## Biomaterial Surfaces & Interfaces
## Room Naupaka Salon 5 - Session BI-MoM

### Biomaterials/Interfaces - 3D Systems

**Moderator: Jenny Malmstrom**, University of Auckland

9:20am **BI-MoM-5 Antifouling Strategies From a Marine Biofouler, Acorn Barnacles (Amphibalanus Amphitrite)***, Q. Lu, E. McGhee, W. Hervey, S. Tuck, D. Leary, C. Spillmann,* ***Kenan Fears,*** US Naval Research Laboratory

Barnacles have long been admired, or hated, for their robust underwater adhesives that allow them to tenaciously adhere to surfaces and endure harsh marine environments. Previously, we revealed that acorn barnacles evolved a remarkable surface cleaning fluid that removes microorganisms ahead of expansion of their base and the deposition of a new ring of cement. This process involves the secretion of a lipidaceous material that phase separates in seawater, into a phenolic laden gelatinous phase that presents a phase rich in lipids and reactive oxygen species to the seawater interface. Biofilms in close proximity to this material rapidly oxidize and lift off the surface as the secretion advances. Proteomics analysis of the adhesive interface reveals the presence of a haloperoxidase, a class of enzyme known to participate in the innate immune response of a wide variety of organisms, which converts chlorine ions to hypochlorite ions (bleach) in the presence of hydrogen peroxide. We performed agar well diffusion assays the assess the susceptibility of marine and terrestrial micro-organisms to hydrogen peroxide with and without the presence of a haloperoxidase. While yeast cells (*P. larentii*) where shown to be quite susceptible to hypochlorite ions at low doses, the oxidation of biofilms of marine bacterium (*V. natrigens* and *M. atlanticus*) by hypochlorite ions did not result in significant cell death. Confocal microscopy of different barnacle species revealed that the surface cleaning mechanisms employed by acorn barnacles is not ubiquitous to all barnacle species. Microbial colonies were present in the basal region of barnacle species in which the secretion of this surface cleaning fluid was not observed, in stark contrast to barnacle with this surface cleaning fluid. Knowledge of these processes could enhance the efficiency of synthetic underwater adhesives and lead to novel environmentally benign antifouling technologies.

9:40am **BI-MoM-6 From Surface to Microbe: The Role of Copper in Marine Biofouling***,* ***Sara Tuck****, K. Fears,* Naval Research Laboratory

Biofouling, the accumulation of unwanted organisms on submerged assets, is a fundamental problem in maritime transport and human health. Biofouling build-up increases fuel consumption, exhaust emissions, and operational costs in addition to facilitating the transfer of environmental and pathogenic bacteria from one location to another. Conventionally, biofouling is inhibited by the application of antifouling coatings, the most popular of which are copper based. In biological systems, copper is tightly regulated and, in an attempt, to exploit this, antifouling coatings contain up to 75% CuO by weight. Despite these high loadings, the efficacy of these coatings is rapidly declining with the emergence and spread of copper-tolerant species. Microbial communities resistant to copper have been found to form mature biofilms on these coatings, which could be altering the interfacial properties to create more favorable conditions for the settlement of a broader biofouling community. To gain an understanding of the mechanisms responsible for the loss of antifouling performance, coated and uncoated polyvinyl chloride panels were submerged at estuarine and marine field test sites and microbial communities were isolated. Biofouling communities were harvested from three test sites and individual species were cultured, isolated, and identified. Copper tolerance was assessed by re-exposing these cells to copper-containing coatings and traditional broth microdilutions. We also investigated copper biocide release from copper-ablative coated glass coverslips over a short time frame under different conditions to better understand the environmental factors that influence copper release.

10:20am **BI-MoM-8 Development of Joint Organoids for the Study of Tissue Integration and Immune Responses***,* ***Gabriella Lindberg****, M. Hofmann, N. Shchotkina, S. South, N. Willett,* University of Oregon **INVITED**

Despite significant advancements in the design of cell-instructive hydrogels to help repair damaged joint tissues with low metabolic activity, such as cartilage, challenges persist in translating these technologies to clinical applications. This presentation will address two key clinical hurdles in cartilage tissue engineering, focusing on articular conditions, particularly osteoarthritis. The first challenge involves insufficient lateral integration between implanted tissue engineered samples and host cartilage, limiting structural integrity and long-term success. The second challenge is reproducing whole-joint disease conditions *in vitro* with patient-specific inflammatory conditions to accelerate the study of immunomodulatory hydrogels therapies.

To tackle these long-standing translational challenges, we've firstly designed a 3D-model to study tissue integration at the surface between mature cartilage tissues. Herein, we designed ECM-hydrogels that enhance integrative cartilage repair strategies using Vitreous humor, Lysyl-oxidase-like-2, and copper to bridge the two tissue surfaces. Secondly, we have employed modern biofabrication tools, including microfluidic technologies and volumetric printing, to recapitulate dynamic interactions between inflammatory cells and diseased cartilage tissues in the joint space, especially at the surface of the tissue. Utilizing our biobank of human cells and tissue samples together with these organo-typic models has allowed us to study demographical factors (age and sex) that may contribute to differences in OA disease pathogenesis and recovery. Cellular health, tissue formation, multiplexed proteomics assays, and spatial transcriptomics have been used to analyze the biological outcomes across our hydrogel platforms.

This series of studies allowed us to develop hydrogels proficient to guide cartilage repair across a variety patient-centric condition. Ultimately, this talk will highlight some of the important advances in hydrogel design for more clinically-relevant cartilage repair and precision medicine, including integrative hydrogels and immunomodulatory hydrogels together with biofabricated 3D-models to inform regenerative needs in catabolic joint environments.

11:00am **BI-MoM-10 Metrology of 3D Cell Culture Systems***,* ***Sally McArthur,*** Deakin University, Australia

In developing 3D cell culture systems for evaluating biomaterials we need to create the matching metrology systems that are reproducible as well as giving us insights into the cells, matrices and biomaterials responses. This talk will explore the challenges, solutions and remaining issues associated with creating versatile, scalable and measurable systems.

## Plenary Session
## Room Naupaka Salon 4 - Session PL-MoM

### Plenary Session

**Moderator: Gregory S. Herman**, Argonne National Laboratory

11:20am **PL-MoM-11 Unlocking Interfacial Water and Dynamics to Design Catalytic Activity and Selectivity***,* ***Yang Shao-Horn,*** MIT **INVITED**

Understanding the role of Interfacial water structure and dynamics on the reaction barrier of (electro)chemical reactions represents an exciting opportunity to transform the designs of catalytic activity and selectivity. In this talk, we will examine the cation-dependent, pKa-dependent or pH-dependent reaction rates including hydrogen evolution and oxidation, oxygen reduction and evolution and $CO_2$ reduction. The origin to these trends will be discussed in the context of local water-ion structures and solvation environments at the interface and the influence on electron transfer and proton-coupled electron transfer barriers. Such work provides molecular insights into potential use of chemical physics of electrolytes to control rates of reactions relevant to making of clean fuels and chemicals.

1. T. Wang, Y. Zhang, B. Huang, B. Cai, R.R.Rao, L. Giordano, S.G. Sun and Y. Shao-Horn, Enhancing the Catalysis of Oxygen Reduction Reaction via Tuning Interfacial Hydrogen Bonds, Nature Catalysis, *Nature Catalysis,* **4**, 753, 2021.
2. B. Huang, R.R. Rao, S. You, K. H. Myint, Y. Song, Y. Wang, W. Ding, L. Giordano, Y. Zhang, T. Wang, S. Muy, Y. Katayama, J. C. Grossman, A. P. Willard, K. Xu, Y. Jiang and Y. Shao-Horn, Cation- and pH-Dependent Hydrogen Evolution and Oxidation Reaction Kinetics, *Journal of the American Chemical Society Au*, [DOI: 10.1021/jacsau.1c00281], 2021.
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4. Ye Tian, Botao Huang, Yizhi Song, Yirui Zhang, Dong Guan, Jiani Hong, Duanyun Cao, Enge Wang, Limei Xu, Yang Shao-Horn, Ying Jiang, Nature Communication, **15**, 7834, 2024.
5. Sunmoon Yu, Hiroki Yamauchi, Shuo Wang, Abhishek Aggarwal, Junghwa Kim, Kiarash Gordiz, Botao Huang, Hongbin Xu, Daniel J

Zheng, Xiao Wang, Haldrian Iriawan, Davide Menga, Yang Shao-Horn, *Nature Catalysis*, **7**, 1000, 2024.

