquid extraction, which involves solute adsorption, complexation reactions and transport across the phase boundary. Being able to quantify surfactant organization is a significant challenge because the distribution of species is broad and highly heterogeneous. As such, in the analysis of molecular dynamics data, there is significant need to develop descriptors that allow statistical analysis of surface organization. This work presents recent developments based upon geometric measure theory and topological data analysis that are able to identify surface assemblies and their dynamic evolution. These methods are revealing intricate dependencies of surface assembly upon solution composition and the impact this has upon transport mechanisms.

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9:00am **CA1+AS+LS+NS+SS+VT-MoM-3 Machine Learning and the Future of Surface Analysis***, J. Jones, M. Caouette,* ***Kateryna Artyushkova,*** Physical Electronics **INVITED**

Machine learning can potentially revolutionize all areas of material science and engineering, including surface analysis, by automating and accelerating data acquisition and analysis. The application of machine learning and artificial intelligence (ML/AI) has been actively evaluated and used in scanning probe microscopic methods[1-2], while the application of AI in surface analysis methods such as AES, XPS, and TOF-SIMS is in the very early stages.[3] In this talk, I will discuss the potential areas where AI will change how we do surface analysis.

With recent instrumental development yielding improvements in sensitivity and throughput, the data acquisition stage of surface analysis has become much faster than the experimental planning or data analysis stages, which bothrequire significant operator time and human-based decisions. Using a spectrometer still requires a human operator with instrument-specific knowledge and experience in how to operate it. More importantly, the operator uses physical and chemical knowledge to decide on what specific data must be obtained and from which locations on the sample, depending on the analytical question being addressed by the experiment. Experienced scientists make these decisions effortlessly during the experiment, but it is a very challenging task for ML algorithms that rely on training data with explicit descriptors.

Initial AI applications to analytical surface analysis will focus on instrument optimization and performance inherent in the analytical workflow. Unlike acquisition parameters based on chemical or material science requiring broader context, tuning, and standardizing the spectrometer can be easily cast into numerical terms processable by AI.

Machine learning can also be utilized as a live data integrity monitoring service during acquisition, recognizing and rejecting "bad data". Systemically erroneous data caused by charging or sample damage are often not discovered until the experiment is complete and the data analyzed by a human. Catching it automatically during the experiment saves valuable operator and instrument time. Here, I will present an initial application wherein ML was used to identify whether ToF-SIMS spectra were correctly calibrated.

1.S.V.Kalinin, *ACS Nano*2021, 15, 8, 12604–12627.

2. S.V.Kalinin, arXiv:2304.02048

3. G Drera *et al* 2020 *Mach. Learn.: Sci. Technol.*1 015008

9:40am **CA1+AS+LS+NS+SS+VT-MoM-5 Complexity to Clarity: Detecting, Identifying and Analyzing Complex Materials with Machine Learning***,* ***Paul Pigram****, W. Gardner, S. Bamford, D. Winkler, B. Muir, R. Sun, S. Wong,* La Trobe University, Australia

Our ability to analyze and understand any physical, chemical, or biological material relies on accurately determining its structure, characteristics, and responses. Contemporary analytical techniques produce large volumes of data from pointwise sample analyses (one dimensional (1D) data), maps of compositional distributions (two dimensional (2D) data), and depth profiles showing composition throughout a sample volume (three dimensional (3D) data).

Correlative analyses linking data from the same sample, obtained by different analytical techniques or different operating parameters, are becoming critically important. Different analytical perspectives on the same sample enhance the richness and depth of the conclusions that can be drawn from it.

Recent advances in analytical science have resulted in an overwhelming avalanche of data – the “big data” problem. In our lab a single time-of-flight secondary ion mass spectrometry (ToF-SIMS) experiment might collect a map (512 x 512 pixels) with 2000 mass spectral peaks of significant intensity in 2 – 10 minutes. These half a billion data points all have differing degrees of significance.

In many cases, only a small number of peaks, 10 – 200, may be judged to be characteristic of a specific sample, and the rest of the data may be discarded. However, there are significant risks that such analyses are biased, and may miss important but subtle trends.

There is a very substantial knowledge gap in our ability to find and make full use of the information and knowledge contained in large scale data sets. This gap is driving rapid international progress in the application of materials informatics and machine learning to analytical surface science.

This presentation will highlight our work on applying artificial neural network approaches to analysis of a variety of very large hyperspectral data sets to better understand complex materials and their interactions.

Nanoscale Science and Technology Division
Room B113 - Session NS1+2D+BI+SS-MoM

Combined Nanoscale Microscopy

Moderators: Adina Luican-Mayer, University of Ottawa, Canada, **Sergei Kalinin**, Oak Ridge National Laboratory

8:20am **NS1+2D+BI+SS-MoM-1 Combined Metrology at the Nanoscale: Advanced Scanning Probe Microscopy to Evaluate Complex Semiconductors***,* ***Fernando A. Castro,*** National Physical Laboratory, UK **INVITED**

The performance of semiconductors is strongly affected by spatial variations that can be introduced during manufacturing or due to degradation processes. In addition to the impact of microstructure and defects on electrical and optical properties, complex semiconductors, such as some compound semiconductors, perovskites or 2D materials, can present dynamic changes in properties during operation. Combining metrology methods is critical to better understand and characterise such complex samples as individual methods provide insufficient information. Ideally these combined measurements should be either co-localised or simultaneous in order to reduce uncertainty associated with post process image registration, spatial heterogeneity, or sample contamination. NPL has been developing a suite of spatially resolved measurement methods to understand critical factors that impact semiconductor performance and reliability. In this presentation, we'll focus on nanoscale methods under controlled operational or environmental conditions, including advanced modes of scanning probe microscopy (SPM) such as time-resolved scanning kelvin probe (tr-SKPM) and tip enhanced optical microscopy (TEOS). After introducing the challenges and recent results from the European project PowerELEC, we'll present two examples of how these combined measurements are applied. First, we'll describe the application of SPM to understand degradation mechanisms in state-of-the-art perovskite solar cells (PSCs). Time-resolved SKPM can be used to distinguish the impact of ionic and electronic charges on dynamic processes and in-situ co-localised measurements under controlled environmental conditions can identify nucleation of nanoscale grains on the perovskite film surface at the start of the degradation process, allowing us to link degradation to the local electrostatic environment. The second example will focus on 2D transition metal dichalcogenide (TMD), which present promise for optoelectronic applications but are often limited by Fermi level pinning effects and consequent large contact resistances upon contacting with bulk metal electrodes. A potential solution for near-ideal Schottky–Mott behavior and concomitant barrier height control has been proposed in the literature by contacting TMDs and (semi-)metals in van der Waals heterostructures. We will show how combined nanoscale measurements allows to directly access interface parameters relevant to the Schottky–Mott rule on a local scale and how we use SKPM and TEOS measurements under simulated operational conditions (e.g. electrostatic doping induced Fermi levels) to enable decoupling and quantification of contributions from the interface dipole and electrode work function.

9:00am **NS1+2D+BI+SS-MoM-3 Correlated Functional Imaging of Printed and Ferroelectric 2D Devices for Ubiquitous Sensing and Neuromorphic Computing***, J. Kim, Z. Zhu, T. Chu, H. Choi, M. Moody,* ***Lincoln Lauhon,*** Northwestern University

The unique properties of 2D materials stimulate the design of devices that exhibit useful new behaviors. However, the correspondence of expected and actual operating principles of devices cannot always be established from simple analysis of temperature-dependent current-voltage characteristics. As a result, the rational optimization of even simple devices such as thin-film transistors, as well as the successful realization of novel neuromorphic devices, benefits from spatially resolved characterization of nanoscale structure and properties to discern the relative contributions of device geometry and 2D material structure and chemistry to device performance. This talk will describe case studies in which Kelvin probe force microscopy (KPFM) and scanning photocurrent microscopy (SPCM) are used to investigate the operating principles of thin-film transistors (TFTs) and source-gated transistors (SGTs) fabricated from MoS_2 and In_2Se_3. In the case of n-type semiconducting 2H MoS_2, model devices constructed from overlapping exfoliated flakes are analyzed to identify factors limiting the performance of printed thin-film transistors (*ACS Nano* 2023, **17**, 575). KPFM analysis is used to isolate the contact, channel, and junction resistances and calibrate a resistor network model of printed thin films. Simulations of the effective mobility and on-current dependence on flake thickness, size, and degree of overlap suggest that the performance of printed TFTs are limited by resistance arising from unpassivated edge states.

In the second use case, KPFM, SPCM, and piezoresponse force microscopy (PFM) are used to pinpoint the origin of resistance modulation in α-In_2Se_3 transistors that exhibit tunable non-volatile channel conductance. Memristive behavior in In_2Se_3 TFTs has been attributed to switching of the channel polarization, but the lack of an obvious threshold for switching raises questions about the evolution of domain structure and the contribution of trap states. Furthermore, the presumed modulation of the Schottky barrier has yet to be confirmed experimentally. We address this gap in understanding through correlated PFM, KPFM, and SPCM measurements. We then fabricate MoS_2-In_2Se_3 transistors with a geometry that induces depletion at the source electrode, i.e. a source-gated transistor, and observe non-volatile switching of the low output current. KPFM, SPCM, and finite element simulations are used to confirm source pinch-off and non-volative multi-level modulation of the effective source resistance. The quantitative correlation of device behaviors with the changes in channel potential at key interfaces usefully constrains the interpretation of the operating principles and builds a foundation for rational design of novel neuromorphic devices and systems.

9:20am **NS1+2D+BI+SS-MoM-4 A Unique New Correlative Microscopy Platform for Combined Nanoscale Microscopy by Combination of AFM and SEM***,* ***Chris Schwalb,*** Quantum Design Microscopy GmbH, Germany*; K. Arat,* Quantum Design, Inc.*; H. Alemansour, A. Alipour,* Quantum Design, Inc., Iran (Islamic Republic of)*; A. Amann,* Quantum Design, Inc., Germany*; L. Montes,* Quantum Design, Inc., Colombia*; J. Gardiner,* Quantum Design, Inc.*; H. Frerichs, L. Stuehn, S. Seibert,* Quantum Design Microscopy GmbH, Germany*; S. Spagna,* Quantum Design, Inc.

The combination of different analytical methods into one instrument is a powerful technique for the contemporaneous acquisition of complementary information. This is especially true for the in-situ combination of atomic force microscopy (AFM) and scanning electron microscopy (SEM), two of the most powerful microscopy techniques available. This combination gives completely new insights into the nanoscale.

In this work, we introduce a highly integrated new corelative microscopy platform, the FusionScope, that seamlessly combines AFM and SEM within a unified coordinate system. The self-sensing piezoresistive cantilever technology used for the AFM scanner results in a purely electrical measurement of the cantilever deflection signal. This allows for concurrent, correlated acquisition of both SEM and AFM images at the region of interest. In addition, a three-axis sample stage and a trunnion provide unique experimental capabilities such as profile view – an 80-degree tilt of the combined sample stage and AFM giving full SEM access to the cantilever tip region.

We will present a variety of novel case studies to highlight the advantages of this new tool for interactive, correlative, in-situ nanoscale characterization for different materials and nanostructures. First results will focus on hard-to-reach samples. FusionScope allows for fast and easy identification of the area of interest and precise navigation of the cantilever tip for correlative SEM and AFM measurements. We demonstrate that approach for analysis of blade radius of razor blades and the characterization of lacunae structures on bone surfaces.

In addition, we will present first results for the in-situ characterization of individual nanowires that will be used for energy harvesting applications. The SEM enables the easy location of individual or multiple nanowires, whereas the in-situ AFM allows the characterization of topography, surface roughness, mechanical, and electrical properties of the nanowire.

Based on the broad variety of applications regarding the inspection and process control of different materials and devices, we anticipate that this new inspection tool to be one of the driving characterization tools for correlative SEM and AFM analysis in the future.

9:40am **NS1+2D+BI+SS-MoM-5 Correlative *in-Situ* Nanoscale Microscopy Using AFM and FIB-SEM for Nanomechanical Property Mapping Throughout a 3D Volume***,* ***Prabhu Prasad Swain****, M. Penedo, N. Hosseini, M. Kangül, S. Andany, N. Asmari, G. Fantner,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

In this work, we present results obtained with an atomic force microscope (AFM) integrated in a focused ion beam- scanning electron microscope (FIB-SEM). The FIB-SEM is a powerful instrument, capable of automated structural analysis and prototyping at nanometer resolution, while the AFM is a well-established versatile tool for multiparametric nanoscale characterization. Combining the two techniques allows unprecedented *in-situ* correlative analysis at the nanoscale. Nanoprototyping and enhanced multiparametric analysis can be performed without contamination of the sample or environmental changes between the subsequent processing steps. The power of the combined tool lies in the complementarity of the two techniques. The AFM offers nanomechanical property mapping with electrical and magnetic characterization of the sample, while SEM offers elemental analysis and FIB enables thin slicing of the of the sample for block face imaging. This enables 3D tomographic imaging of complex samples mapping composition and mechanical properties throughout the 3D volume. Controlling both these instruments with open-hardware controller (OHC), allows us to perform automated *in-situ* AFM-FIB-SEM characterization. The setup is aimed to provide true 3D correlative information and mapping, with increased resolution for a larger volume. We will demonstrate the capabilities of correlative AFM/SEM/FIB imaging through a series of correlative experiments on polymers, 2D materials, nanowires and rock sediments.