## Renewable Energy and Energy Storage
## Room Naupaka Salon 4 - Session RE1-MoM

### Electrochemistry and Photocatalysis I

**Moderator: Craig Perkins**, National Renewable Energy Laboratory

8:40am **RE1-MoM-3 Hot Carrier-Driven Plasmonic Photoelectrochemical Processes*, Jeong Young Park,*** KAIST, Republic of Korea **INVITED**

The detection of hot electrons and understanding the correlation between hot electron generation and surface phenomena are challenging questions in the surface science and catalysis community. Hot electron flow generated on a gold thin film by photon absorption (or internal photoemission) appears to be correlated with localized surface plasmon resonance. It has been found that the hot electron flux generated under photon absorption and exothermic chemical reaction is the major mediator of energy conversion process [1-3]. In this talk, I introduce the research direction to attempt to detect the surface plasmon driven hot carrier at the nanometer scale by using scanning probe microscopy. To detect and utilize the hot electron flows at the macroscale level, the metal-semiconductor nanodiodes were constructed. At the nanometer scale, we utilized photoconductive atomic force microscopy to observe photoinduced hot electrons on a triangular Au nanoprism on n-type TiO2 under incident light. This is the direct proof of the intrinsic relation between hot electrons and localized surface plasmon resonance. We observed surface plasmon induced hot hole by using the system of Au nanoprism on p-type GaN [4]. I will discuss the impact of hot carriers in the photocatalytic activity under photoelectrochemical water splitting by using Au-based plasmonic nanostructures [5].

**References**

[1] K. Song et al. Advanced Materials Interfaces, 2400273 (2024).

[2] H. Lee et al. of Chemical Research 55, 24, 3727 (2022).

[3] S. W. Lee et al. Surface Science Reports 76 100532 (2021).

[4] H. Lee et al. Advanced Science 7, 2001148 (2020).

[5] K. Song et al. ACS Energy Lett. 6, 4, 1333–1339 (2021).

9:20am **RE1-MoM-5 Next-Generation Electrocatalysts Derived from Metal-Organic Frameworks for Hydrogen Production and Conversion*, Di-Jia Liu,*** Argonne National Laboratory

Metal-organic frameworks (MOFs) have found their ever growing applications in today's economy and industrial applications. In this presentation, I will discuss some of the recent technological breakthroughs in applying MOFs for green hydrogen applications. I will focus on the discussion on our recent progresses in applying MOFs for a) platinum group metal free (PGM-free) and ultralow platinum metal cathodic catalysts in the proton exchange member fuel cell (*Science*, 2018) and b) new application of PGM-free catalyst as the replacement for iridium for hydrogen production operated in proton exchange membrane water electrolyzer (*Science*, 2023). The talk will cover rational catalyst design, electrocatalytic performance, understanding of the catalytic mechanism, and prospects of these emerging technologies in green hydrogen production and application.

9:40am **RE1-MoM-6 Defective Metal Oxides for Electrochemical Ammonia Synthesis *, Emma Lovell,*** University of New South Wales, Australia

There is a growing and urgent need to decarbonize large-scale industrial process, such as the Haber-Bosch process, used to synthesize ammonia. By using electricity to drive this process and avoiding the requirement for fossil fuel-derived hydrogen, the large scale production of fertilizers can be done sustainably.

Our recent work uncovered an approach to produce ammonia using air and water. By plasma activating air into water, an aqueous solution of $NO_x$ (nitrate and nitrite) can be generated. This solution can then be electrocatalytically reduced to produce ammonia (NOxRR). This hybrid plasma/electrochemical approach can overcome the limitations of direct nitrogen reduction to ammonia (NRR), such as the relative insolubility and stability of nitrogen [1].

The development of active, selective and stable catalysts for NOxRR is essential for the application of this hybrid ammonia synthesis approach. In this talk, our recent work on designing metal oxide catalysts for NOxRR will be discussed [2-4]. By using flame spray pyrolysis (FSP) metal oxides with tunable properties were produced. For example, Ru-doped $Co_3O_4$ was produced with Ru being shown to be incorporated into the $Co_3O_4$ lattice. This doping resulted in an ease in generating oxygen vacancy defects during electrochemical preconditioning which facilitated nitrate adsorption and enhanced Faradaic Efficiency towards ammonia production [3].

[1] Sun et al., (2021) Energy & Environmental Science 14 (2), 865-872

[2] Bui et al., (2023) Advanced Materials 35 (28), 2205814

[3] Lim et al., (2024) Small, 2401333

[4] Rahman et al., (2021) Energy & Environmental Science 14 (6), 3588-3598

## Renewable Energy and Energy Storage
## Room Naupaka Salon 4 - Session RE2-MoM

### Surfaces and Interfaces in Photovoltaics

**Moderator: Elisa Miller**, National Renewable Energy Laboratory

10:20am **RE2-MoM-8 Stabilizing Zinc Powder Anodes via Functional Mxene Towards Flexible Zinc-Ion Batteries*, ZIXUAN YANG,*** Deakin University, Australia*; Z. Wang,* RMIT University, Australia*; J. Razal,* Deakin University, Australia

The global energy crisis demands the development of sustainable and efficient energy storage technologies. Zinc-ion batteries (ZIBs) have emerged as a promising alternative to traditional lithium-ion batteries due to their intrinsic safety, environmental benignity, and the abundance of zinc resources. Among the available anode materials, zinc powder offers distinct advantages over conventional zinc foil, such as enhanced flexibility and processability, which are critical for flexible energy storage devices. However, zinc powder anodes face significant challenges, including dendrite growth, corrosion, and limited cycling stability, which hinder their widespread application.To overcome these issues, we propose a strategy to functionalize zinc powder anodes with MXene, leveraging their high conductivity and ease of surface modification. This functionalization improves the electrochemical performance of zinc powder by facilitating efficient charge transfer, mitigating dendrite formation, and enhancing cycling stability. The MXene-functionalized zinc powder anodes demonstrate remarkable structural integrity and electrochemical efficiency over extended cycling, positioning them as a stable and reliable option for flexible ZIBs.By addressing the fundamental limitations of zinc powder anodes, this study provides a viable solution for next-generation flexible energy storage systems, contributing to the broader goal of resolving global energy challenges through the development of sustainable, high-performance battery technologies.

10:40am **RE2-MoM-9 Hard X-Ray Photoemission Spectroscopy Possibilities at Scienta Omicron*, Tamara Sloboda,*** Scienta Omicron, Sweden*; P. Amann,* Scienta Omicron, Germany*; M. Lundwall, D. Allansson,* Scienta Omicron, Sweden*; X. Zhang, A. Yost,* Scienta Omicron

X-ray photoemission spectroscopy (XPS) is a powerful method in investigations of chemical nature of materials' surfaces. During the past decade, increased attention has been shown to hard X-rays in the photoelectron spectroscopy (HAXPES) field which opens a path towards increased information depth and allows probing high binding energy core levels. This promoted the investigation of buried interfaces occurring in, e.g., device electronics or the work with elevated pressure or solid-liquid interfaces is difficult as the energy of the created photoelectrons is not high enough and scattering inside the material bulk limit the detected signal intensity.

This talk will give an overview on the Scienta Omicron HAXPES Lab system. Having access to HAXPES and XPS X-ray sources enables measurements of different core levels of the same element, including deep core levels. After excitation, electrons with enough kinetic energy escape the material and reach the detector. With an XPS source, the kinetic energy of most elements is low, thus the obtained information is very surface sensitive. However, with high energy X-rays it is possible to be both surface and bulk sensitive, as electrons stemming from deep core levels will have lower kinetic energy and contain more surface sensitive information. Similarly, electrons stemming from shallow core levels will have higher kinetic energy and contain more bulk sensitive information. This is especially valuable when detecting artefacts formed by sample exposure to different environments (e.g. air, moisture, heat, cold etc.) or by preparation steps known to induce chemical changes on the surface (e.g. sputtering). Scienta Omicron's HAXPES Lab uses a monochromatic Ga Ka metal jet source with excitation energy of 9.25 keV, therefore enabling artefact-free investigations with superior information depth, which clearly extends beyond limits of conventional XPS surface analysis. This unlocks a comprehensive and effective characterization of materials. Combined with a hemispherical electron analyzer with a ±30 degree acceptance angle, investigation of buried interfaces, operando devices and real-world samples becomes easily achievable.

Over the years it has proven invaluable in research of semiconductor materials in thin film electronic devices including the operando characterization of bias induced changes in chemical composition of material interfaces. Other applications include polymer materials, metal surfaces and coatings, or even food processing and pharmaceutical industry. This presentation will give an overview of the HAXPES Lab system and common applications of HAXPES method.

11:00am **RE2-MoM-10 Low Dos Tails Dominate Band Alignments in State-of-the-Art Cd(Se,Te) Solar Cells***, Craig Perkins,* National Renewable Energy Laboratory

As the efficiency of single junction CdTe-based solar cells approaches the thermodynamic limit, further device improvements depend heavily on identifying the limiting aspects of cell architectures.Device modeling is the main tool for apportionment of efficiency losses and for guiding research into which aspects of cell designs need improvement.State-of-the-art device models though require numerous input parameters related to both bulk and interfacial properties, many of which are not known.Detailed characterization of an interface in any completed thin film solar cell presents a challenge but is particularly difficult in CdTe-based solar cells where the heterojunction is formed first, evolves during subsequent processing, and ultimately gets buried between mm-thick glass and microns of other materials.In this contribution, we show how an unusual sample preparation method coupled with electron spectroscopic methods was used to tease out details of the front interface of new record efficiency CdTe solar cells.A combination of X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), low energy inverse photoemission spectroscopy (LEIPS), and Auger electron spectroscopy (AES) was used to probe the electronic and structural properties of the front oxide-Cd(Se,Te) interface in fully completed solar cells.Prior to our destructive analysis of the front interface, operating cells were fully characterized by transport measurements, which when modeled, allowed independent assessment of band positions measured by surface analytical techniques.Band alignments based mainly on X-ray excited valence band spectra do not agree with alignments estimated from device modeling, whereas measurements using UPS-derived band edges do agree.A major conclusion from this is that low density of states (DOS) tails can be missed by X-ray excited valence band measurements, even when XPS data are used in conjunction with theoretical total DOS.The low DOS tails detected directly by UPS are found to be present in several different materials and structures found in modern CdTe solar cell designs, including $SnO_2$, a material used widely in other solar cell designs as well as in gas sensors and other electronic devices.It is believed that the low DOS band edges critical to this work are present in many other electronic materials.For that reason, our work has important implications for the use of electron spectroscopy in understanding and improvement of a wide variety of semiconducting devices.

## Biomaterial Surfaces & Interfaces
## Room Naupaka Salon 5 - Session BI1-MoE

### Biomaterials/Interfaces - Characterization

**Moderator: David G. Castner**, University of Washington

5:40pm **BI1-MoE-1 Molecular Structure of Sputtered Species with Large Cluster Ions***, **Jiro Matsuo**,* Quantum Science and Engineering Center, Kyoto University, Japan **INVITED**

Molecular-imaging techniques are now of interest for life science, pharmaceutical and medical applications and organic industrial materials, such as functionalized polymers and organic semiconductors. SIMS (Secondary Ion Mass Spectrometry) is one of the powerful techniques, due to high lateral resolution, high sensitivity and high surface sensitivity. However, ion dose is limited with conventional keV primary ion beam, which destroys molecules of samples with high energy ion impacts. Therefore, SIMS measurement should be completed before organic molecules on the surface are completely damaged. Recently, large cluster ions are utilized for SIMS as a primary ion beam, because there is no limitation in ion dose. It has been demonstrated that large cluster ion beams have a great capability to sputter organic molecules without any residual damage on the surface, because cluster ion beams are equivalently low energy ion beams. Extremely high energy density and multiple collisions are responsible for “cluster effects”, which play an important role during their sputtering process of organic molecules. Practical applications, such as organic depth profiling and 3-dimensional molecular analysis in XPS or SIMS have been demonstrated. Nevertheless, high sensitivity is required in all applications, and high sensitivity is becoming an important issue in SIMS technique as well. It is quite important to increase secondary molecular ion yields, which are usually very low(<1E-4). GCIB technique can generate clusters of not only Ar gas but also a variety of gas molecules and various gas molecules are being utilized in the GCIB technique to improve secondary ion yields. Unfortunately, it is still not enough. Most of sputtered species are neutral, but there is no report on molecular structure of sputtered species from organic materials. Due to low ionization yields, SIMS spectra never tell us molecular structure of sputtered species.We have concerned that organic molecules sputtered with large cluster ions are destroy, or not. Capturing of neutral species and electrospray ionization mass spectrometry (ESI-MS) technique were utilized to explore molecular structure of sputtered neutral species. We have, for the first time, measured the molecular structure of sputtered neutral species and the results clearly show that there are many neutral species maintaining their molecular structure. 10% of neutral particles maintains their molecular structure. If those neutral species are ionized, sensitivity of SIMS would improve by several orders of magnitude.

6:20pm **BI1-MoE-3 GCIB-SIMS Analysis of Skin Cancer Samples***, **John S. Fletcher**, K. Sjögren Cehajic, K. Dimovska Nilsson, O. Zaar, D. Katasarelias, J. Paoli, R. Olofsson Bagge, N. Neittaanmäki,* University of Gothenburg, Sweden

The use of gas cluster ion beams (GCIBs) for secondary ion mass spectrometry (SIMS) analysis provides softer ejection of biomolecular ions and has created opportunities for meeting the challenges of clinical researchers who require chemical specific imaging of different sample type from cells to tissue biopsies. Here we use a J105 Buncher-ToF SIMS instrument (Ionoptika Ltd, UK) to perform in situ lipidomics of skin cancer samples. GCIB-SIMS analysis enabled detailed spatial-lipidomics that could be directly correlated with conventional histopathological analysis of consecutive H&E slides. Here we present work where melanoma cancer samples were the target in order to investigate the chemical changes associated with disease progression and also to investigate if different metastatic pathways could be distinguished based on the chemical signature of the tumours. Primary tumours were analysed along with "healthy/normal" skin from the same subject along with metastatic tumour samples that had spread via either the lymphatic system or through the blood. Significant differences in the lipid profiles were found in primary compared to metastatic melanomas, notably an increase in phosphatidylethanolamine lipids relative to phosphatidylinositol lipids and an increase in GM3 gangliosides in the metastatic samples. Furthermore, analysis of the data from in-transit versus distant metastases samples highlighted that specific glycerophospholipids, and a difference in the long versus shorter chain GM3 gangliosides, discriminated the metastatic routes. The data is also compared to other skin cancer samples including such as aggressive basal cell carcinoma. Challenges related to data processing and spectral annotation are also discussed.

6:40pm **BI1-MoE-4 Depth Correction of 3D SIMS Depth Profiling Images of Biomaterials Using Only Secondary Ion Signal Intensities***, M. Brunet, B. Gorman, **Mary Kraft**,* University of Illinois Urbana-Champaign

We have developed a depth correction strategy for three-dimensional (3D) SIMS depth profiling images of biomaterials that solely employs secondary ion signal intensity. In this approach, the secondary ion images that were collected during depth profiling are used to create a model of the sample’s morphology at the time that each depth profiling image was acquired. Then these models of the sample’s morphology are used to shift the voxels in the 3D image to the correct z-position. Comparison of the morphology models created using the secondary ions and the secondary ion images the usage of secondary ion signals with high intensities tends to produce more accurate morphology models. However, even 3D SIMS images that were depth corrected using secondary ions with relatively low intensities were more accurate than uncorrected 3D SIMS depth profiling images. This ability to use secondary ion images to depth correct 3D SIMS depth profiling images in the absence of correlated measurements of sample topography or knowledge of sputter rate expands the range of SIMS depth profiling data sets that may not be depth corrected.

7:00pm **BI1-MoE-5 Label-Free High-Resolution Molecular Imaging of Sex Steroid Hormones in Zebrafish by Water Cluster Secondary Ion Mass Spectrometry (Cluster SIMS)***, **Kate McHardy**, N. Sano,* Ionoptika Ltd., UK*; E. Lau, M. Bailey,* University of Surrey, U.K.

Sex steroid hormones are essential biomolecules for vertebrates and are involved in the maintenance of pregnancy, development of secondary sexual characteristics and diseases such as osteoporosis and breast cancer. Visualising the distribution of steroids contributes to further understanding of disease. However, analysis of steroids is difficult; their low polarity leads to poor ionisation efficiency, meaning they need to be derivatised for conventional analyses. Furthermore, the steroid signals overlap with a MALDI matrix background.

Water Cluster SIMS is a high-sensitivity mass spectrometry technique for imaging complex-mixture materials without derivatisation or the use of matrix. We demonstrate imaging of sex steroid hormones in zebrafish (an ideal vertebrate model organism) with a Water Cluster SIMS instrument.

An adult female zebrafish was prepared for this work. It was embedded while fresh in 0.75% HPMC and 0.25% PVP embedding media to facilitate sectioning. The whole block was flash-frozen in a dry-ice and isopropanol bath. The sample was sectioned to 20 µm at -25 °C and thaw-mounted onto a conductive indium-tin-oxide (ITO) coated glass. The section was dried while frozen in a vacuum desiccator, and then directly analysed without any matrix application for the analysis. The Cluster SIMS analyses were then performed with the J105 SIMS Cluster SIMS (Ionoptika Ltd), using a 70 keV $(H_2O)$n beam, where n is in the range of 15,000-35,000, and also separately with a 40 keV $C_{60}$ beam. High-resolution images were acquired with a pixel size of < 1 micron.

Water Cluster SIMS uses a high-energy beam of ionised clusters of water to sputter and ionise molecules from a surface. It is far less damaging and generates far fewer fragment ions than traditional ToF SIMS, but retains many of the benefits of that technology such as high-spatial-resolution imaging. As a result, detailed images of the distribution of sex steroid hormone molecules in the zebrafish are visible. Preliminary data shows that it is possible to map the chemical distribution of steroids in the ovary area. In addition, we also detected lipid ions related to the embryo or oocyte around the ovary area as unique distributions.