10:00am **NS1+2D+BI+SS-MoM-6 Anisotropic Friction Effects of Perovskite Nanoplatelets on a vdW Substrate*, Sidney Cohen,* *N. Itzhak, I. Rosenhek-Goldian, O. Brontvein, E. Joselevich,* Weizmann Institute of Science, Israel**

Interest in 2D materials can be attributed to their unique properties such as electrical, optical, and mechanical characteristics, which can be harnessed in small devices. Assembly of these materials can be challenging. vdW epitaxy is a promising approach, in which nano-sized crystalline structures are grown on a 2D vdW substrate which has minimal interaction energy, resulting in low strain. The epitaxial growth still provides sufficient interaction to favor specific geometries according to lattice directions. In this presentation, the system is $CsPbBr_3$ platelets grown on vdW $ReSe_2$.This combination is of fundamental and applied interest due to special optoelectronic properties of these 2D-3D mixed semiconductor systems. The mechanism of the nanoplatelet growth leading to their shape and orientation on the surface remains to be fully revealed . Here, we present tribological studies performed by monitoring the force required to push the platelets along the surface. We observed a significant directional effect expressed in the lateral forces required to slide the platelets along the surface. In particular, forces 4-5 times those required to push rectangular platelets along the $ReSe_2$ surface along the long axis were insufficient to move the same platelets along their short axis. STEM images showed that this correlated with commensurability of the two lattice structures.Some of the experiments were performed in an ambient AFM system. Because sliding along the surface can be hindered by atomic steps and defects, unbiased analysis of this effect requires searching for small steps of atomic height along the sliding path. Scanning electron microscopy is a convenient way to search for these defects: thus, comparative experiments were performed in-situ in a combined AFM-SEM system. This combination had the additional advantage of allowing rapid overview of the surface to locate regions of interest.

In the process of evaluating the measurements, those performed in vacuum requiredmuch higher (by as much as an order of magnitude) forces to support pushing along the surface in comparison with comparable measurements made in the ambient AFM system.These measurements will be presented in the context of the characterization of the 2D substrate and platelet nanostructure as revealed by the two correlative measurement techniques.

Nanoscale Science and Technology Division
Room B113 - Session NS2+2D+BI+EL+SS-MoM

Chemical Identification with Scanning Probe Microscopy

Moderators: Sidney Cohen, Weizmann Institute of Science, Israel, **Harald Plank**, Graz University of Technology

10:40am **NS2+2D+BI+EL+SS-MoM-8 Nanoscale imaging with photo-induced force microscopy*, Eric Potma,*** University of California Irvine **INVITED**

Imaging with molecular contrast at the nanoscale is important for a myriad of applications, yet it remains a technical challenge. Over the past two decades, various flavors of optical spectroscopy combined with atomic force microscopy have been developed, each offering hope for a more routine nanospectroscopy technology. One of these approaches is photo-induced force microscopy (PiFM), a non-contact scan probe technique that is sensitive to the light-induced polarization in the material. PiFM has been used to generate molecular maps with 5 nm resolution, based on absorption contrast or on contrast derived from nonlinear optical interactions. Nonetheless, questions remain about the origin of the signal, in particular the possible contribution of forces that result from the thermal expansion of the sample. In this presentation, we will discuss various physical mechanisms that contribute to the PiFM signal and highlight several applications that are unique to the PiFM technique.

11:20am **NS2+2D+BI+EL+SS-MoM-10 Near-field Optical Microscopy Imaging and Spectroscopy at 10nm Spatial Resolution*, Artem Danilov,*** Attocube Systems Inc.

Fourier-transform infrared (FTIR) spectroscopy is an established technique for characterization and recognition of inorganic, organic and biological materials by their far-field absorption spectra in the infrared fingerprint region. However, due to the diffraction limit conventional FTIR spectroscopy is unsuitable for measurements with nanoscale spatial resolution. Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) allows to overcome the diffraction limit of conventional light microscopy or spectroscopy enabling optical measurements at a spatial resolution of 10nm, not only at IR frequencies but also in the whole spectral range from visible to terahertz. s-SNOM employs an externally-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample and detection of the elastically tip-scattered light yields nanoscale resolved near-field images simultaneous to topography.Use of material-selective frequencies in the mid-IR spectral range can be exploited to fully characterize polymer blends or phase change polymers with nanometer-scale domains. Quantification of free-carrier concentration and carrier mobility in doped semiconductor nanowires, analysis of 2D (graphene) nanostructures, or study phase propagation mechanisms in energy storage materials is achieved by amplitude- and phase-resolved near-field imaging. Furthermore, here we introduce correlative tip-enhanced nanoscopy, enables complete collocal vibrational analysis of both IR- and Raman-active modes at the same spatial scale. Our instrument allows for a straight-forward implementation of nano-PL measurements using background suppressing provided by the demodulation of detector signal utilized in nano-FTIR detection scheme. Combining Raman, TERS, nano-FTIR and nano-PL measurements in the same instrument significantly reduces the effort of correlating the resulting datasets, enabling complete optical analysis at nanoscale, which has not been possible so far.

11:40am **NS2+2D+BI+EL+SS-MoM-11 Correlative Nanoscale Chemical, Mechanical and Electrical Property Mapping on a Single AFM-IR Platform***, C. Li,* ***Martin Wagner****, C. Phillips,* Bruker Nano Surfaces Division

Chemical identification on the nanoscale is a long sought after capability from the inception of AFM. AFM-IR has proven to be uniquely successful in achieving this among all other attempts. It uses a mid-IR laser that is focused onto the AFM tip. Light absorption by the sample results in photothermal expansion that causes a detectable cantilever deflection change of the AFM probe. The obtained IR spectra correlate with conventional FTIR spectroscopy but are associated with sub-10nm spatial resolution.

However, a single data set rarely tells the full story and multiplexed analysis is essential to fully understand a material. We use an AFM-IR microscope with image registration and overlay capability to return to the same position on a sample when changing AFM probes, enabling extensive multimodal analysis. Data on a two-component polymer sample PS-LDPE comprising polystyrene and polyethylene reveals nanoIR spectra that correlate well with FTIR, while nanoIR maps at different IR wavenumbers provide the spatial distribution of each component. Further, we show that they are directly correlated at the nanometer level through PeakForce QNM elastic modulus and adhesion maps, as well as work function (surface potential) and dielectric maps with FM-KPFM (frequency-modulated Kelvin probe force microscopy). Many of the properties can be conveniently obtained simultaneously, while others are preferably obtained sequentially in a colocalized manner with the optimal probe choice and parameter settings for each AFM mode. Data on real-world industrial samples is then discussed, e.g. SBR (styrene-butadiene rubber) with carbon-black additives for car tires, exemplifying how ratio-map and multimodal property mapping unravel information not seen through one technique alone. In another use case chemical identification is complemented by nDMA, a mode where viscoelastic nanoscale sample properties are measured that match bulk dynamic mechanical analysis (DMA) data.

Chemical Analysis and Imaging of Interfaces Focus Topic
Room A105 - Session CA+AS+LS+NS+SS+VT-MoA

Environmental and Energy Interfaces

Moderators: Musahid Ahmed, LBNL, **Xiao-Ying Yu**, Oak Ridge National Laboratory, USA

1:40pm **CA+AS+LS+NS+SS+VT-MoA-1 In situ Spectroscopies of Interfacial Reactions and Processes in Batteries***, **Feng Wang**,* Argonne National Laboratory **INVITED**

The performance and lifetime of batteries, whether they are traditional lithium-ion, solid-state, or other types, strongly depend on the effectiveness and stability of electrochemical interfaces within the devices. To design battery materials and interfaces with desired functionality, it is crucial to have a mechanistic understanding of the interfacial reactions and processes occurring during battery operation. This necessitates developing advanced techniques capable of characterizing local structures and capturing *non-equilibrium* dynamics at electrochemical interfaces, with the relevant spatial, time resolution and chemical sensitivity, both to light elements (H, Li, O) and heavy ones. Herein, we present the development and application of *in situ* spectroscopies specialized for probing interfacial reaction and processes in lithium-ion and solid-state batteries. With specific examples from our recent studies, we will show how to correlate the structure and function of electrochemical interfaces through *in situ* spectroscopy characterization, thereby gaining insights into the design and processing of battery materials, electrolytes and other components. Towards the end of this talk, we will discuss emerging opportunities in data-driven experimentation, analysis, and modeling for closed-loop battery development to accelerate the transition from lab discovery to commercial deployment.

2:20pm **CA+AS+LS+NS+SS+VT-MoA-3 Novel Strategies for the Characterization of the Next-Generation Energy Storage Materials by ToF-SIMS: From an in-Situ Exploration to an Operando Measurement***, **Tanguy Terlier**, Q. Ai, S. Sidhik, A. Mohite, J. Lou,* Rice University **INVITED**

Recently, advances in instrumentation and sample preparation have permitted a rapid development for characterizing a wide range of applications such as next-generation energy storage materials. Developing new materials is one of the most crucial topics for emerging technologies. However, the complexity of these materials in their structures makes them particularly challenging for numerous characterization and analytical techniques. Exploring chemical composition and the potential chemical reactions such as degradation, diffusion, or doping is crucial to understand advanced materials and to transfer the new technologies to the industry. Among the most suitable characterization tool, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a very sensitive surface analytical technique providing detailed elemental and molecular information about the surface, thin layers, interfaces, and full three-dimensional analysis of the samples.

Thanks to the advances in ToF-SIMS characterization, understanding of the chemical composition and the different components in the complex structures, permit a deeper exploration and a better knowledge in the next-generation energy storage materials such as batteries, perovskites, and 2D materials.

Firstly, we will focus on the characterization of batteries. Initially, we will discuss the sample preparation and our specific setup for transferring the specimens from the inert atmosphere in the glovebox to the ultra-high vacuum chamber of our instrument. We will illustrate the possibility to study the reversibility of the chemical composition between pristine, charged, and discharged batteries using surface mass spectrometry by ToF-SIMS in operando conditions. Then we will compare three methods of cross-sectioning used to identify the interfacial species in a composite cathode.

Secondly, we will show a study of an in-depth distribution of the 3D/2D heterostructures for perovskite solar cells where we have been able to identify individually the 3D and 2D heterostructures along with the depth of the film. Then, we will illustrate the characterization of interdiffusion in quasi-2D perovskite light-emitting diodes as a function of the organic ligand layer inserted into the perovskite crystals.

Finally, we will demonstrate how the retrospective analysis using ToF-SIMS can be very powerful and useful for exploring any single feature in 2D materials. Typically, ToF-SIMS acquisition is recording a full mass range spectrum per pixel (or voxel), which permits to isolate and to decorrelate specific regions of interest for resolving interfaces, diffusion, and doping in thin 2D structures. We will present how to treat a 3D volume image of a multilayer perovskite device for extracting useful information.

3:00pm **CA+AS+LS+NS+SS+VT-MoA-5 Advanced In-Situ and Ex-Situ S/TEM Probing of Interfacial Process in Rechargeable Batteries***, **Chongmin Wang**,* Pacific Northwest National Laboratory

In-situ diagnosis appears to be one of the essential methods for gaining insights as how an electrode material failure, therefore feeding back for designing and creating new materials with enhanced battery performances. In this presentation, I will highlight recent progress on ex-situ, in-situ and operando S/TEM for probing into the structural and chemical evolution of interfacial process in energy storage materials. Both ex-situ and In-situ high resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass, charge and electron transport, providing insights as how active materials failure during the cyclic charging and discharging of a battery. In perspective, challenges and possible direction for further development of the in-situ S/TEM imaging and spectroscopic methods for energy storage materials and other field will also be discussed. Most importantly, integration of different analytical tools appear to be the key for capturing complementary information.