## Biomaterial Surfaces & Interfaces
## Room Naupaka Salon 5 - Session BI2-MoE

### Biomaterials/Interfaces - Sustainable Materials

**Moderator: Gabriella Lindberg**, University of Oregon

7:40pm **BI2-MoE-7 Advanced BioAFM for Temporal Analysis***, **Amy Gelmi**,* RMIT University, Australia **INVITED**

Electrical stimulation, a physical stimulation which can be delivered via a conductive biomaterial interface, directs human mesenchymal stem cell (hMSC) differentiation towards different cell tissue types.[1] Electrical stimulation conditioning offers a promising approach in directing stem cell fate. Conductive biomaterials are commonly used to provide either a passively conductive substrate, or actively provide 'smart' electrical stimulation of stem cells for tissue engineering. However, the mechanisms in which cells transduce these electrical signals into specific phenotype differentiation are poorly understood, restricting the intelligent design of stimulation protocols for targeted differentiation.

How the stem cells transduce an electrical signal into a biological response is explored via different classes of conductive biomaterials. Immediate changes in the stem cells during and post-stimulation is characterised, using live cell bio-AFM for morphological and biomechanical changes, complemented with standard biological characterisation. The advanced bioAFM technique delivered unprecedented intracellular biomechanical information of live cells undergoing simultaneous electrical stimulation.

For the first time we have characterised the transient mechanical response of hMSC to electrical stimulation, and related that to controlling stem cell differentiation towards osteogenesis. The knowledge gained from this study helps to further the intelligent design of stimulation parameters for targeted differentiation outcomes when using a conductive biomaterial.

[1] Gelmi, A., Schutt, C. E., Stimuli-Responsive Biomaterials: Scaffolds for Stem Cell Control. Adv. Healthcare Mater. 2020, 10, 2001125.

8:20pm **BI2-MoE-9 Development of an Active Sustainable Polymer Based on Crosslinked Gelatin***, **Monique Lacroix,*** INRS Armand Frappier Health Biotechnology, Canada

Gelatin is a potential sustainable polymer for packaging development. Due to its biological origin this polymer is highly biocompatible and biodegradable. However, films based on gelatin have poor mechanical properties, high water solubility and permeability. Crosslinking reaction can help to overcome these limitations. In this study, ionization as a non - toxic physical treatment has been used to induce gelatin crosslinking reaction in presence of riboflavine to improve the functional properties of this biopolymer. Riboflavine is a photosensitive compound who can promote crosslinking of proteins during ionization treatment. Concentrations from 0.3 to 1.2 % of riboflavine have been used and doses from 5 to 15 kGy have been applied. Results demonstrated that 0.75% of riboflavine and a dose of 5 kGy were the optimal conditions to improve positively the tensile strength, the water resistance and water barrier properties of the films. The infrared spectroscopy evaluation suggests the formation of a more compact protein structure. A mixture of essential oils and silver nanoparticles were then added in the crosslinked gelatin before film formation. The active film was used for a *in situ* test on fresh meat. Results showed that this active film can increase the shelf life of the fresh meat by more than 6 days. This study suggests that crosslinking of gelatin during ionization treatment in presence of riboflavine is an effective green technology for the development of sustainable bioactive packaging.

8:40pm **BI2-MoE-10 Sustainability Inspired Development of Next Generation Neural Interfacing and Neurostimulation Electrodes via Reactive Hierarchical Surface Restructuring***, **Shahram Amini,*** Pulse Technologies Inc.*; S. Shahbazmohamadi, H. Choi, A. Blagojevic, M. Maniscalco, P. Tavousi,* University of Connecticut

Over the last two decades, platinum group metals (PGMs) and their alloys have been the preferred materials for electrodes in long-term implantable neurostimulation and cardiac rhythm management devices due to their superior conductivity, mechanical and chemical stability, biocompatibility, corrosion resistance, radiopacity, and electrochemical performance. Despite these benefits, the manufacturing processes for PGMs are extremely costly, complex, and present potential health hazards. Additionally, the volatility in PGM prices, high supply risk, and their scarce concentration of approximately 0.01 ppm in the earth's upper crust, combined with limited mining geographical areas, highlight their classification as critical raw materials. Effective recovery or substitution of PGMs is thus of paramount importance. Since postmortem recovery from deceased patients and refining PGMs used in electrodes and microelectrode arrays is rare, challenging, and costly, the substitution of PGM-based electrodes with other biocompatible materials that can match or surpass their electrochemical performance is the only viable and sustainable solution. In this context, we demonstrate for the first time how the novel technique of “reactive hierarchical surface restructuring” can be applied to titanium—widely used in non-stimulation medical device and implant applications—to create biocompatible, low-cost, sustainable, and high-performing neurostimulation and cardiac rhythm management electrodes. Our study shows that titanium electrodes, which initially exhibit poor electrochemical performance, undergo significant compositional and topographical transformations through this technique, resulting in electrodes with outstanding electrochemical performance. This innovation offers a promising path to reducing and ultimately substituting PGMs in long-term implantable neurostimulation and cardiac rhythm management devices.

## Thin Films and Surface Modification
## Room Naupaka Salon 4 - Session TF1-MoE

### Thin Films - Materials I

**Moderator: Ryo Toyoshima**, The University of Tokyo

5:40pm **TF1-MoE-1 Plasma Diagnostic-Based Plasma Processing for Semiconductor and Nanomaterial Manufacturing***, **Hyo-Chang Lee,*** Korea Aerospace University, Republic of Korea **INVITED**

Plasma has been actively used in semiconductor and nanomaterial manufacturing. As the structures of nanostructures and semiconductor devices become more complex, plasma process technology based on plasma characteristic measurement is needed. In this invited talk, several key plasma process results, including analysis of the correlations between process results and plasma variables, are presented.

6:20pm **TF1-MoE-3 Tailoring High Temperature Anti-Oxidizing Coatings by Sol-Gel Chemistry for Enhanced Aeronautic Efficiency***, L. Lager,* University Lyon 1, France*; S. Senani-De Monredon, J. Delfosse,* Safran Tech, France*; S. Benayoun,* Ecole Centrale de Lyon, France*; **Berangere Toury,*** University Lyon 1, France

Reducing polluting gases emissions is a major strategic challenge for the aeronautic industry. Two approaches exist to achieve this : increasing engine operating temperatures and/or reducing the total mass of the aircraft. Titanium alloys, due to their low density, good damage tolerance, and excellent fatigue resistance, are particularly attractive for use up to temperatures of 500°C.

To date, the scientific challenge concerning these alloys is to extend their operating temperature resistance up to 600-700°C while maintaining or improving their specific properties required for the aimed application. One of the main causes of degradation in these alloys when used at high temperatures is related to oxidation. Actually, for these materials, oxidation can occur in two distinct ways : firstly, the formation of an external oxide layer ($TiO_2$), and secondly, significant oxygen diffusion within the underlying alloy. This second phenomenon is linked to the high solubility of oxygen in titanium. In both cases, without additional protection, the use of titanium alloys at high temperatures considerably reduces their mechanical properties, especially ductility.

In this context, the main goal of this study is focused on the design, synthesis and characterization of a high temperatures anti-oxidizing coating based on rare earth aluminate for enhanced titanium alloys used in aeronautics. In this work, we are interested in the synthesis of protective coatings by using the sol gel process, which is a versatile method allowing direct enduction of the sol on metallic substrates. Thus, leveraging precise control over sol chemistry enables the reach of coatings with desired stoichiometry. The morphology of the coatings is meticulously examined via SEM. Additional characterizations utilizing XPS, solid NMR, and thermal analyses where used to understand curing mechanisms. Initial oxidation tests reveal promising prospects for the application of these coatings in aeronautic contexts, potentially enhancing engine efficiency while mitigating environmental impact.

6:40pm **TF1-MoE-4 Fabrication and Characterizations of Aluminum Doped Cadmium Oxide (Cdo:Al) Thin Film Using Sol-Gel Spin-Coating Method***, **Moniruzzaman Syed**, J. Massey, M. Hurd,* LeMoyne Owen College*; M. syeda,* University of Memphis

Aluminum-doped cadmium oxide (CdO:Al) thin films are deposited on silica substrates by the sol–gel spin-coating method as a function of spin coater’s rpm (revolution per minute). Cadmium acetate dihydrate and Aluminum nitrate have been taken as the precursor material and a source of Al-dopant respectively. CdO:Al thin films are characterized by x-ray diffraction (XRD), Fourier Transform Infrared (FT/IR), Field emission scanning electron microscopy (FE-SEM) and SEM-EDX. XRD result indicates the highest crystallinity at 6000 rpm with a crystallite size of 31.845 nm, cubic phase formation, and strain of ~$1.6 \times 10^{-2}$. FE-SEM/SEM/EDX shows the well-faceted homogeneous surface structure at 6000 rpm having an average particle size of 130.05 nm. FT/IR confirms the presence of CdO:Al in the film with the peak position shifting to higher wavenumbers.