3:20pm **CA+AS+LS+NS+SS+VT-MoA-6 Investigating sp^2 and sp^3 Carbon Ratios by XPS: A Study of the D-Parameter and a New Second Plasmon Loss (2PL) Parameter***, **Alvaro Lizarbe**, G. Major, B. Clark,* Brigham Young University*; D. Morgan,* Cardiff University, UK*; M. Linford,* Brigham Young University

The D-parameter provides a useful estimate of the ratio of the sp^2 and sp^3 carbon in a sample. It is the energy difference between the maximum and minimum of the derivative of the C KLL Auger peak. The D-parameter can be an important analytical resource for diamond samples, as the quality of diamond depends on the sp^3 to sp^2 carbon ratio and any lattice impurities. For example, the highly sought after type 2a diamonds, which are colorless and free from impurities, consist almost entirely of sp^3 carbon. According to the universal curve for XPS, electrons with different kinetic energies have different mean free paths. Thus, electrons with different kinetic energies sample materials at different depths. In the case of carbon, the KLL Auger peak comes shallower in a material compared to the C 1s signal, which is a result of electrons with much higher kinetic energies. That is, a limitation of the D-parameter is that it is based on the C KLL Auger peak, found at around 1220 eV, while it is often related to the C 1s peak located at approximately 284.8 eV. Thus, the D-parameter is much more sensitive to adventitious carbon contamination. In an effort to derive a parameter that will be more representative of the amounts of sp^2 and sp^3 carbon in a material, we have examined the plasmon loss peaks of the zero-loss C 1s peak of direct current chemical vapor deposition (DC-CVD) diamonds, carbon nanotubes, and graphitic materials such as HOPG. By analyzing the second plasmon loss signal of the C 1s narrow scan, we obtain a new parameter for analyzing carbonaceous materials: the 2PL parameter. The 2PL parameter is the difference in energy between the second plasmon loss signal and the C 1s peak. We compare the traditional D-parameter with the 2PL parameter for various materials. They correlate quite well. We have also investigated various mathematical methods of deriving the 2PL parameter, including via a weighted average of the second plasmon loss and C 1s signals. Ultimately, because the 2PL parameter involves signals that are closer to the C 1s photoemission binding energy, we believe it may be more representative of the full chemistry of carbonaceous materials.

4:00pm **CA+AS+LS+NS+SS+VT-MoA-8 Solid-Liquid Interfaces for Energy-efficient Chemical Separation of Critical Minerals and CO_2 Conversion***, **Manh-Thuong Nguyen**, V. Prabhakaran, D. Heldebrant, G. Johnson,* Pacific Northwest National Laboratory **INVITED**

Chemical separations consume around 15% of the energy used by industry today. It is thus critical to develop energy- and material-efficient approaches for large-scale separations. In the first part of this presentation, I will illustrate how we employ modified 2-dimensional materials and solvents to separate critical minerals including rare earth elements. Polar functional groups present at the interface of graphene oxide laminate membranes are demonstrated to improve the selectivity of metal cations separated by both adsorption and sieving. Hydrophobic ionic liquid molecules including 1-ethyl-3-methylimidazolium chloride, when used as a minor solvent component, are shown to increase the energy efficiency of the desolvation of aqueous lanthanide cations in electrochemical separations. In the second part, I will present studies exploring the use of functionalized hexagonal boron nitride (h-BN) membranes to separate CO_2

from multicomponent gas mixtures. Strategies for improving CO_2 separation selectivity and efficiency, such as chemical functionalization and engineering the dimensions of interlayer transport channels, will be discussed. Finally, I will present studies on the electrochemical conversion of CO_2 into value added chemical feedstocks such as methanol on membrane-supported catalysts. Insights into the effects of local structure modification and confinement on catalytic processes will be presented.

4:40pm **CA+AS+LS+NS+SS+VT-MoA-10 Buried Interfaces of Ir Photodetector Devices Analyzed with Lab-Based Xps/Haxpes***, **Roman Charvier**, M. Juhel,* STMicroelectronics, France*; O. Renault,* Univ. Grenoble-Alpes, CEA, Leti, France*; A. Valery, D. Guiheux, L. Mohgouk Zouknak,* STMicroelectronics, France*; B. Domenichini,* ICB UMR 6303 CNRS-Université de Bourgogne, France

The development of new IR photodetectors should respond to challenges in order to reach best performances. A major objective is to understand critical interfaces that play an important role in the final device properties. This work addresses to chemical analysis of molybdenum oxide (MoO_{3-x}) used as hole transport material which is deposited between a photosensitive material and top electrode often made of indium-tin oxide (ITO). Such critical interfaces are typically located under 20 to 50 nm under the surface.

In the case of MoO_{3-x}, the stoichiometry is generally controlled by X-ray photoelectron spectroscopy (XPS) which is well-known to obtain chemical data close to the material surface (analysis depth < 10 nm). Two methods can be used to analyse deeper buried layers: (i) the use of hard X-rays to perform Hard X-ray PhotoElectron Spectroscopy (HaXPES) and thus generate photoelectrons having a kinetic energy able to go through several tens of nm; (ii) the etching of the surface by means of an Ar^+ beam (having an energy from 0.5 to 3 keV) in order to remove the superficial layers giving access to the underlying layers. In the former case, the analyzed thickness remains far below 100 nm while in the latter case, the chemistry of the surface atoms are often modified by argon ion beam. It is then necessary to mix the two approaches to allow the chemical analysis of buried interfaces. This analysis way is used here to characterize the stoichiometry of MoO_{3-x} thin films buried under 50 nm of ITO using chromium $K\alpha$ hard-X-ray from lab-based HaXPES.

5:00pm **CA+AS+LS+NS+SS+VT-MoA-11 Detection and Discrimination of Aquatic Toxins Targeting Voltage Gated Sodium Channels Using Static ToF-SIMS Imaging***, **Jiyoung Son**, K. Engbrecht, J. Mobberley,* PNNL

Neurotoxins from aquatic microorganisms, such as cyanobacteria and algae, have been a public health concern due to their harmful impacts on the nervous systems of animals, including humans. A subset of these neurotoxins, including saxitoxin and brevetoxin, bind to and alter the function of voltage-gated sodium channels, which are essential to generating the cell membrane action potential. Existing detection and categorization methods, such as PCR and antibody-based enzyme-linked immunosorbent assays, are too specific and they require live animals like the mouse bioassay. They also require time-consuming and expensive sample preparation for analysis using LC-MS/MS and HPLC. In this project, we developed a method to detect the activity of the aquatic sodium channel neurotoxins, brevetoxin and saxitoxin, using a cell-based process. We specifically examined the impact of these two neurotoxins on HEK-293 cells, a robust cell line that has been transfected with a voltage-gated sodium channel gene, SCN1A, in order to better study neurotoxins. We cultured a layer of cells onto disinfected silicon chips, exposed the cells to neurotoxins, performed chemical fixation, and then air-dried the chips. We also prepared mock exposed samples where the cells on the silicon chips were not exposed to neurotoxins, but just the solutions each neurotoxin was resuspended in, either a 3mM HCl solution (mock saxitoxin) or a 50:50 ACN: water solution (mock brevetoxin). Control samples, which just exposed cells to cell culture media only, gave us a baseline reference. Dried samples were analyzed with mass spectral imaging using time-of-flight secondary ion mass spectrometry (ToF-SIMS). After collecting a series of spectral data, we utilized an in-house MATLAB tool to run principal component analysis (PCA) as previously described (Yu et al., 2020). Our initial statistical analysis of SIMS spectral data using PCA shows a noticeable difference in peak trends between neurotoxin and mock-exposed cells as well as neurotoxin-exposed and control cells. Our approach utilizes chemical imaging to develop a threat-agnostic model system for detecting and classifying neurotoxin activity. The technology and protocols developed from this work could transition to other rapid cellular assays for pathogenic and chemical threats.

Reference

Yu, J., Zhou, Y., Engelhard, M. *et al.In situ* molecular imaging of adsorbed protein films in water indicating hydrophobicity and hydrophilicity. *Sci Rep***10**, 3695 (2020). https://doi.org/10.1038/s41598-020-60428-1

Nanoscale Science and Technology Division
Room B113 - Session NS+EM+MN-MoA

Nanoscale Devices, Structures and Materials

Moderators: Aubrey Hanbicki, Laboratory for Physical Sciences, **Deep Jariwala**, University of Pennsylvania

1:40pm **NS+EM+MN-MoA-1 Integrated Nanophotonics Temperature Metrology Platform***, **Nikolai N. Klimov**, K. Douglass, D. Barker, T. Bui, S. Robinson, T. Herman, K. Quelhas,* National Institute of Standards and Technology (NIST)

Temperature, being, perhaps, the second most measured physical property after time and frequency plays a crucial role in various aspects of modern technology ranging from medicine and Earth's climate to semiconductor industry and advanced manufacturing process control. While there have been great strides in developing novel thermometry approaches, resistance-based thermometry remains the standard method for disseminating the SI unit of temperature at the highest level of precision. The fundamental limitations of resistance thermometry, as well as the desire to reduce sensor ownership cost, have ignited a substantial interest in the development of alternative technologies such as photonics-based temperature sensors.

At the National Institute of Standards and Technology (NIST), we are developing a new photonics-based temperature measurement solution that has the potential to revolutionize how temperature is realized and disseminated to customers. One of the key elements of our Photonic Thermometry program is an ultra-Sensitive Photonic Thermometer (SPoT) – an on-chip integrated silicon nanophotonic resonator, whose optical resonance frequency shifts with temperature due to high thermo-optic coefficient of silicon and can be used to trace temperature variations with high precision. Our goal is to evolve SPoT into a robust, field-deployable device that is on par or better than the state-of-the-art resistance thermometer.

In this work, we describe the performance of SPoT thermometer, as well as a new photonic readout for SPoT. In our new read-out scheme, we employ a novel offset-locking technique for reading out the resonance wavelength of the SPoT. This method provides extremely high accuracy for relative temperature changes on a short time scale (<< 1s).Our results indicated that the packaged on-chip integrated SPoT can detect temperature fluctuations as small 2 μK over 200 ms integration time. This methodology as well as other proposed methods will be discussed.We also show a benchmark comparison of SPoT thermometer to Standard Platinum Resistance Thermometer (SPRT) – the best-in-class resistance thermometer, in various fixed-point cells of ITS-90, evaluating temperature resolution and repeatability

2:00pm **NS+EM+MN-MoA-2 AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient Talk: Breaking the Efficiency Bottleneck of Micro-LEDs Through Nanoscale and Excitonic Engineering***, **Yixin Xiao**[1], R. maddaka, Y. Wu, Y. Malholtra, Y. Guo, S. Yang, K. Sun, A. Pandey, J. Min, Z. Mi,* University of Michigan, Ann Arbor

The performance of conventional optoelectronic devices, such as LEDs and laser diodes, is extremely sensitive to the presence of defects and dislocations. For these reasons, it has remained challenging to achieve high efficiency nanoscale LEDs and laser diodes. For example, while conventional broad area LEDs can exhibit external quantum efficiency (EQE) in the range of 80-100%, the EQE of submicron scale LEDs is often <1%, due to the dominant nonradiative surface recombination. The operation of conventional LEDs involves the radiative recombination of free electrons and holes in the active region. It is known that an exciton, a bound state of an electron and hole through strong Coulomb interaction, can drastically enhance the radiative recombination efficiency, which can be potentially exploited to make micro and nanoscale LEDs relatively immune from the presence of defects/traps. Recent studies have shown that the exciton oscillator strength can be increased by nearly two orders of magnitude in small size InGaN nanowires, due to efficient strain relaxation. Here we demonstrate that the efficiency bottleneck of μLEDs can be fundamentally addressed by utilizing bottom-up III-nitride nanostructures. We report on

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[1] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

the demonstration of micrometer scale green and red LEDs with an external quantum efficiency of 25% and 8%, respectively, which are the highest values ever reported to the best of our knowledge. We employ selective area plasma-assisted molecular beam epitaxy as the material synthesis platform. Due to efficient strain relaxation, such bottom-up nanostructures are largely free of dislocations. By exploiting the large exciton binding energy and oscillator strength of quantum-confined InGaN nanostructures, we show that the external quantum efficiency of a green-emitting micrometer scale LED can be dramatically improved from ~4% to >25%. The dramatically improved efficiency is attributed to the utilization of semipolar planes in strain-relaxed nanostructures to minimize polarization and quantum-confined Stark effect and the formation of nanoscale quantum-confinement to enhance electron-hole wavefunction overlap. We have further developed a new approach that included an InGaN/GaN short period superlattice together with an InGaN quantum dot active region to achieve high efficiency red emission. A maximum quantum efficiency of >7% was measured. Our studies offer a viable path to achieve high efficiency micrometer scale LEDs for a broad range of applications including mobile displays, virtual/augmented reality, biomedical sensing, and high-speed optical interconnects, that were difficult for conventional quantum well based LEDs.