7:00pm **TF1-MoE-5 Structural and Electronic Impact on Various Substrates of Tio2 Thin Film Using Sol-Gel Spin Coating Method***, **Afrika Leiws**, T. Crosby, J. Muhammad,* LeMoyne Owen College*; M. Syeda,* University of Memphis*; M. Syed,* LeMoyne Owen College

Titanium dioxide ($TiO_2$) thin films have been deposited on Corning 7059 glass and Fused quartz silicate substrates using the Sol-Gel spinning coating technique. On glass substrates, there are four Raman active bands are observed: 3Anatase [A<149cm-1>, A<523cm-1> and A<646cm-1>] and 1 Rutile B<401 cm-1>. On silica substrates, additional two more bands which are R<859 cm-1> and B<1068 cm-1> detected. The deposited films show polycrystalline nature with high XRD intensity peaks in (110), (200) and (211) orientation corresponding to anatase and rutile phases respectively with tetragonal BCC structure. The other orientations (101), (111), (210), (211), (220), (201), (002), (204) and (116) are also observed for all films with low intensities. XRD crystal sizes are found to increase with increasing annealing temperature on both substrates. Maximum crystal sizes are found to be ~31 nm on silica substrates and ~23 nm on glass substrates at 500oC. On glass substrate, $TiO_2$ thin film shows the agglomeration of various non-uniform flaky type of structures. On silica substrate, the FESEM micrographs show the following observations: (i) particles are spherical in shape with forming different islands (ii) particles are soft agglomerates/spongy in nature with uniform surface, (iii) each spherical agglomerate contains many particles in the nanometric range and (iv) the agglomerate size is in between 40 and 110 nm. FE-SEM $TiO_2$ particles size distribution at 500oC showed that the average particle size is 89.55 and 110.35 nm on glass and silica substrates respectively.

## Thin Films and Surface Modification
## Room Naupaka Salon 4 - Session TF2-MoE

### Thin Films - Characterization

**Moderator: Chen-Hao Wang**, National Taiwan University of Science and Technology

7:40pm **TF2-MoE-7 In-Situ/Operando Soft X-Ray Measurements for Hydrogen Related Surface Functional Materials***, **Ryo Toyoshima**,* The University of Tokyo, Japan **INVITED**

Chemical reactions at surfaces have been widely used for chemical processes such as catalytic synthesis, energy conversion, environmental cleanup, and sensor. Surface science techniques enable us to understand physicochemical fundamental processes on surfaces. However, one drawback of such surface science techniques is that the experiments are carried out under vacuum in many cases. We have developed some in situ / operando experimental techniques for observing surface reactions on liquid/solid and gas/solid interfaces in energy range from infrared to soft X-ray. We have focused on the development and understanding of heterogeneous catalysts using hydrogen gas as a reducing agent [1], and sensing materials to detect small molecules such as hydrogen [2], by ambient pressure X-ray photoelectron spectroscopy (AP-XPS). The experiments were carried out at a beamline BL-13 at the Photon-Factory of High Energy Accelerator Research Organization (KEK-PF). The AP-XPS system is consisted of a high-pressure chamber, preparation chamber and load-lock chamber. An important technical point of the AP-XPS system is that the high-pressure chamber, where quasi-atmospheric gases are introduced, and the electron analyzer are separated by a small aperture and pumped by a differential pumping system. It keeps the pressure of electron analyzer under ultra-high vacuum, and it also reduces the scattering of photoelectrons in the gas atmosphere. Recently, a sensor material has been developed that can detect $H_2$ gas in air and breath with high sensitivity (1 ppm) using nanometer-thick platinum-based thin films [2]. Figure 1 shows a result of operando AP-XPS measurement for H2 sensing Pt-Rh thin-film sensor. The Pt-Rh sensor detects the atmospheric concentration of H2 gas by changing in electric resistivity. Here, a 10 nm-thick Pt–Rh thin-film deposited on a SiO2 substrate was used for the measurements. Figure 1(a) shows time evolution of relative electric resistivity (ΔR/R). The resistivity decreases with exposing H2 gas to the sensor surface, whereas it increases with exposing O2 gas. Figure 1(b) shows corresponding Rh 3d and Pt 4f XPS. Before the gas dosing (i), the surface was dominated by Rh oxide. When the surface was exposed to the H2 gas, the chemical state clearly changed. The Rh oxide was completely reduced to the metallic state. When, the surface was exposed to the O2 gas, the oxygen-induced species grew up again. Those findings indicate the surface chemical state strongly relate to the material functions.

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8:20pm **TF2-MoE-9 NAP HAXPES from Tender X-Ray Energies***, **Paul Dietrich**,* SPECS Surface Nano Analysis GmbH, Germany

X-ray photoelectron spectroscopy (XPS) is a powerful technique for investigating a wide range of materials' chemical composition and electronic structure. The information depth of XPS is contingent upon the inelastic mean free path (IMFP) of the photoelectrons in solid matter. The IMFP as a function of kinetic energy exhibits a pronounced minimum at kinetic electron energies between 40 and 100 eV. The maximum kinetic energy of photoelectrons in an XPS experiment depends on photon energy. In this context, typical photon energies employed in laboratory settings and at synchrotron radiation facilities range up to 1500 eV. In such experiments, the inelastic mean free path is typically around a few nanometers making conventional XPS a surface-sensitive technique. It is necessary to increase the kinetic energy of electrons by using higher photon energies for excitation to gain access to properties at the bulk and interface levels. In hard X-ray photoelectron spectroscopy (HAXPES), photon energies typically range between 3 keV and 15 keV, thereby extending the information depth to 10–30 nm.

The µFOCUS 450 is a versatile small-spot multi-wavelength X-ray monochromator for surface analysis and depth profiling applications. This fully computer-controlled device allows for in situ switching between different emitters for Al, Ag, and Cr excitation, thus providing X-rays with high flux density for various applications such as small, medium, and high energy XPS. This new monochromator is an all-in-one solution for (NAP) XPS and (NAP) HAXPES systems. It combines the high performance of the standard aluminum Kα excitation (1487 eV) with silver Lα and chromium Kαexcitation lines at 2984 eV and 5414 eV, respectively. The new design hosts up to three anodes and the corresponding monochromator optics in one Rowland circle based housing.

Due to signal absorption in the surrounding gas, NAP XPS is one of the most challenging applications in surface analysis. High-performance analyzers, such as the AEOLOS 150 NAP, require a matched X-ray source, fitting the small analyzer field of view and the need for a high flux density on the smallest spots. The µFOCUS 450 is designed to cover these requirements for highly efficient NAP XPS and NAP HAXPES measurements. The combination of our monochromatic three-color X-ray source µFOCUS 450 with Al, Ag, and Cr anodes together with the high transmission hemispherical analyzer AEOLOS 150 NAP is ideally suited for studies of interfaces under reactive conditions extending the information depth from the surface into the bulk. We will present a selection of recent (NAP) HAXPES results from different types of samples.

8:40pm **TF2-MoE-10 Redox XPS;Progressive *proxime situ* Oxidation in XPS (and SIMS) as an Aid to Spectrum Interpretation***, **Peter Cumpson**,* La Trobe University, Australia*; D. Devadasan,* Thermo Fisher Scientific, UK*; S. Gazzola,* University of Bath, U.K.*; T. Nunney,* Thermo Fisher Scientific, UK*; R. Weatherup,* Oxford University, UK

We have developed a method of exposing surface analysis samples to a progressive series of oxidation steps in the entry-lock of a UHV instrument (e.g. ThermoFisher K-Alpha and NEXSA XPS instruments). Shortwave UV and part-per-million ozone are used in automated steps to progressively oxidise specimens so that one obtains a series of narrow-scan XPS spectra representing increasingly oxidised states. This makes it easier to interpret the superposition of chemical states that existed in the original spectrum of an "as received" specimen, and indeed, to numerically extract spectra representing the pure components. This is not done *in situ* in the analyser, or *ex situ* outside the instrument, but rather *proxime situ* in the entry lock without having to take the sample out of the instrument. This allows Redox XPS to be done automatically and unattended, rather like a depth-profile. To be clear, this is not done to study the chemistry of UV or ozone exposure, but just to elucidate the chemical components of the specimen surface before that exposure.

After a brief review of the experimental arrangement we present a comprehensive analysis of spectral unmixing in Redox XPS, focusing on the treatment of spectra in the presence of the inelastic background. The study introduces novel approaches for analyzing narrowscan XPS spectra of progressively oxidized samples, offering significant insights into the decomposition of complex spectral data into its constituent chemical states. By leveraging advanced computational techniques, this approach significantly improves the accuracy and reliability of chemical state identification in XPS analysis, and should address some of the important issues raised in the community recently regarding the reliability of peak-fitting performed by those new to XPS.

This progressive gas-phase oxidation offers even more opportunities in the understanding of SIMS spectra, given the more specific ozonolysis chemistry of complex organics. We look at the opportunities (with data - if we have it by December).

## Biomaterial Surfaces & Interfaces
## Room Naupaka Salon 5 - Session BI1-TuM

### Biomaterials/Interfaces - Biointeractions

**Moderator: Kaori Sugihara**, Institute of Industrial Science, the University of Tokyo

8:40am **BI1-TuM-3 Dynamic Supramolecular Gels for 3D Cell Culture***, A. Chalard, H. Porritt,* University of Auckland, New Zealand*; A. Taberner,* The University of Auckland, New Zealand*; J. Fitremann,* CNRS, France*; **Jenny Malmstrom,*** University of Auckland, New Zealand

Cells sense and adapt to forces and physical constraints imposed by the extra cellular matrix. Such mechanotransduction plays a crucial role in cell function, differentiation and cancer. In our research group we are developing materials to achieve spatiotemporal control over mechanical properties.