2:20pm **NS+EM+MN-MoA-3 Modeling Gas Phase Etching in High Aspect Ratio Stacked Nanostructures for Semiconductor Processing: Stacked SiGe Layer Etching**, ***Zach Zajo***, Stanford University; *D. Mui, J. Zhu, M. Kawaguchi,* Lam Research Corp.; *E. Shaqfeh,* Stanford University

Gate all around (GAA) nano-transistors offer better channel control and increased current carrying capacity compared to FinFETs (Field Effect Transistor) which are currently the standard in the semiconductor industry. However, the need for precise control of their nanoscale features poses a challenge in manufacturing such GAA nano-transistors. The high material selectivity required in fabricating these transistors makes gas phase etching much more appealing in comparison to liquid phase and plasma-based etching techniques. An etching configuration that is of particular interest is one consisting of alternating layers of Si and SiGe from which the SiGe layers are selectively etched by fluorine gas. In the etching of these structures, it is important to have a uniform etch-rate for SiGe layers from top to bottom, to maintain consistency of the etched features. This consistency is essential for the superior performance of the GAA devices. The key gas phase processing challenge then is to determine and maximize the number of SiGe-Si layers that can be stacked in a single structure while still maintaining a nearly uniform etch-rate from top to bottom in the stack. While experiments have offered insights in terms of the effect of layer thickness, number of layers, gas pressure etc. on the viability of the process, such experiments are quite expensive and tedious. We propose and develop computer simulations as a tool to predict the etch profile evolution over time in a gas phase etching process. The tool is based on a mathematical model which considers the transport processes and surface interactions involved in the gas phase etching process – which at the nanoscale is primarily governed by Knudsen diffusion in the free molecular flow regime. Thus, the transport model is formulated as a boundary integral equation which takes into account the direct flux of etchant molecules that any given point on the exposed surface receives from the bulk gas phase as well as the re-emission flux from other parts of the structure itself. We compared the applicability of two different surface reaction models - a model where the local etch rate is linear in the flux at a point and a Langmuir adsorption/reaction model- to connect the net flux received at a point on the surface to the local etch rate. Our results show that the re-emission of etchants at the etching interface plays a vital role in determining the differential etch rates observed across layers at different depths in the stacked feature. In addition, we have characterized the effect of layer thickness and the spacing between adjacent stacks as these impact the etch rates observed from layer to layer.

2:40pm **NS+EM+MN-MoA-4 Fabrication of Silicon Microfluidic Gratings for Neutron Imaging**, *S. Robinson, R. Murphy,* National Institute of Standards and Technology (NIST); *Y. Kim,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park; *J. LaManna, C. Wolf, K. Weigandt, D. Hussey,* ***Nikolai N. Klimov***, National Institute of Standards and Technology (NIST)

In this work, we describe the development of a spatial modulator for x-ray and neutron beams. Current technology for x-ray and neutron phase imaging uses individual source gratings with a fixed period to modulate the beams. Each fixed-period, or “static” source grating, has a limited range in spatial resolution at a specific length scale, thus, a relatively larger set of individual static source gratings is required to achieve high-resolution imaging. Our team is developing a neutron imaging technique that will probe heterogeneous samples across multiple length scales. To address the need for a large variability of source grating periods, we are building a silicon microfluidic-based device, DynAmic ReconfIgUrable Source grating (DARIUS), that itself is capable to adjust, with high resolution, the grating period from 20 µm to 20,000 µm. With such on-demand tunability, a single DARIUS has the potential to replace more than 500 static source gratings, minimizing the need of fabricating, installing, and aligning a new source grating for the required period. To achieve such functionality, DARIUS features over 5,000 microfluidic grating channels that are etched on both the front and back sides of a 100 mm silicon wafer. Each of these grating channels can be selectively infilled with a neutron and/or x-ray absorbing fluid, and provide real-time reconfigurable spatial modulations for neutron and x-ray beams. In this work, we present updates on the double-sided deep silicon etch (on the front and the back of the wafer), as well as the front-to-back alignment of the silicon channels. We also describe the progress towards wafer bonding to seal the front and back sides of DARIUS device. Due to the challenges of both the microfluidic control and tight fabrication tolerances, we are evaluating the design specifics to address larger grating periods.

3:00pm **NS+EM+MN-MoA-5 The Small Shift Matters – Submilliradian Tilt Goniometry in Scanning Electron Microscopy**, ***Andrew Madison***, *J. Villarrubia, D. Westly, R. Dixson, C. Copeland,* National Institute of Standards and Technology (NIST); *J. Gerling, K. Cochrane, A. Brodie, L. Muray,* KLA-Tencor; *J. Liddle, S. Stavis,* National Institute of Standards and Technology (NIST)

Electron optical aberrations degrade the accuracy and reliability of scanning electron microscopy. Among multiple aberrations of potential concern, an axial tilt of the electron beam shifts the apparent positions and deforms the intensity profiles of features in scanning electron micrographs. Measurement of the beam tilt can enable either a physical correction of beam deflection or an analytical correction in a measurement function. In this study, we report a novel reference structure and image analysis method to measure such shifts, among other key effects. Our new concept has the potential to improve accuracy in scanning electron microscopy, with multifunctional standards enabling integrative calibrations of beam tilt and beyond. Such advances will be of particular interest in semiconductor manufacturing metrology, where even the small shift matters.

We explore conical frustum arrays as multifunctional reference structures, using physical theory to guide ongoing experiments. For a tilt inclination ϑ, a centroid shift s between the top and bottom edges of a conical frustum shows the effect of tilt. For a frustum height h, the measurement function is simply $\vartheta = \sin^{-1}(s/h) \approx s/h$, yielding a null-tilt sensor and self-calibrating goniometer. To understand the limiting random effect of shot noise, we simulate frustum images using a physical model of electron scattering and emission. At a dose of 60 electrons per nm^2, model shifts show the possibility of submilliradian accuracy for sidewall angles greater than approximately 40 mrad. In experimental measurements, charge accumulation and hydrocarbon contamination may limit the achievable electron dose, while conical asymmetry among other systematic effects will ultimately limit accuracy. In initial experiments, we fabricate submicrometer frustum arrays in silicon using electron-beam lithography and reactive ion etching and demonstrate use of the reference structure in calibrations of a typical scanning electron microscope.

In an integrative calibration, frustum arrays are optimal structures for correlative atomic force, super-resolution optical, and scanning electron microscopy. This workflow yields reference heights and positions that allow calibration of scale factor and correction of scanfield distortion, improving the accuracy of centroid shifts to show electron beam tilt and spatial variation thereof across the imaging field.

4:00pm **NS+EM+MN-MoA-8 On Point – Accurate Integration of Quantum Dots and Bullseye Cavities**, ***Craig Copeland***, *A. Pintar, R. Dixson, A. Chanana, K. Srinivasan, D. Westly, B. Ilic, M. Davanco, S. Stavis,* NIST-Gaithersburg

Self-assembled quantum dots are promising light sources for quantum networks and sensors. These emerging technologies require the accurate integration of quantum dots and photonic structures, but epitaxial growth forms quantum dots at random positions in semiconductor substrates. Optical localization of these random positions can guide the placement of photonic structures by electron-beam lithography. This integration process requires the reliable registration of position data across microscopy and lithography systems. However, large errors can result from multiple sources, including lithographic and cryogenic variation of reference dimensions for microscope calibration, as well as localization errors from optical distortion. Such errors tend to increase across an imaging field, presenting a critical impediment to exploiting the throughput and scalability of widefield microscopy. In this study, we target this problem and show how our solution enables accurate integration to improve device performance and process yield. We develop our methods of traceable localization to calibrate a cryogenic localization microscope – an optical microscope with the sample and objective lens inside of a cryostat, and custom optics outside of the cryostat. We fabricate and characterize arrays of submicrometer pillars in silicon, creating microscopy standards with both traceable reference positions and traceable reference data for thermal expansion coefficient. We image these arrays with the cryogenic microscope at approximately 1.8 K, localize the pillar positions, and use the reference data to calibrate the microscope. Our calibration determines the scale factor of the imaging system and corrects position errors due to complex distortion, among other aberration effects. We combine the results of this cryogenic calibration with our previous assessment of fabrication accuracy by electron-beam lithography, introducing a comprehensive model of the effects of registration errors on Purcell factor. This performance metric quantifies the radiative enhancement that occurs upon integration of a quantum dot into a bullseye resonator. The Purcell factor reaches a maximum value of approximately 11 for error-free registration of the quantum dot and resonator center. Our model demonstrates the possibility of greatly improving Purcell factor across a wide field. Depending on the Purcell factor threshold, on-point integration can increase yield by one to two orders of magnitude. This foundation of accuracy will enable a transition from demonstration devices to efficient processes, leading to the reliable production and statistical characterization of quantum information systems.

4:20pm **NS+EM+MN-MoA-9 Nanostructured Gas Sensors for the Detection of Meat Spoilage***, **Ken Bosnick**,* National Research Council of Canada

The sustainability of the food industry will remain a key societal challenge in the decades ahead. In North America, over 20% of meat produced is wasted, mostly at the later stages in the supply chain [1]. When meat begins to degrade, it releases biogenic amines (e.g., putrescine, H_2N-$(CH_2)_4$-NH_2) for which early detection provides a means to sense the onset of spoilage [2]. Early detection of meat spoilage through the sensing of such amines can proactively assure quality in the food production process and potentially eliminate the need for food recalls and other waste. At the heart of these envisioned quality assurance strategies are portable devices that are capable of rapid detection of low levels of biogenic amines and that can be easily deployed at various stages in the production process. New material technologies with a selective response to low levels of biogenic amines are needed to enable these envisioned devices.

The use of MOS-type gas sensing technology represents a promising avenue for portable gas sensors with many advantages over competing sensing technologies and over more traditional analysis methods. We have investigated the application of Pd-decorated ZnO nanoflowers in a chemiresistive sensing mechanism and found an excellent response of 99.5% at 250 °C towards 400 ppm methylamine [3]. The device also shows a promising response of 45% at room temperature, making it a candidate sensing material for early detection of spoilage in meat-based products. Towards improved performance at room temperature, ZnO nanocantilevers [4] are being investigated for amine sensing and will also be discussed.

[1]FAO. 2011. “Global food losses and food waste – extent, causes and prevention”

[2]Fernanda Galgano, Fabio Favati, Malvina Bonadio, Vitina Lorusso, Patrizia Romano, “Role of biogenic amines as index of freshness in beef meat packed with different biopolymeric materials”, Food Res. Int., 42 (2009) 1147

[3]Jennifer Bruce, Ken Bosnick, Elham Kamali Heidari, “Pd-decorated ZnO nanoflowers as a promising gas sensor for the detection of meat spoilage”, Sens. Actuators B Chem. 355 (2022) 131316

[4]Kissan Mistry, Viet Huong Nguyen, Mohamed Arabi, Khaled H. Ibrahim, Hatameh Asgarimoghaddam, Mustafa Yavuz, David Muñoz-Rojas, Eihab Abdel-Rahman, and Kevin P. Musselman, “Highly Sensitive Self-Actuated Zinc Oxide Resonant Microcantilever Humidity Sensor”, Nano Lett. 22 (2022) 3196

4:40pm **NS+EM+MN-MoA-10 From Natural to Fabricated Gas Sensing Photonic Nanostructures: Unexpected Discoveries and Societal Impact***, **Baokai Cheng**, J. Brewer, B. Scherer, R. Potyrailo,* GE Research Center

Existing gas sensors often degrade their performance in complex backgrounds. Thus, new sensing approaches are required with improved sensor selectivity, accuracy, and stability for demanding applications ranging from homeland security, to industrial process monitoring and safety, and to monitoring of outdoor and indoor pollutants and volatile biomarkers.

In this talk, first, we will demonstrate and analyze capabilities of natural photonic nanostructures as sensors for detection of different gases and the origins of these capabilities. Next, we will demonstrate that this new acquired knowledge from studies of natural nanostructures allowed us to develop design rules to fabricate nanostructures for needed gas selectivity and stability for numerous gas monitoring scenarios at room and high temperatures. These design rules for selective gas sensors bring a multivariable perspective for sensing, where selectivity is achieved within a single nanostructured sensing unit, rather than from an array of separate sensors. We fabricated bioinspired nanostructures using several contemporary technologies and have achieved several new functionalities beyond Nature.By utilizing individual nanostructured sensors rather than sensor arrays we also have improved sensor stability by eliminating independent aging factors in separate sensors and their arrays.The use of existing and our new machine learning (a.k.a. multivariate analysis, chemometrics) tools further advanced our sensor designs and performance in detection of multiple gaseous species. The achieved performance capabilities of our developed bio-inspired photonic gas sensors complete with the capabilities of existing commercially available gas sensors and their arrays. These colorimetric sensors can be tuned for numerous gas sensing scenarios in ambient and high temperatures, in confined areas or as individual nodes for distributed monitoring.

5:00pm **NS+EM+MN-MoA-11 Argon-Plasma Dry Etch of sub-Micron Feature-Size Waveguides in Thin-Film Lithium Niobate***, **Sesha Challa**, N. Klimov, P. Kuo,* NIST-Gaithersburg

Lithium Niobate (LN) possesses exceptional properties such as a wide transparency range, large non-linear coefficient, and high-electro-optic efficiency. These properties along with successful implementation of periodic poling in LN have spurred the development of devices finding applications in spectroscopy, remote sensing, and quantum communications.