Stiffness patterning of hydrogel scaffolds, through the use of stiffness gradients for instance, allows the modelling and studying of cellular responses to fibrotic mechanisms. Gelatine methacryloyl (GelMA) has been used extensively in tissue engineering for its inherent biocompatibility and the ability to precisely tune its mechanical properties. We have developed a method to photopattern the mechanical properties of GelMA hydrogels with visible light and using physical photomasks and projection with a digital micromirror device. This method allows to create hydrogels with areas of different stiffnesses and hydrogels with precise stiffness gradients. The mechanical properties of the resulting hydrogels have been characterised using force indentation with atomic force microscopy, which demonstrated the efficiency to spatially pattern the elastic modulus of GelMA according to the photomask or the projected pattern. (1)

In addition to pattern mechanical properties, it is interesting to include a dynamic aspect to cell-laden biomaterials, since native ECM is constantly reshaped by cells. Composite hydrogels are developed to bring different combinations of structures and properties to a scaffold by using different types and sources of materials. We have combined GelMA with biocompatible supramolecular fibers made of a small self-assembling sugar-derived molecule (*N*-heptyl-D-galactonamide, GalC7). The GalC7 fibers were directly grown in the GelMA through a thermal process, and it was shown that the presence of the fibrous network increased the Young's modulus of GelMA. Due to the non-covalent interactions that govern the self-assembly, these fibers were observed to dissolve over time, leading to a dynamic softening of the composite gels. Cardiac fibroblast cells were successfully encapsulated into composite gels for 7 days, showing excellent biocompatibility and fibroblasts extending in an elongated morphology, most likely in the channels left by the fibers after their degradation. These novel composite hydrogels present unique properties and could be used as tools to study biological processes such as fibrosis, vascularization and invasion. (2)

1) Chalard, Malmström, et al. Frontiers in Cell and Developmental Biology 2022, 10.

2) Chalard, Malmström, et al. BioMaterials Advances, 2024, accepted

9:00am **BI1-TuM-4 Supercritical Angle Raman Microscopy (SAR-M): A Versatile Tool to Study Molecular Conformations at Surfaces on the Example of Amyloid and α-Synuclein Proteins***, N. Münch, S. Das, **Stefan Seeger,*** University of Zurich, Switzerland

Supercritical Angle Raman Microscopy (SAR-M) emerges as a transformative technique for the in-depth study of molecular conformations at surfaces, providing unparalleled spatial resolution and sensitivity. This presentation explores the application of SAR-M to investigate the structural dynamics of amyloid and synuclein proteins, which are pivotal in neurodegenerative diseases such as Alzheimer's and Parkinson's. Utilizing the unique capabilities of SAR-M, we demonstrate its proficiency in capturing subtle conformational changes and aggregations of these proteins at the nanoscale, which are critical to understanding their pathological roles as well as the role of ions like Calcium.

Amyloid and synuclein proteins are known for their propensity to misfold and aggregate, forming insoluble fibrils that are toxic to neuronal cells. Traditional microscopy techniques often fall short in providing the necessary resolution and chemical specificity to study these proteins' surface interactions and early aggregation stages. SAR-M overcomes these limitations by exploiting the supercritical angle fluorescence to enhance Raman scattering signals, thereby achieving superior surface sensitivity.

Through a series of experiments, we detail the conformational mapping of amyloid-beta peptides and alpha-synuclein at different aggregation stages. The results reveal distinct molecular signatures and structural transitions, offering new insights into the mechanisms driving protein misfolding and aggregation. Additionally, SAR-M's capability to monitor these processes in real-time opens avenues for investigating the effects of potential therapeutic agents aimed at inhibiting or reversing protein aggregation.

Serrano D, Seeger S, Light: Science and Applications (2017) 6, e17066

Dubois A, Serrano D, Zhang X, Seeger S, Analytical Chemistry (2020) 4963

Münch NS, Das S, Seeger S, PCCP (2024), in press

9:20am **BI1-TuM-5 Biomimetic Leaf Surfaces as a Platform Technology to Study Bio-Interactions***, **Volker Nock,*** University of Cantebury, New Zealand*; S. Sale,* University of Canterbury, New Zealand*; A. Garrill,* University of Cantebury, New Zealand*; M. Bernach,* University of Cantebury, New Zealand, Germany*; M. Remus-Emsermann,* Freie Universität Berlin, Germany **INVITED**

Spatial and temporal variability of leave surfaces modulates plant-microbe and microbe-microbe interactions, creating diverse microenvironments for microbial colonizers such as bacteria and fungi. Mimicking leaf complexity on artificial surfaces greatly aids in the study of microorganisms residing on plant leaf surfaces [1]. Over the years, a number of surrogate surfaces aiming to replicate leaf surface topography have been proposed, ranging from simple nutrient agars to complex casts [1]. These surrogate surfaces are often used to deconstruct leaf surfaces into individual aspects, as this enables bio-interactions to be studied in separation [2].

In this paper I will discuss ongoing efforts to develop biomimetic leaf surfaces as a platform technology to study bio-interactions. In particular, I will focus on work related to bacterial colonization [2-4] and invasion by pathogenic rusts [6]. To date, this has involved *Arabidopsis thaliana* [2,3], as well as wheat, poplar, eucalyptus and mānuka mimics [5]. Incorporating properties such as leaf topography or hydrophobicity, these mimics all aim to promote colonizer survival in the absence of a living plant host. Characterizing agarose, polydimethylsiloxane (PDMS) and gelatin, we have determined PDMS to be one of the most suitable materials for leaf replicas [6]. Diffusion of water and nutrients to the surface of PDMS can be optimized by addition of fillers [7]. Increasing permeability, we have been able to demonstrate the possibility of delivering fructose to the surface, thus allowing division and distribution of bacteria to be affected [2]. Such leaf replicas have since also enabled us to culture in-vivo biotrophic rusts, normally considered "un-culturable" on artificial substrates due to the need for a living host [5], as well as helped to demonstrate that RNAi can be used to inhibit infections by these rusts [8].

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8. Degnan, R.M., et al., Mol. Plant Pathol. 24:191-207, 2022.

## Biomaterial Surfaces & Interfaces
## Room Naupaka Salon 5 - Session BI2-TuM

### Biomaterials/Interfaces - Biosensing

**Moderator: Volker Nock**, University of Cantebury

10:20am **BI2-TuM-8 Mechanochromic Polymer, Polydiacetylene, for Force-, Bio-Sensing Applications***, **Kaori Sugihara,*** Institute of Industrial Science, the University of Tokyo, Japan **INVITED**

The forces around us, such as grip forces, loads on buildings and machines, and friction, are closely related to our health and safety. While technologies exist to measure such forces, there are still many types of forces that cannot be measured with existing technologies, such as molecular forces at nanoscale or the detection of curved or anisotropic forces. Mechanochromic materials are expected to play a pivotal role in these niches. In my talk, I will introduce the mechanism and applications of a mechanochromic lipid polymer called polydiacetylene towards biosensing.$^{1-2}$

References

1. Juhasz, L.; Ortuso, R. D.; Sugihara, K., Quantitative and Anisotropic Mechanochromism of Polydiacetylene at Nanoscale. *Nano Lett* **2021,** *21* (1), 543-549.
1. Chen, J. L.; Zheng, J. L.; Hou, Y. G.; Sugihara, K., Colorimetric response in polydiacetylene at the single domain level using hyperspectral microscopy. *Chem Commun* **2023,** *59* (25), 3743-3746.

11:00am **BI2-TuM-10 Inspired by Nature: Next-Gen Multiplex Biosensing with Biomimetic Surfaces*, Saimon Moraes Silva,*** 1/6 Patterson Street, Bonbeach, Australia **INVITED**

A major issue faced by electrochemical surfaces that need to function in biological fluids remains the biofouling of electrode surfaces. In this presentation, I will demonstrate how lubricin (LUB) can mitigate the biofouling issue and enable the development of biosensors that function in unprocessed whole blood. LUB is a cytoprotective glycoprotein present in synovial fluids and coating cartilage surfaces in articular joints.[1] It displays a distinguishing chemistry, conformational and molecular structure, and also the ability to self-assemble in a well-organized manner on substrates of different materials.[2,3] When attached to a conductive surface, LUB presents the capability of preventing biofouling and at the same time allowing good electrochemistry with the advantage of a simple and one-step coating preparation.[4] This makes LUB an interesting surface coating for applications such as bionic implants and electrochemical biosensors. In this presentation, I highlight both recent technological advances associated with the LUB coatings for use in electroactive surfaces and a number of recent advances toward point-of-care diagnostics enabled by this unique biomimetic surface coating.