Despite these valuable properties and possessing large second-order non-linearity, LN has taken a backseat to compete integrated photonic platforms, such as silicon, which has no second-order nonlinearity.This was due to difficulties in fabrication of a low-loss LN waveguides (WGs), integration, as well as processing on a wafer-scale.

With commercial TFLN wafers now being accessible, in parallel with the rapid advancement of scalable micro-/nano fabrication techniques, TFLN photonic devices are steadily emerging. By offering tighter conifinement compared to ion-exchanged WGs, TFLN WGs boost the performance of devices such as EOMs to have bandwidth with smaller power consumption.

Etching LN is however challenging, hence, making it difficult to fabricate low-loss WGs. In particular poor etch induces substantial roughness and non-vertical side-wall angles contributing to high propagation losses in the WGs. Low-loss LN WGs have been demonstrated over the past several years. Most of these WGs were fabricated using argon gas inductively coupled reactive ion plasma (ICP-RIE) etching. Etch recipe optimization is of utmost importance to reduce optical losses. Initial demonstrations have shown that TFLN devices can match or exceed the performance of traditional silicon or indium phosphide devices. However, low-loss TFLN waveguides are not widely available.

As a part of the effort to develop low-loss TFLN devices, we perform a systematic study of fabrication high-quality LN WGs. The main goal of this investigation is to reduce the WG’s surface roughness while keeping an optimum side-wall angle profile that minimizes light propagation loss. In particular, our efforts are focused on three criteria: (1) selecting appropriate mask materials to reduce the transfer of mask defects into LN WGs, (2) establishing the optimal plasma chemistry by detailed study of various ICP-RIE etch parameters, and, (3) determining the optimum chemical cleaning protocol to remove the redeposited during ICP-RIE etch material on the WG’s side-wall. In this presentation, we discuss the details of all three fabrication aspects to make high-quality TFLN devices and structures.

Nanoscale Science and Technology Division
Room B113 - Session NS+2D+EM+MN+SS-TuM

Scanning Probe Microscopy

Moderators: Aubrey Hanbicki, Laboratory for Physical Sciences, **Fernando Castro**, National Physical Laboratory, U.K.

8:00am **NS+2D+EM+MN+SS-TuM-1 AVS Medard W. Welch Award Talk: Microscopy is All You Need: The Rise of Autonomous Science***, **Sergei Kalinin**[1],* University of Tennessee Knoxville **INVITED**

Making microscopes automated and autonomous is a North Star goal for areas ranging from physics and chemistry to biology and materials science – with the dream applications of discovering structure-property relationships, exploring physics of nanoscale systems, and building matter on nanometer and atomic scales. Over the last several years, increasing attention has been attracted to the use of AI interacting with physical system as a part of active learning – including materials discovery and optimization, chemical synthesis, and physical measurements. For these active learning problems, microscopy arguably represents an ideal model application combining aspects of materials discovery via observation and spectroscopy, physical learning with relatively shallow priors and small number of exogenous variables, and synthesis via controlled interventions. I introduce the concept of the reward-driven experimental workflow planning and discuss how these workflows can be implemented via domain-specific hyper languages. The applications of classical deep learning methods in streaming image analysis are strongly affected by the out of distribution drift effects, and the approaches to minimize though are discussed. The real-time image analysis allows spectroscopic experiments at the predefined features of interest and atomic manipulation and modification with preset policies. I further illustrate ML methods for autonomous discovery, where the microstructural elements maximizing physical response of interest are discovered. Complementarily, I illustrate the development of the autonomous physical discovery in microscopy via the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed. These concepts and methods can be extended from microscopy to other areas of automated experiment.

8:40am **NS+2D+EM+MN+SS-TuM-3 Dielectric Constant Measurement Sensitivity in Electrostatic Force and Force Gradient Microscopy-Based Modes***, **Gheorghe Stan,*** National Institute of Standards and Technology (NIST)*; C. Ciobanu,* Colorado School of Mines

Understanding of the nanoscale electrostatic interaction between a conductive atomic force microscopy (AFM) probe and a dielectric film is central to the operation of various nanoscale dielectric microscopies and determination of dielectric properties of the film. There is no simple analytical description of the electrostatic interaction generated in the confined probe-sample geometry of neither the static nor dynamic AFM modes used for dielectric measurements. An accurate description of the involved physics is obtained only by means of a finite element analysis modeling of the system. However, the alternative of using numerical analysis is not very popular being slower and requiring relatively high computation resources. In this work we revised the contributions from different parts of the AFM probe to the probe-sample capacitance by both analytical and numerical methods. We tried to reconciliate the two approaches and observed the differences as a function of geometry and material parameters. Under various noise levels, the efficiency of an analytical model was tested against finite element analysis that captures in detail the electrostatic interaction in AFM-based dielectric measurements. The investigation was performed in both spectroscopic force-distance curves and constant height scans with measurements for the deflection and frequency of the AFM probe. The obtained measurement sensitivities are relevant in selecting the optimal scanning mode and its operational parameters for given film thicknesses and dielectric constants but are also showing the critical role of the numerical analysis to the correct interpretation of the measurements.

9:00am **NS+2D+EM+MN+SS-TuM-4 Measuring and Understanding the Nanomechanical Properties of Halide Perovskites and Their Correlation to Structure***, I. Rosenhek-Goldian,* Dept. of Chemical Research Support, Weizmann Inst. of Science, Israel*; I. Buchine, N. Prathibha Jasti,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ., Israel*; D. Ceratti,* Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel & CNRS, UMR 9006, IPVF, Institut Photovoltaïque d'Ile-de-France*; S. Kumar,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ. Ramat Gan Israel. & Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel*; D. Cahen,* Bar-Ilan Inst. for Adv. Mater. and Nanotechnol & Dept. of Chem. Bar-Ilan Univ. & Dept. of Mol. Chem. & Materials Science, Weizmann Inst. of Science, Israel*; **Sidney R. Cohen,*** Dept. of Chemical Research Support, Weizmann Inst. of Science., Israel

Halide perovskites, HaP, and especially Pb-based ones exhibit a plethora of remarkable properties. Of these, their photovoltaic properties are the most widely studied due to the proven potential these materials hold for significant technological impact. In addition to photoresponse, this material class is characterized by interesting physical properties, of which mechanical properties enjoy special attention, not only because of potential use in flexible devices, but also from a fundamental science point of view. The mechanical response can shed light on the materials' behavior including dynamic processes and strain-related effects on optoelectronic behavior.

In the context of these studies, particular emphasis has been placed on environmental factors which can alter, especially degrade, material functionality and device performance. Exposure to humidity, light, and oxygen rank prominently amongst these factors.

In this study we measure the humidity influence on the mechanical properties, i.e., elastic modulus (E) and hardness (H), for two series of lead halide perovskite single crystals, varying either by cation or by anion type. Our conclusions are based on comparing results obtained from several different nano-indentation techniques, which separate surface modulus from that of the bulk, and probe different manifestations of the hardness. These studies reveal the different crystalline parameters governing influence of humidity on the mechanics at the surface and in the bulk.

An atypical inverse correlation between E and H was measured (as seen in the supplementary figure a). Furthermore, humidity influenced these two properties in opposite fashion – humidity exposure led to lower H, but to higher E (supplementary figure b). This trend is opposite to that found in most materials where hydration lowers both E and H. We suggest a link between dynamic disorder, self-healing, and the intriguing relation between E and H.

9:20am **NS+2D+EM+MN+SS-TuM-5 3D Nanoprinting of Advanced AFM Nano-Probes***, **Harald Plank**, M. Brugger-Hatzl, R. Winkler, L. Seewald,* Graz University of Technology, Austria

The demand for correlative microscopy is still increasing, as it enables a superior ensemble of information by using various methods to combine individual strengths. The highest level of that approach are hybrid microscopes, which enable individual characterization at the very same spot in a consecutive or even parallel way. With that, however, comes the demand of a conflict-free integration of different microscopes, which require a radical redesign of the instrumentation. A major step in that direction is a recently introduced dual system called FUSIONScope, which is a deeply integrated scanning electron microscopy (SEM) and atomic force microscopy (AFM) solution. While the former enables high-resolution guidance towards the region of interest, the latter complements SEM capabilities by true quantitative 3D surface information, which together exploit their full potential by the possibility to precisely land the AFM tip on highly exposed regions. Even more importantly, advanced AFM modes such as conductive AFM (CAFM), magnetic force microscopy (MFM), electrostatic / Kelvin force microscopy (EFM/KFM), scanning thermal microscopy (SThM) or mechanical mapping, provide functional information beyond SEM capabilities. For that, special nano-probes are required, which typically achieve their intended functionality by additional thin film coatings, which contains two main disadvantages. First, they increase the apex radii and limit the lateral resolution, which is in conflict with the still decreasing feature sizes. Secondly, coatings are prone to delamination during operation, which affects resolution, lateral correlation and reliability. Therefore, to exploit the full potential of advanced AFM modes, it is of great interest to develop new approaches for the fabrication of functional nano-probes. Following that motivation, we joined forces with industry and apply the additive direct-write technology focused electron beam induced

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[1] **Medard W. Welch Award Winner**

deposition (FEBID) for the development of novel 3D nano-probe concepts with industrial relevance. In this contribution, we briefly discuss the 3D nano-printing process and then go through a variety of advanced, FEBID-based tip concepts for CAFM, EFM, MFM and SThM. The joint element for all probes is the coating-free character, which eliminates the aforementioned risks during operation. Additionally, the apex regions are routinely in the sub-10 nm regime, which allows for high-resolution imaging. Aside of comparisons to traditionally used nano-probes, which reveal the superior performance of FEBID-based nano-tips, we discuss on currently ongoing research towards multi-functional AFM tips, based on FEBIDs flexibility.

11:00am **NS+2D+EM+MN+SS-TuM-10 Chemical, Mechanical, and Morphological Evolution of Nanostructures on the Surfaces of Asphalt Binders***, L. Lyu, J. Pei,* Chang'an University, China*; E. Fini,* Arizona State University*; L. Poulikakos,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; **Nancy Burnham**,* Worcester Polytechnic Institute

Bitumen (asphalt binder) holds roads together. It is a complex, dynamic, nanostructured material that comes from the bottom of an oil refinery stack—a non-renewable resource. It ages, and it ages more quickly under the influence of heat and light. Can additives made from waste materials increase the longevity of bitumen, and thus roads?

In this study, atomic force microscopy (topography, phase imaging, PF-QNM) and its combination with infrared spectroscopy (AFM-IR) were used to explore the chemical, mechanical, and morphological evolution of the surface of bitumen without and with additives. Aging is assumed to begin at the surface.

Samples of bitumen were made with and without introducing bio-modified rubber additives. Each sample was exposed to several thermal and UV aging protocols. Evolution of surface under aging was studied. Depending on the additive and type of aging (thermal, UV, or combined), the nanostructures changed their chemistry, mechanical properties, and size. Furthermore, the matrices and phases immediately surrounding the nanostructures evolved differently upon aging than the included nanodomains. In general, carbonyl and sulfoxide IR bands became more prevalent, the samples became stiffer and less adhesive, and the phase immediately surrounding the nanostructures became smaller. One additive made from two different waste materials was found to enhance the stability of the surfaces.

By understanding the evolution of asphalt binders and which additives promote their stability, longer lasting roads might be designed and built, thereby lowering the need for a non-renewable resource.

11:20am **NS+2D+EM+MN+SS-TuM-11 Identifying Potential Carbon Sources for Direct Carbon Material Production by AI Assisted HR-AFM***, **Percy Zahl**,* Brookhaven National Laboratory*; Y. Zhang,* ExxonMobil Technology and Engineering Company*; S. Arias,* Brookhaven National Laboratory

High-resolution Atomic Force Microscopy (HR-AFM) has proven to be a valuable and uniquely advantageous tool for studying complex mixtures such as petroleum, biofuels/chemicals, and environmental or extraterrestrial samples. However, the full potential of these challenging and time-consuming experiments has not yet been fully realized. To overcome these bottlenecks and enable further research into solutions for the energy transition and environmental sustainability, automated HR-AFM in conjunction with machine learning and artificial intelligence will be crucial [1].

In this study, we focus on identifying potential carbon sources suitable for more direct carbon material production by analyzing various pitch fractions based on their solubility in toluene. Specifically, we present the first comprehensive AI-assisted study of hydrocarbon fractions derived from petroleum and coal tar pitch, using and refining our previously introduced "Automated HR-AFM" tools. We explored four classes derived from Petroleum Pitch (PP) and Coal Pitch Tar (CPT), separated into toluene soluble (TS) and toluene insoluble (TI) fractions. Our analysis revealed differences in the structural characteristics of the molecules, which we binned based on the number of aromatic rings.

(Please see also the in our supplemental document included figures 1 and 2)

Overall, our results demonstrate the potential of automated HR-AFM and AI-assisted analysis for understanding complex mixtures and identifying potential carbon sources for direct carbon material production. This work represents an important step towards more sustainable and environmentally-friendly energy solutions.