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11:40am **BI2-TuM-12 Polyaniline-Gold Nanocomposite as an Electrode Material for Supercapacitor and Escherichia Coli Detection*, Md Zaved Hossain Khan,*** Jashore University of Science and Technology, Bangladesh

The present work is focused on detection and quantification of low-density E. Coli using a new supercapacitor-based biosensor. Herein, gold nanoparticles (AuNPs) doped pseudo capacitive PANI-PS composite has been synthesized by in situ oxidative deposition of PANI-ES in the presence of AuNPs in aqueous H2SO4. The novel nanocomposite AuNPs@PANI-PS exhibits excellent supercapacitor performance and bio-electrochemical sensing of E. Coli, which is only possible for chronoamperometry deposition respective charging event on electrode surface. In addition, AuNPs@PANI-PS electrode shows high specific capacitance (812.96 F/g, with 2.5 mA/g, current density) and 207.43 Wh/kg energy density respective 6.05 KW/kg power density. In E. Coli detection, AuNPs@PANI-PS based sensor can exhibit a wide linear range of 10-108 CFU/ml with a limit of detection of 1.0 CFU/ml. Except laboratory strain, we also detect it in urine medium. The proposed whole cell biosensor provides high selectivity for the detection of E. Coli bacteria in the presence of E. Coli DH5-α, E. Coli ATCC, S. Typhi DMS_A1, P. Aeruginosa, S. Flexneri, and others. Finally, the smartphone-based application of this biosensor showed excellent performance. Therefore, the proposed composite can serve as an effective material in supercapacitor and the monitoring of E. Coli

## Renewable Energy and Energy Storage
## Room Naupaka Salon 4 - Session RE1-TuM

### Electrochemistry and Photocatalysis II

**Moderator: Craig Perkins**, National Renewable Energy Laboratory

9:00am **RE1-TuM-4 Tuning Optoelectronic Properties of 2D Transition Metal Dichalcogenides and p-Conjugated Polymers*, Elisa Miller,*** National Renewable Energy Laboratory **INVITED**

This talk will review recent research tuning optoelectronic properties of 2D transition metal dichalcogenides (TMDCs) and p-conjugated polymers to ultimately control energy conversion processes. First, a major roadblock to the commercial deployment of TMDC monolayers for next generation electronic devices has been the inability to controllably dope these materials at wafer scale as can be done with traditional semiconductors. We demonstrate dedoping with high spatial fidelity in wafer-scale monolayer $MoS_2$ upon illumination with a mechanistic understanding. Second, the p-conjugated polymer n-type N2200 and P90 polymers (alternating naphthalene dicarboximide (NDI) acceptor and bithiophene (T2) donor units, where NDI units in P90 alternately feature methyl end-capped heptaethylene glycol (90%) and 2-octyl dodecyl (10%) side chains) are studied to understand how electrolyte cation insertion influences the polymer electronic behavior, which is necessary for energy conversion applications.

9:40am **RE1-TuM-6 Transition Metal Doped NiOx Faceted Nanosheets for Electrocatalytic Water Oxidation***, K. Ruecker,* German Aerospace Center Oldenburg, Germany*; D. Taffa,* Carl von Ossietzky University of Oldenburg, Germany*; E. Brim, D. Hayes,* Colorado School of Mines, USA*; J. Lorenz,* German Aerospace Center Oldenburg, Germany*; S. Alia, B. Pivovar,* National Renewable Energy Laboratory*; M. Risch,* Hemholtz Center Berlin, Germany*; C. Harms,* German Aerospace Center Oldenburg, Germany*; M. Wark,* Carl von Ossietzky University of Oldenburg, Germany*;* ***Ryan Richards,*** Colorado School of Mines, USA

The ability to manipulate earth abundant metal oxides presents an important potential technology to develop sustainable materials with novel properties. These materials are of interest due to the coordination environments that can be achieved and to the high degree of control over properties that can result from tailoring the exposed facets of metal oxides. Here, recent highlights regarding nanostructured metal oxides and their applications in electrocatalysis will be presented.Water electrolysis enables the production of green hydrogen as part of the energy transition. Moving to alkaline media using an anion exchange membrane (AEM) enables the usage of non-precious metal electrocatalysts and thereby limitations in the availability and the cost of catalyst materials required for proton exchange membrane water electrolysis. The oxygen evolution reaction (OER) at the anode involves multiple electron and proton transfer steps and thus suffers from a higher overpotential than the hydrogen evolution reaction at the cathode, making catalyst development for the OER critical for water electrolysis. Transition metal oxide (TMO) catalysts are promising as efficient electrocatalysts for the OER in alkaline media, since they are relatively active and the material is comparably inexpensive. It has been shown, that the electrocatalytic activity of nickel-based catalysts is strongly influenced by the morphology, by the crystallographic orientation of the material and by the combination of different transition metals into the nickel oxide host structure.

In this study, NiO nanosheets predominantly oriented in the (111) crystallographic planes were synthesized by either hydrothermal (HT) or microwave-assisted (MW) routes, to investigate the influences of faceting as well as the enhancements by doping with transition metals (Fe, Mn, Co), where especially doping with small amounts of Fe (e.g. 5 mole %) enhanced the OER activity. Furthermore, the syntheses were adopted to produce Fe, Mn and Co doped NiO (111) nanosheets with various dopant concentrations. The Fe and Co doped NiO (111) nanosheets outperformed the pure NiOx materials during the testing, whereas the Mn doping decreased the electrocatalytic activity of the materials. Structural characterization by synchrotron-based X-ray absorption spectroscopy and X-ray photoelectron spectroscopy before and after electrochemical testing were used to elucidate underlying processes like phase transformation and oxidation state changes.

## Renewable Energy and Energy Storage
## Room Naupaka Salon 4 - Session RE2-TuM

### Materials for Energy Conversion

**Moderator: Ryan Richards**, Colorado School of Mines

10:20am **RE2-TuM-8 Physical Properties Control of Metal-Hydride Thin Films and Application of Autonomous Synthesis Systems*, Ryota Shimizu,*** The University of Tokyo, Japan **INVITED**

Hydrogen-containing compounds have been attracting considerable attention. Until now, extensive research has focused on hydrogen energy applications such as hydrogen storage systems and fuel cells. However, recent research has diversified into various fields. For example, among various hydride materials, the ionic conductivity of $Li^+$ and $Na^+$[1] ions and hydride ($H^-$) ions[2] has been reported, with potential applications in electrochemical devices. Furthermore, discoveries of optoelectronic properties in rare-earth oxyhydrides[3] and high-temperature superconductivity under ultrahigh pressure[4] have opened new directions in solid-state physics and solid-state chemistry.

One unique characteristic of hydrogen is its flexible charge state. Hydrogen has an intermediate electronegativity among all elements, allowing it to exist as $H^+$ (proton), H (atomic), or $H^-$ (hydride) depending on the surrounding environment. Therefore, if this charge state can be controlled by external fields, it is possible to develop devices with dramatically altered physical properties.

Our aim is to create epitaxial thin films of these intriguing metal hydrides and explore their applications in material property research and electronic devices. To date, we have successfully achieved the epitaxial growth of metal hydrides such as $TiH_2$, NbH, $MgH_2$ (hydrogen storage materials), $YH_2$ (smart mirrors), and $EuH_2$ (ferromagnetic semiconductors)[5] using reactive sputtering techniques. We have also succeeded in the epitaxial growth of yttrium oxyhydrides ($YO_xH_y$)[6] and calcium nitride hydrides ($Ca_2NH$)[7] through anion complexation with reactive gases like $O_2$ and $N_2$. We will present these deposition techniques and discuss the intriguing physical properties associated with hydride thin films involving electrons and ions.

Furthermore, aiming to accelerate the rapid discovery of such novel thin film materials, we have developed an autonomous synthesis system that integrates AI and robotics. In this talk, I will discuss future perspectives regarding a materials exploration system integrated with various measurement instruments.

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11:00am **RE2-TuM-10 Non-Precious Metal Electrocatalysts for Anion Exchange Membrane Fuel Cells***, **Jin-Song Hu**,* Institute of Chemistry Chinese Academy of Sciences, China

Under the carbon neutrality scenarios, the demand for fuel cell electric vehicles (FCEVs) is rapidly growing. According to the IEA report, the transportation section will demand more than 15,000 thousands of FCEVs by 2030. Besides continuing to improve the fuel cell performances, the fuel cells cost and FCEVs running cost come into attention. Anion exchange membrane fuel cells (AEMFCs) offer the opportunities for using non-precious metal based electrocatalysts for both anodic and cathodic reactions to reduce the fuel cell cost and relieve the concerns on the Pt scarcity.

This presentation will be focused on our recent efforts on the development of non-precious metal based electrocatalysts for alkaline oxygen reduction reaction (ORR) and the CO-tolerant electrocatalysts for hydrogen oxidation reaction (HOR). A couple of new strategies will be introduced to develop the efficient electrocatalysts, including a molecular-based cascade anchoring strategy for general mass production of high-density metal-nitrogen single-atomic catalysts, metastable rocksalt oxide mediated synthesis of high-density well-armored transition metal nanoparticle electrocatalysts, and interface assembly strategy for achieving high-density binary single-atomic catalysts with much improved active site utilization. Moreover, the binary active sites electrocatalysts will be introduced to synergistically boost the elementary reactions of the alkaline HOR. These results may provide new insights for the rational design and bottom-up synthesis of cost-effective and high-performance electrocatalysts for AEMFCs.