Reference:

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11:40am **NS+2D+EM+MN+SS-TuM-12 Automated Microscopy for Physics Discovery: From High-Throughput to Hypothesis Learning-Driven Experimentation***, **Yongtao Liu**, R. Vasudevan, M. Ziatdinov, S. Kalinin,* Oak Ridge National Laboratory

In this work, we explore the ferroelectric polarization switching in relation to the applied pulse bias including bias voltage and time in scanning probe microscopy (SPM). We perform two types of automated and autonomous experiments. First, we conduct automated high-throughput experimentation to gain a comprehensive understanding of the relationship between pulse biases and ferroelectric domain growth. Second, we employ an autonomous experimentation driven by machine learning (ML) algorithm to optimize experimental conditions based on real-time experiment results.

SPM has proven to be a powerful tool for manipulating and visualizing ferroelectric domains at the nanoscale. Investigations of ferroelectric domain size and stability can advance our knowledge of ferroelectrics application in memory devices, such as operating time, retention time, and bit size. However, conventional SPM measurements have been time-intensive and dependent on experienced researchers to perform repetitive tasks and make real-time decisions regarding measurement parameters. For example, researchers determine and manually tune the parameters for next iteration of experiment according to the previous results.Here, we perform automated and autonomous experiments in SPM to explore the mechanism of ferroelectric polarization. The first experiment is a high-throughput experiment of applying various bias pulse conditions to write ferroelectric domains followed by imaging domain structure using piezoresponse force microcopy. In this automated experiment, we systematically adapt the bias pulse parameters to gain a comprehensive understanding of their relationship with the resulting domain structures. We discovered different polarization states that show up upon different bias conditions. In the second experiment, we implement a hypothesis active learning (HypoAL) algorithm based on structured Gaussian process to control the SPM for ferroelectric domain writing. The HypoAL analyzes the relationship between the bias pulse conditions and the written domain size in real-time experiments, and determines the bias pulse parameters for the next iteration. The goal of HypoAL is to establish the best physical hypothesis for the material's behaviour within the smallest number of experiment step.The HypoAL identifies that the domain growth in a $BaTiO_3$ film is governed by kinetic control. The approaches developed here have the potential to be extended to other experiments beyond SPM in the future to accelerate the discovery of new materials and advances in physics.

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 $\sim 10^7$ cells/mL. Our results demonstrate how mass-produced diffraction gratings can be used as low-cost detection systems for the continuous detection of contamination in liquids, opening the door for autonomous monitoring for a range of different applications.

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

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

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

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

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

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

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

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

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

References

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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.

[1] Park, et al. „Recent Advances of Point-of-Care Devices Integrated with Molecularly Imprinted Polymers-Based Biosensors: From Biomolecule Sensing Design to Intraoral Fluid Testing". Biosensors 12, Nr. 3 (22. Februar 2022): 136. https://doi.org/10.3390/bios12030136.

Nanoscale Science and Technology Division
Room B113 - Session NS1+2D+EM+MN-TuA

Nanofabrication and Characterization of Low-Dimensional Materials

Moderator: Georg Fantner, EPFL

2:20pm **NS1+2D+EM+MN-TuA-1 Atomic-Scale Design and Defect Networks at the 2D/3D Interface*, Kate Reidy*,** MIT **INVITED**

'Mixed dimensional' 2D/3D van der Waals heterostructures, where 3D metallic nanostructures are integrated with suspended two-dimensional (2D) van der Waals materials, show unique functionalities including light-matter coupling, charge transfer, and enhanced catalytic activity. To enable such integration, an understanding of how structure and defects at the 2D/3D interface affect heterostructure properties is required. Moreover, 2D/3D heterostructures display fluctuations of opto-electronic properties in nanometer spatial range; and it is advantageous to probe position-dependent properties at the same spatial scales. In this seminar, I will share work exploring the local properties of the 2D/3D interface using a combination of atomic resolution scanning transmission electron microscopy (STEM), in situ ultra-high vacuum (UHV) TEM, and monochromated high-energy resolution electron energy-loss spectroscopy (EELS). We demonstrate epitaxial, single-crystalline metallic nanoisland growth of technologically relevant metals (Au, Ti and Nb) with with ultra-low defect density interfaces and facetted morphologies on several thin suspended 2D materials. We then explore the key parameters of 2D/3D growth, including the role of temperature, defects, moiré, surface chemistry, and thermodynamic equilibrium shapes. Lastly, we fabricate more complex heterostructure stacks with defect densities controlled by the compliance of the 2D material substrate. Through fundamental understanding of the structure-property-performance relationship, we suggest that future electronic, magnetic, and optical nanodevices will utilize versatile fabrication of 2D/3D heterostructures with well-characterized interfaces and morphologies.

3:00pm **NS1+2D+EM+MN-TuA-3 Highly Asymmetric Doping of Epitaxial Bilayer Graphene by Targeted Bonding of the Intercalated Gadolinium*, Marek Kolmer,*** Ames National Laboratory*; J. Hall,* Ames National Laboratory and Department of Physics and Astronomy, Iowa State University*; S. Chen, M. Tringides,* Ames National Laboratory, Department of Physics and Astronomy, Iowa State University

Heterostructures consisting of vertically stacked two-dimensional (2D) materials have recently gained large attention due to their highly controllable electronic properties. Particularly, mechanically stacked multilayered systems offer exceptional control over a stacking sequence or interlayer twist angles. On the other hand, epitaxially grown 2D materials express unprecedented quality and stability over wafer-scale lengths. In both cases controlling the interlayer coupling can generate novel electronic and topological phases and its effective implementation is commonly done with a transverse electric field. However, phases generated by high displacement fields are elusive.

Here, we introduce an exceptionally large displacement field by structural modification of a model system: AB-stacked epitaxial bilayer graphene (BLG) on a SiC(0001) surface. We show that upon intercalation of gadolinium with two specific interlayer locations, electronic states in the top two graphene layers exhibit a significant difference in the on-site potential energy (~1 eV), which effectively breaks the interlayer coupling between them. As a result, for energies close to the corresponding Dirac points, the BLG system behaves like two electronically isolated single graphene layers. We prove this fact by a comprehensive multi-technique methodology based on low-temperature scanning tunneling microscopy/spectroscopy (STM/S) and angle-resolved photoelectron spectroscopy, which are corroborated by density functional theory, tight binding, surface diffraction and multiprobe STM transport. The work presents charge transfer from intercalated metal atoms as a promising approach for the synthesis of 2D graphene heterostructures with electronic phases generated by giant displacement fields.

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4:20pm **NS1+2D+EM+MN-TuA-7 AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient Talk: Exfoliated 2D Nanosheets for Large-Area, Solution-Processed Optoelectronics*, Lidia Kuo*[1]***, S. Rangnekar, V. Sangwan, M. Hersam,* Northwestern University

Two-dimensional (2D) materials exhibit thickness-dependent optoelectronic properties due to their atomically thin nature, unlike their bulk layered crystalline counterparts. In particular, semiconducting MoS_2 undergoes an indirect to direct bandgap transition as the thickness is decreased to the monolayer limit, leading to enhanced optical absorption and emission at the atomically thin scale. Liquid-phase exfoliation (LPE) is a scalable and cost-effective method for obtaining 2D materials from bulk crystals. However, the yield of monolayer sheets by LPE has been impractically low in previous work. The resulting LPE-processed optoelectronic devices have fallen short compared to nanosheets derived from mechanical exfoliation or chemical vapor deposition. Here, we demonstrate that LPE coupled with megasonic exfoliation – i.e., processing at megahertz frequencies compared to the kilohertz frequencies commonly utilized for LPE – yields an unprecedentedly high fraction of monolayer MoS_2. As a result, megasonic exfoliation enables ultrahigh responsivity in printed MoS_2 photodetectors as well as the first demonstration of electroluminescence for large-area, solution-processed MoS_2 films. This work establishes megasonic exfoliation as a scalable and generalizable approach for achieving optoelectronic-grade 2D semiconductors via LPE.

Nanoscale Science and Technology Division
Room B113 - Session NS2+2D+EM-TuA

Light-Matter Interactions at the Nanoscale

Moderator: Nancy Burnham, Worcester Polytechnic Institute

4:40pm **NS2+2D+EM-TuA-8 Highly Tunable Room-Temperature Exciton-Polariton Strong Coupling from Monolayer Wse_2 in Nanocavities***, P. Schuck, **Thomas Darlington,*** Columbia University **INVITED**

In the interaction of light and matter, strong coupling occurs when exchange between a photon and electronic transitions exceeds the relative loss rate leading to hybridization of the optical and electronic states. The behavior is well known in cavity quantum electrodynamics (QED), and is a fundamental ingredient in single photon quantum logic gates. In solid-state systems, many strong coupling phenomena have been explored between different material excitations. Plasmons in particular have attracted great interest owing to their small mode volumes, allowing for strong coupling of a plasmon and single quasi-particles excitations such as excitons, potentially recreating in the solid-state, at the nanoscale, and at elevated temperatures many of the phenomena previously studied in traditional trapped atom QED.

Here, I describe our investigations of strong coupling between TMD excitons and a tunable plasmonic nanocavity formed between a plasmonic tip and gold substrate. Strong coupling between plasmons and excitons has been observed in excitons systems: e.g., J-aggregates, and colloidal quantum-dots. While these systems offer large coupling strengths, the exciton transition energies are largely fixed, and vary randomly depending on variations in growth conditions. By contrast, TMDs offer strong exciton emission and large tunability of exciton energy by applied strain. We utilized this tunability to control coupling strengths in nanocavities in a proof-of-principle nano-electro-mechanical system (NEMS) platform, demonstrating the ability to continuously tune, between weak and strong coupling conditions where we observe both upper and lower polariton bands.

5:20pm **NS2+2D+EM-TuA-10 Surface Plasmon Characterization in Ag Nanotriangles for Evaluation of Fano Resonance Conditions*, Nabila Islam,*** Department of Physics, Portland State University*; R. Word,* Department of Physics, Portland State University, Portland, Oregon*; E. Abdul, S. Rananavare,* Department of Chemistry, Portland State University*; R. Könenkamp,* Department of Physics, Portland State University

Surface plasmon resonances in metal nanostructures allow confinement of the electromagnetic field well below the light diffraction limit and have

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[1] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

attracted research interest for a broad range of sensing applications [1]. The comparably broad spectral width of surface plasmon based sensors can be improved by coupling the plasmon resonance to other resonances to generate Fano resonances with the distinctive and sharp asymmetric Fano line-shape. We used photoemission electron microscopy to explore the spectral and spatial behavior of plasmon resonances in structures consisting of a single nanoscale triangular platelet on a substrate providing coupling to a waveguide layer or to an optically active excitonic layer. In our experiments stationary and propagating surface plasmons are optically excited in the nano-triangle at wavelengths around 820-900nm, and multi-photon electron-emission is used to obtain images of the lateral surface plasmon distribution. An aberration-corrected photoemission microscope allowed us to obtain a spatial resolution of ~15nm and a femtosecond pulsed Ti-sapphire laser provided the photon intensities needed for the 3-photon photoemission imaging process [2]. The analysis of the obtained images is done in optical simulations of the same experimental set-up and by calculating the plasmon electric field distribution which is then used to analyze and interpret the photoemission micrographs. The analysis allows to identify the prominent surface plasmon modes and to analyze their interaction to form stationary resonance patterns and propagating modes. Fano-resonances are established in the simulation by placing the triangles in the vicinity of an optical waveguide using an appropriate spacer layer [3]. The simulation then allows to optimize this type of arrangement and to determine locations where the Fano-resonance amplitudes are most pronounced. Simulations of this kind were also applied to the case of gold triangles on substrates provided with exciton and spacer layers. Our results indicate that both the high plasmon field strengths typical for single nanoparticle structures and the sharp spectral features available in Fano-resonances can be combined in these single nano-particle structures, thereby allowing improved resolution in sensor applications.

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5:40pm **NS2+2D+EM-TuA-11 Interconnected Plasmonic Nanogap Antennas for Photodetection via Hot Carrier Injection***, **John Grasso**, R. Raman, B. Willis,* University of Connecticut

Modern integrated circuits have active elements on the order of nanometers; however, optical devices are limited by diffraction effects with dimensions measured in wavelengths. Nanoscale photodetectors capable of converting light into electrical signals are necessary for the miniaturization of optoelectronic applications. Strong coupling of light and free electrons in plasmonic nanostructures efficiently confines light into sub-wavelength volumes with intense local electric fields. Localized electric fields are amplified in nanogap regions between nanostructures where enhancements can reach over 1000. Hot carriers generated within these high field regions from nonradiative decay of surface plasmons can be injected into the conduction band of semiconductors at room temperature, enabling sub-bandgap photodetection. The optical properties of these plasmonic photodetectors can be tuned by modifying antenna materials and geometric parameters like size, thickness, and shape. Electrical interconnects provide connectivity to convert light into electrical signals. In this paper, we will describe the optical properties of plasmonic nanostructures with electrical interconnects and compare experiment and theory using finite-difference time-domain (FDTD) simulations. We will present experimental extinction data and FDTD simulations to elucidate how geometric structure and dielectric properties influence optical properties. We will present sub bandgap photodetection for nanostructures integrated with ALD deposited TiO_2, and investigate both wavelength and polarization dependence. We will also discuss how plasmonic heating effects contribute to photocurrent generation. These plasmonic nanogap antennas are subwavelength, tunable photodetectors with sub-bandgap responsivity for a broad spectral range.

Nanoscale Science and Technology Division
Room Oregon Ballroom 203-204 - Session NS-TuP

Nanoscale Science and Technology Poster Session

NS-TuP-1 AVS Dorothy M. and Earl S. Hoffman Awardee Talk: Scalable and Sustainable Synthesis of ZnO Nanowires via Hot Water Treatment for Photocatalytic Applications*, **Ranjitha K. Hariharalakshmanan**[1], F. Watanabe, T. Karabacak,* University of Arkansas at Little Rock

There is growing interest in developing cost-effective and sustainable methods to synthesize photocatalysts that can be immobilized on substrates. In this study, we present a novel and ultra-scalable method for synthesizing ZnO nanowires that are immobilized on the surface of Zn plates using a hot water treatment (HWT) technique. This straightforward synthesis method involves immersing Zn coupons in deionized water at 75 °C without any chemical additives or precursors. SEM, TEM, EDS, XRD, XPS, and UV-Vis spectroscopy analysis on the surface of Zn after 5 hours of HWT showed the formation of well-developed, hexagonally-faceted, stoichiometric, and crystalline ZnO nanowires with a bandgap of 3.26 eV. To evaluate the photocatalytic activity of these ZnO nanowires, we performed methylene blue degradation tests under UV light. 93% of methylene blue was degraded in 120 minutes with a reaction rate constant of 0.021 min^{-1}. Overall, our findings demonstrate the potential of HWT as a scalable and environmentally-friendly method for synthesizing ZnO nanostructures with excellent photocatalytic properties.

NS-TuP-2 Nanopore Arrays Patterned by Thermal Scanning Probe Lithography for Electrochemical Biosensing*, **Ken Bosnick**, J. Canlas, E. Kamali,* National Research Council of Canada

The use of nanopore arrays for electrochemical sensing represents an exciting avenue for improved detection of biomolecules. Through chemically modifying the nanopore arrays, sensitive and selective platforms can be engineered that exploit a transport-modulation-based amplification, whereby one analyte molecule can block multiple electrochemical reporter molecules [1]. This poster will report on the fabrication of such nanopore arrays using thermal scanning probe lithography in ultrathin dielectric layers on electrochemically active conductors (e.g., ALD SiO_2 on ITO).

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NS-TuP-3 Tunable Gold- and Aluminum-Nanocrescents as a Platform for Circular Dichroism Spectroscopy*, **Anh Nguyen**,* University of Utah

Gold (Au) has been a common material for plasmonic nanostructures studies. Although aluminum (Al) has several advantages over gold and is a promising material for nanoscience studies, the complication of the ubiquitous alumina film in Al nanostructures’ fabrication limits its use. With the copper mask nanosphere template lithography fabrication method, our group has successfully fabricated both Au- and Al-nanocrescents (NCs) despite the challenges that arise from the native oxide layer of Al. Both Au- and AlNCs exhibit multimodal, polarization-dependent plasmons that can be tuned in different spectral regions. However, AuNCs' plasmon resonances are red-shifted compared to AlNCs due to the difference in surface properties. Moreover, chiral plasmonics is recently an area of particular interest in the rich and diverse field of plasmonic nanostructure studies. The fundamental focus of chiral plasmonics is to probe the difference in the nanostructures' ability to absorb left vs. right circularly polarized light. Au- and AlNCs have shown the properties of extrinsic chiral nanostructures, which have CD response when titled to out-of-plan incident angles with respect to the incident circularly polarized light. At $\theta=\pm30^\circ$ out-of-plane incident, the Au- and AlNCs' true CD responses are equal in ellipticity but opposite in handedness. In addition, the Au- and Al-NCs exhibit the opposite chiral response when rotated 180°relatives to the sample's orientation at $\theta=\pm30^\circ$. There is no handedness response for true CD of both Au- and AlNCs at normal incidence, which confirms the extrinsic chiral optical properties of the system. Conversely, there is negligible handedness response for the birefringence of Au- and Al-NCs at both normal and out-of-plane incident angles. These optical phenomena define that the nanocrescents system is an isotropic orientation averaging where there is little to no change in the original substrate surface forward/backward CD response as well as exhibits true CD behavior. These results have produced novel insight into understanding the chiral optical and resonant plasmonic support in nanostructures and opens further investigation into the use of Au- and Al-nanostructures in sensing and detection.

NS-TuP-4 Towards Artifact-Free Atomic Force Microscopy Images*, **Nancy Burnham**,* Worcester Polytechnic Institute*; L. Lyu,* Chang'an University, China*; L. Poulikakos,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Atomic force microscopy (AFM) is based upon a simple operational principle. However, the presentation and interpretation of AFM images can easily suffer from consequential artifacts that are easily overlooked. Here we discuss results from AFM and its companion variations PF-QNM (peak-force quantitative nano-mechanical mapping) and AFM-IR (AFM combined with infrared spectroscopy) by imaging “bee” structures in asphalt binder (bitumen) as examples. We show how common problems manifest themselves, with the intent that authors can present their results clearly and avoid interpreting artifacts as true physical properties, thereby raising the quality of AFM research.

NS-TuP-5 Probing Metal Substrate Effects on the Adsorbate Conformations of a Nonplanar Tetrabenzoporphyrin Molecule by Ultra-high Vacuum Tip-Enhanced Raman Spectroscopy*, **Soumyajit Rajak**, N. Jiang, D. Liu, L. Li,* University of Illinois - Chicago

Tetrabenzoporphyrin molecules are one of the most widely studied model biomolecules in organic optoelectronics for modern-age electronic device applications and catalysis. Opto-electronic properties in the nanoscale are controlled by the local nanostructures of a molecular arrangement. The local nanostructures are determined by the real-space molecular conformations. It is really challenging to determine the real-space surface adsorbed conformations of a molecule using ensemble-averaged surface science techniques. The molecular structure and the 2-dimensional crystalline arrangements of the tetrabenzoporphyrins are primarily defined by the symmetry of the porphyrin molecule and the steric and electronic nature of the groups linked at meso-positions and β-positions of the ring. The flexibility of the σ-bonded peripheral groups in the meso-positions can induce dynamic behavior in the porphyrin molecule and may give rise to different binding configurations on different metal substrates or sometimes even on one substrate. Herein we present a combined topographical and chemical analysis of different surface-adsorbed conformations and surface-sensitive arrangements of a symmetric tetrabenzoporphyrin molecule using angstrom-scale resolution scanning tunneling microscopy (STM) and ultra-high vacuum tip-enhanced Raman spectroscopy (UHV-TERS). Low temperature (77K) scanning tunneling microscopic images and localized surface plasmon resonance enhanced Raman signals reveal different adsorbate conformations of single molecule entities and a fundamental view of adsorbate-substrate binding interactions.

NS-TuP-6 Studies of Chemistry and Materials Approaching the Atomic Scale with Cryogenic Ultrahigh Vacuum Scanning Near-Field Optical Microscopy Methods*, **Jeremy F Schultz**,* National Institute of Standards and Technology (NIST)*; L. Li, S. Mahapatra, N. Jiang,* University of Illinois Chicago*; A. Centrone,* National Institute of Standards and Technology (NIST)

Optical spectroscopies can be used to probe and characterize the composition as well as the physical and electronic structure of molecules and materials. By confining light-matter interactions into the near-field of a scanning probe microscope (SPM) the diffraction limit of light can be circumvented and the resulting measurements can consider composition and subtle local phenomena down to the nanoscale. In ultrahigh vacuum (UHV) and at cryogenic temperatures the spatial resolution of these methods can be pushed towards the atomic scale.

Scanning tunneling microscopy (STM) and tip-enhanced Raman spectroscopy (TERS) were used to investigate the behavior and chemistry of molecular adsorbates with surfaces. Spectroscopic imaging provides the ability to visualize highly localized phenomena, while vibrational fingerprints can be used to understand their effects on a molecule’s or material’s structure. This yields insight into adsorbate-substrate interactions crucial to the growth of nanostructures through surface chemistry, as well as the functionalization or modification of 2D materials.

Moving beyond UHV-STM-TERS, ongoing work focuses on the development of a new versatile cryogenic UHV-SPM platform for other measurements of light-matter interactions, specifically STM-induced luminescence (STML) and coupling pulsed infrared light into the tip-sample junction. STML leverages the atomically sharp STM tip as a probe to locally excite light emission and captures spectra that can be used to characterize excitonic

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[1] **AVS Dorothy M. and Earl S. Hoffman Awardee**

behavior and vibronic structure. On the other hand, many relevant quantum phenomena occur in the infrared regime, which remains relatively unexplored with atomic scale near-field microscopy. Together, these capabilities are expected to result in a platform capable of studying properties of materials that would otherwise be inaccessible.

NS-TuP-7 Novel Air Spacer Technology for Parasitic Bit-Line Capacitance Reduction*, **Dongmin Han,*** Department of Semiconductor and Display Engineering The Graduate School Sungkyunkwan University, Republic of Korea*; B. Choi,* Department of Electrical and Computer Engineering, Sungkyunkwan University, Republic of Korea

In this study, a novel air spacer using plasma nitridation (PN) technique for dynamic random acess memory (DRAM) device is investigated to minimize parasitic bit-line capacitance (Cb). The ratio of Cb to cell capacitance (Cs) is increasing due to smaller cell size. Thus, DRAM development faced great difficulties due to the decrease in bit-line sensing margin [1]. The Cb/Cs is a key factor in determining the bit-line sensing margin. In addition, Cs is expected to continue to decrease due to the physical limitations of cell capacitor technology, so technology that can lower Cb has become a key technology [2]. 20nm DRAM developed bit-line air spacer technology and greatly improved Cb [1]. However, Cb still needs additional improvements due to the continued reduction in bit-line spacer dimension. We improved the Si3N4 transition layer by using the plasma nitridation techniques before the deposition of the outer Si3N4 film. The pre-plasma nitriding treatment process forms an inter-diffusion and additional protective layer and improves the surface properties of the deposited film [3]. We used this technology to the air spacer. As shown in figure 1, it was expected to maximize the air layer thickness formed in the subsequent process by reducing the thickness of the transition layer formed during outer Si3N4 deposition. The Cb was measured using the test element group, which can measure air spacer pattern and non-air spacer pattern. the Cb improved by 2%, as shown in figure 2. It is considered that the portion of air thickness is increased through surface transition layer improvement. This is a simple and innovative approach to improve the characteristics of DRAM. This study proposed a new direction to improve the Cb/Cs Characteristic for a sub 20 nm DRAM device.

Reference

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NS-TuP-8 Understanding Interaction Forces at Silicon Wafer Interfaces to Optimize Nanoscale Cleaning Processes*, D. Miano,* CEST GmbH, Austria*; L. Palla, A. Seltenhammer,* TU Wien, Austria*; **Pierluigi Bilotto,*** CEST GmbH, Austria*; B. Loidl, S. Garvey,* Lam Research Corp., Austria*; M. Valtiner,* TU Wien, Austria

Miniaturization of electronics at the wafer surface is a possible answer to the growing demand of fast, cheap, and environmentally friendly devices. This strategy arises a question on how nanometer size particles, which could impact the yield of nanoscale electronics, could be removed from the wafer surface. The current state-of-the-art in wafer cleaning processes is based on subsequents streams of solvents (e.g., mega-sonic cavitation[1]) on rotating disks,[2] but such protocols can alter the surface to a level which is significant for nanoscale electronics, and do not affect nanoscale level particles. More than ten years ago, it was discussed that surface nanobubbles can remove nano particles,[3] but the understanding is still limitated to a qualitative description of the phenomenon.
In this project, we aim to shed light on the interaction between surface nanobubbles and nanoparticles, in order to finally clarify the physical-chemical interaction at the interface which can lead to a nanoscale-cleaning-process.
In this poster, I will show our innovative design of a microfluidic system applied to an atomic force microscope.
We utilize thiol functionalization to define model systems and mimic the different interaction forces, explaining according to the DLVO theory, and that might take place onto a wafer surface during its industrial cleaning process.
In parallel we also cover with different size nanoparticles our surfaces, that should reproduce the possible impurity of a real Si surface, we study if it is possible to use the solvent exchange for remove these objects and we try to understand how to implement the cleaning process protocol. I will display our results and comments on what are the possible key elements participating in the nanoscale-cleaning-process.
The finding of this work are not only relevant from a fundamental point of view, but have a clear industrial application which is why we collaborate with top industrial partners in the field of semiconductor and wafer cleaning.

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NS-TuP-9 The Design of Thermal Cloak Using Nanoporous Thin Films*, **Yue Xiao,*** Advanced Cooling Technologies, Inc.*; Q. Chen, Q. Hao,* University of Arizona

In recent years, nanoporous thin films are widely studied as an effective way to manipulate the thermal transport within thin-film-based devices. In practice, nanoporous patterns can effectively cut off the heat flow and thus guide the thermal transport along the desired direction. However, a better design of these thermal devices is not addressed, such as thermal cloaking as the thermal counterpart for optical invisibility cloaks. In existing designs based on the Fourier's law, composite materials with varied structures are often introduced to achieve the required location-dependent thermal conductivities to distort the heat flux. At the micro-to nano-scale, such designs are difficult to be implemented and factors such as the interfacial thermal resistance must be further considered. In this work, inverse thermal designs of a nanoporous material are used to achieve the thermal cloaking effect for 2D materials or 3D thin films, without introducing any other variation of the composition or material to tune the local thermal conductivity. This simple approach can be widely used for thin-film-based devices to protect heat-sensitive regions or function as thermal camouflaging devices. The proposed nanoporous structures can also be used to tune the local properties of a thin film for general applications, such as graded thermoelectric materials.

NS-TuP-11 Control and Manipulation of Superconducting Vortex Lattices from Nano to Mesoscales*, S. Song, J. Yan,* Oak Ridge National Laboratory*; W. Ko,* University of Tennessee Knoxville*; E. Dumitrescu, G. Halasz,* Oak Ridge National Laboratory*; H. Fangohr,* Max Planck Institute for Structure and Dynamics of Matter, Germany*; C. Ha, B. Lawrie, **Petro Maksymovych,*** Oak Ridge National Laboratory

When a magnetic field larger than a lower critical field is applied to a type-II superconductor, magnetic fluxes will pass through the volume of the superconducting material, creating a vortex state. Vortices exhibit a rich structural diagram, with the possibility of vortex liquid, glass, and lattice states determined by the material properties and external parameters. On a fundamental level, single and few vortex manipulation opens a pathway to understand vortex properties and to tailor their dynamics to prospective applications in quantum computing.

We will discuss two experiments using scanning tunneling microscopy (STM) which demonstrate direct control over vortex positions in FeSe superconductor. First, we observed that the twin boundary in the FeSe superconductor traps a relatively high density of vortices and acts as a barrier that aligns the vortices on the terrace parallel to the twin boundary. The alignment effect causes various phases of vortex lattice structures such as rectangular and one-dimensional vortex lattices – both with ordering qualitatively different from the commonly observed vortex glass. The analysis of these interactions also reveals further clues regarding vortex dynamics, inter vortex interaction, and vortex pinning, and directly points to strain fields as possible effective approach for accurate control over vortex structures. Second, we found that the vortex shape can be controllably varied with the imaging conditions in STM, particularly at the extreme limit of very large local current density. We attribute the observations as direct evidence of vortex manipulation, by contrasting the behaviors of various types of vortices in proximity to twin boundaries on FeSe. Altogether we suggest that precise control over the high tunneling current, combined with specific structural topological defects, can translate into an effective strategy for vortex manipulation approach without destruction of the superconducting state, enabling STM to become a quantitative nanoscale probe of vortex dynamics and a platform to explore vortex manipulation in the context of topological quantum computing.

Work supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. Experiments were carried out as part of the user project at the Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, which is a US Department of Energy Office of Science User Facility.

S. Y. Song, C. Hua, L. Bell, W. Ko, H. Fangohr, J. Yan, G. B. Halász, E. F. Dumitrescu, B. J. Lawrie, P. Maksymovych, *Nano Lett.*23(2023)2822.

NS-TuP-12 Exploring the Complex Chemistry and Degradation of AscorbicAcid in Aqueous Nanoparticle Synthesis*, **Debashree Roy**, L. Moreau,* Washington State University

While ascorbic acid (AA) has been the ubiquitous choice as a mild reductant in the aqueous synthesis of noble metal nanoparticles (NPs), its role beyond the reducing powers has been mostly overlooked. Despite the fact that reduction kinetics of metal salt precursors are most susceptible to modifications by reducing agents, it has frequently been relegated to concentration and pH variations for AA, without delving into the more complex chemistry associated with the latter. The mechanism behind AA-mediated reduction is often stymied by an oversimplified presentation in literature wherein the diprotic acid is assumed to undergo consecutive oxidations via a radical intermediate to form dehydroascorbic acid (DHA). In reality, these assumptions may not accurately describe the aqueous behaviour of AA in a wide array of synthetically relevant conditions.

We show that facile degradation of ascorbic acid has considerable impacts on the formation and properties of aqueous silver NPs and discuss implications for the use of ascorbic acid in NP synthesis. Briefly, experimental evidence shows that the alkaline degradation of AA at no point converges to yield DHA, which follows an independent degradation pathway altogether. While DHA at different stages of degradation consistently results in the formation of spherical/quasi-spherical Ag NPs, it is interesting to note that AA aged for > 12h gives rise to anisotropic plate-like morphology, furthering the hypothesis that a different degradation pathway is followed for both. The role of various plausible degradation products has been additionally studied to inform AA's assumed behaviour in NP synthesis. These findings have profound implications for the understanding of AA in NP systems, and the mechanisms behind its role as a reductant and surfactant.

NS-TuP-13 Exploiting Mixed-Dimensionality in Hybrid Van Der Waals Heterostructures*, **Emanuele Orgiu,*** Institut National de la Recherche Scientifique / University of Quebec, Canada

2D Quantum Materials are held together by weak interplanar van der Waals (vdW) interactions. The incorporation of molecules in such materials holds an immense potential to understand and modify the fundamental physical properties of the pristine materials while creating new artificial materials. Whilst nature offers a finite number of 2D materials, an almost unlimited variety of molecules can be designed and synthesized with predictable functionalities. The possibilities offered by systems in which continuous molecular layers are interfaced with inorganic 2D materials to form hybrid organic/inorganic van der Waals heterostructures (H-vdWH) are emphasized. Similar to their inorganic counterpart, the hybrid structures have been exploited to suggest novel device architectures. Moreover, specific molecular groups can be employed to modify intrinsic properties and confer new capabilities to 2D materials. In particular, I will highlight how molecular self-assembly at the surface of 2D materials can be mastered to achieve precise control over position and density of (molecular) functional groups, paving the way for a new class of hybrid functional materials.

In particular, I will show how the presence of ordered supramolecular assemblies bearing different functional groups can modify the pristine Shubnikov-De Haas oscillations [1] occurring in graphene or tune the magnetoresistance in a given transition metal dichalcogenide [2].

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NS-TuP-14 Circuit-Level Device Modeling for Framework Analyzing Hot Carrier Injection Failure in Gate-All-Around (GAA) Charge Trapping Flash (CTF) Memory Devices Based on New Experimental Methodology*, **Sunghwan Cho,*** Samsung Electronics Co., Inc., Republic of Korea

To overcome the limitation of conventional planar flash memory in scaling down, gate-all-around (GAA) charge trapping flash (CTF) memory gradually become the most promising alternative due to remarkably larger storage and less disturbance. However, as stacking more layers vertically and getting smaller in feature size, it is inevitable that device failures attributed to interference or leakage such as band-to-band tunneling (BTBT) and hot carrier injection (HCI) increase rapidly. Furthermore, a suitable framework to analyze failure mechanisms and optimize design by using circuit simulation is insufficient. In this paper, we proposed circuit-level device modeling as a framework focused on HCI failure analysis in GAA CTF, which is achieved by establishing new method in measuring HCI effect and optimizing model parameters by derived formula. As shown in Fig. 1, threshold voltages in non-programmed memory cell can be increased unexpectedly by HCI effect, which results in critical failure and degradation of performance. In conventional junction-less GAA CTF memory devices, electrons generated by BTBT in a large gap in boosted channel potential and high electric field in vertical direction contribute to HCI effect. As a result, circuit-level modeling for accurate calculation of boosted channel potential and determination of gate voltages in a cell string is essential in analyzing HCI effect. Fig. 2(a) and (b) illustrate single modeling structure and equivalent circuit attaching voltage-controlled-current sources which execute essential current flow in GAA CTF such as Fowler-Nordheim (FN) tunneling, BTBT and HCI leakage by using derived formula in our work. By connecting single modeling units serially as shown in Fig. 2(c), circuit-level modeling structure with a cell string unit is proposed which makes prediction of boosted channel potential and BTBT/HCI current more accurate. Fig. 3 presents mechanisms of HCI in the proposed experimental method. Since the amount of HCI leakage is determined by 2 dominant conditions which are potential difference in lateral direction generating BTBT and electric field in vertical direction, we separated 2 measurement conditions, as shown in Fig. 3(a) and (b), to extract model parameters compactly by breaking down 2 terms. Furthermore, since HCI failure commonly occurs at the end of channel, we enhanced experimental progress by measuring near gate select line (GSL) transistor, as shown in Fig. 3(c). Finally, the fitting results show good agreement with experimental data, as shown in Fig. 4, which means the proposed model would equip circuit designer of GAA CTF by analyzing failure mechanism and optimizing the performance.

NS-TuP-15 Statistic Analysis of Nanoscale Tunneling Electrical Contacts Based on Transmission Line Model*, **Bingqing Wang**, P. Zhang,* Michigan State University

The rising interest in innovative electronic circuits utilizing low-dimensional materials, like carbon nanotubes (CNTs), has made nanoscale contact engineering increasingly important. This study investigates the influence of contact resistances between carbon nanotubes (CNTs) on electron transport and electrical conductivity of carbon nanofibers (CNFs), which profoundly impacts the performance of CNT thin film field effect transistors (FETs)[1]. Utilizing a self-consistent contact model, we integrate a transmission line model with tunneling current model [2] to calculate the plethora of parallel CNT-CNT contacts within individual fibers. A statistical analysis is conducted, using Gaussian distributions to account for variations in contact lengths, gap distances, and single CNT aspect ratios, and producing data on CNT-CNT contact resistance and the overall resistance of CNT fiber. By scaling our model to a macroscopic level, our results are in significant alignment with experimental measurements [3]. Our calculation suggests that while increasing overlap length diminishes individual CNT-CNT contact resistance, it paradoxically increases macroscopic CNT fiber resistance, given a constant CNF mass density. Similarly, greater gap distance also increases both individual and fiber resistance. This research provides a tool for exploring CNT fiber electrical properties, promoting advancement in low-dimensional material-based electronic circuit development. Future work could leverage machine learning for establishing the correlations between different parameters and identify the optimal parameter values that most accurately represent the experimental results.

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* Work is supported by the Air Force Office of Scientific Research (AFOSR) Award No. FA9550-22-1-0523.

NS-TuP-16 Instrumentation of Ptychographic Microscopy at the Atomic Scale*, **Chien-Nan Hsiao**, F. Chen,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan*; T. Chung,* Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Taiwan*; C. Chen,* Department of Engineering and System Science, National Tsing Hua University, Taiwan

Ptychographic electron microscopy at atomic-scale resolution had been established. A hybrid pixelated detector and remote controlled electron beam scanning coil were integrated on an aberration corrected scanning transmittance electron microscopy with a circular C2 aperture of 10 µm. Experimental results shown that the 128×128 steps of electron probe interval (1 Å) in real space with the size of each diffraction pattern is 512×512 pixels in high dynamical range. The 4D cube data of sampling areas were stable acquired at 200 kV with high diffraction space resolution. In addition, phase retrieval algorithms were developed to improve the point resolution of coherent diffraction imaging. Moreover, the lattice strain mapping was simultaneously interpreted with the high angle annual dark field image in nanostructural characterization by analysis the convergent beam electron diffraction patterns.

NS-TuP-17 Influence of Defects on Oxidation of Rhodium*, **Allison Kerr**, M. Gillum, D. Killelea,* Loyola University Chicago

Due to the importance of oxide surfaces in heterogeneously catalyzed oxidation reactions, it is necessary to gain a fundamental understanding and behavior of oxygen on transition metal surfaces. Additionally, the atomic arrangement of the metal surface plays an important role in the behavior of the oxygen on the surface, which provides a need to study high defect density surfaces that are more akin to industrial catalysts. The research presented herein utilizes a curved rhodium crystal c-Rh(111) with two different well-defined defects on either side to conduct a systematic study of the influence of defect geometry on the kinetics and dynamics of different oxygen species present on the surface. Scanning tunneling microscopy (STM), low energy electron diffraction (LEED), temperature programmed desorption (TPD), and Meitner-Auger electron spectroscopy (MAES) will be used to look at the surface on an atomic scale and to observe what chemical species are on the surface after introducing oxygen into the vacuum environment.

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.

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.

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 $<1 \times 10^{16}$ 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 $Ar/SiH\text{-}_4$ 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)

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