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11:20am **RE2-TuM-11 Elucidating Early-Stage Lithium Growth and Dendrite Suppression Strategies in Lithium Metal Batteries***, **Seung-Yong Lee**,* Hanyang University, Korea **INVITED**

Lithium metal batteries (LMBs) offer significant advantages over traditional lithium-ion batteries due to their high theoretical capacity and energy density. However, their practical application is hindered by the formation of lithium dendrites during charging, which leads to poor performance, reduced lifespan, and severe safety risks. Current research aims to understand and mitigate these challenges to unlock LMBs' full potential, but a comprehensive understanding of the fundamental mechanisms driving lithium dendrite formation remains elusive.

In this study, we employed various air-free techniques, including cryo-transmission electron microscopy (cryo-TEM), to investigate the early-stage growth behaviors of lithium metal. By enabling direct lithium deposition on copper TEM mesh grids within coin cell batteries, we examined lithium growth without additional sampling processes that could introduce artifacts and damage. Preliminary experiments showed that the stepped edges of certain TEM mesh grids served as preferential nucleation sites, guiding lithium growth within confined spaces. This finding highlights the potential of TEM mesh grids as effective 3D hosts for lithium metal anodes and underscores the need for caution in interpreting lithium growth kinetics using this method.

Further investigations using this approach revealed mechanisms behind lithium dendrite suppression with a lithium nitrate electrolyte additive. Air-free cryo-TEM experiments, including energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS), along with air-free X-ray photoelectron spectroscopy (XPS), identified the predominant phases of the solid-electrolyte interphase (SEI) formed with the electrolyte additive. These analyses indicated that an inorganic SEI layer significantly suppresses dendritic growth, transforming lithium deposition into a more spherical morphology. Additional controlled experiments confirmed the influence of the inorganic SEI layer on lithium morphology.

Our research advances battery technology by providing in-depth mechanistic insights and practical strategies to overcome the limitations of LMBs. By addressing the fundamental challenges of lithium dendrite formation, we pave the way for developing safer, high-performance energy storage solutions essential for future technological advancements.

## Biomaterial Surfaces & Interfaces
## Room Naupaka Salon 1-3 - Session BI-MoP

## Biomaterial Surfaces & Interfaces Poster Session

**BI-MoP-1 Fabrication of Hydrogel-Based Optical Biosensor for Smart Intraocular Lens*, **Soongeun Kwon**, Y. Eom, H. Choi, J. Ahn, S. Park, H. Lim, G. Kim, K. Choi, J. Lee,* Korea Institute of Machinery and Materials, Republic of Korea

Due to the high biocompatibility, facile chemical modification and excellent responsiveness, hydrogel materials have received great deal of attention as wearable or implantable biosensor substrates. To fabricate a hydrogel-based biosensor, a stable bond at the interface of hydrogel and a functional sensing material is essential. In this study, we demonstrated fabrication and application of hydrogel-based optical sensor with a biocompatible micro-grating pattern for implantable medical devices.

To fabricate a functional micro-grating pattern, photolithographic patterning of a photoresist (PR) was performed to define the micro-scale line and spacing pattern. Gold (Au) nanoparticles spin-coated on the PR pattern were patterned by ligand exchange and lift-off process, resulting in an Au micro-grating pattern on a silicon (Si) wafer. The as-fabricated Au micro-grating pattern showed a rabbit ear morphology by controlling the thickness of the PR pattern. Subsequently, molding of a hydrogel precursor into the Au micro-grating pattern on a Si wafer was conducted to transfer the Au micro-grating pattern to the target hydrogel substrate.

The rabbit ear morphology and porous structure of the Au pattern enabled large interfacial contact area between hydrogel precursor and Au nanoparticles, resulting in stable bonding at the interface of Au micro-grating pattern and hydrogel substrate. Due to the biocompatibility of Au and hydrogel, this hydrogel-based biosensor can be used as for implantable medical devices.

As a case study, we demonstrated the application of hydrogel-based optical sensor composed of Au micro-grating pattern for smart intraocular lens (IOL). A pH-responsive hydrogel sensor with Au grating pattern was attached to an IOL to measure the micro-displacement of reactive hydrogel in response to pH changes by optical Moiré pattern detection. With the optical Moiré pattern detection scheme, the proposed hydrogel-based biosensor provides novel implantable optical sensor without external battery, highlightening its potential as a versatile tool for detecting various disease-specific biomarkers.

**BI-MoP-2 Correlative Microscopy Without the Instrument Manufacturer; Using Computer-Readable Fiducial Markers to Navigate Specimens Irrespective of Who Made the Sample Stage*, **Peter Cumpson**,* La Trobe University, Australia

In the diverse field of microscopy, researchers often face challenges in correlating data across different instruments, each with proprietary hardware and software. This work introduces a novel, manufacturer-agnostic solution for correlative microscopy using computer-readable fiducial markers, facilitating seamless navigation and analysis across various microscopy platforms.

Our approach employs laser-etched fiducial markers on sample holders, enabling precise localisation of sample features. This methodology eliminates the need for instrument-specific solutions, significantly enhancing workflow efficiency and accuracy.

We have demonstrated the effectiveness of our system across multiple microscopy techniques, including Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS), and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Our results indicate that this "GPS map for microscopy" not only improves the precision of correlative microscopy but also significantly reduces the time and costs associated with manual sample alignment and calibration.

In collaboration with the National Physical Laboratory (NPL) and University of Durham in the UK we have begun a project to demonstrate and verify the accuracy of this technique. This model considers various scales and imaging modalities, ensuring traceable measurement accuracy and enhancing the reliability of our method.

Our system offers significant advantages for a wide range of applications, from material science and battery research to biomedical and pharmaceutical studies. By enabling precise and consistent navigation across different microscopes, we facilitate interdisciplinary collaboration and accelerate scientific discoveries.

**BI-MoP-3 Supervised MVA and Random Forests for Analysis of GCIB-SIMS Data from Bacteria*, **John Fletcher**,* University of Gothenburg, Sweden

Antibiotic resistance can rapidly spread through bacterial populations via bacterial conjugation. The bacterial membrane has an important role in facilitating conjugation, thus investigating the effects on the bacterial membrane caused by conjugative plasmids, antibiotic resistance, and genes involved in conjugation is of interest. Analysis of bacterial membranes was conducted using gas cluster ion beam–secondary ion mass spectrometry (GCIB-SIMS). The complexity of the data means that data analysis is important for the identification of changes in the membrane composition. Pre-processing of data and several analytical methods for identification of changes in bacterial membranes have been investigated. GCIB-SIMS data from *Escherichia coli* samples were subjected to principal components analysis (PCA), principal components–canonical variate analysis (PC-CVA), and Random Forests (RF) data analysis with the aim of extracting the maximum biological information. The influence of increasing replicate data was assessed, and the effect of diminishing biological variation was studied. Optimized *m*/*z* region-specific scaling provided improved clustering, with an increase in biologically significant peaks contributing to the loadings. PC-CVA improved clustering, provided clearer loadings, and benefited from larger data sets collected over several months. RF required larger sample numbers and while showing overlap with the PC-CVA, produced additional peaks of interest. The combination of PC-CVA and RF allowed very subtle differences between bacterial strains and growth conditions to be elucidated for the first time. Specifically, comparative analysis of an *E. coli* strain with and without the F-plasmid revealed changes in cyclopropanation of fatty acids, where the addition of the F-plasmid led to a reduction in cyclopropanation.

**BI-MoP-4 Establishing Semi-Oriented Crimped Dual-Sized Fibrous Skeleton for Soft Tissue Engineering Scaffolds*, **Han Wang**, L. Ren,* Deakin University, Australia, China*; S. Zhao,* Deakin University, Australia*; H. Yang,* Wuhan Textile University, China*; L. Kong,* Deakin University, Australia

Soft tissues, such as blood vessels and heart valves, exhibit unique mechanics stemming from their intricate fibrous network architecture. Replicating harmonious structure-function relationships with synthetic analogs remains an unmet challenge. In this work, semi-oriented crimped dual-sized poly(lactic-co-glycolic) acid fibrous membranes with soft-tissue-like mechanical biocompatibility were fabricated by optimizing the organization of the polymer molecular chains and fibers. This is achieved by controlling the entanglement and conformational adjustment of molecular chains. Mechanical properties (modulus: 39.46 ± 11.01 MPa, strength: 3.19 ± 0.33 MPa, toughness: 0.66 ± 0.17 MJ/m$^3$) of submicron (145 - 863 nm) and micron (0.66-5.60 μm) crimped fiber membranes with an orientation of 38.91-47.38% were not significantly different from those of valve soft tissues. This fibrous skeleton provides inspiration for the development and design of soft tissue scaffolds with superior structure and performance.

## Renewable Energy and Energy Storage
## Room Naupaka Salon 1-3 - Session RE-TuP

## Renewable Energy and Energy Storage Poster Session

**RE-TuP-1 Graphene-Based Solar Cell Energy Harvester Intermittently Recharges a Battery-Powered Temperature Sensor System*, **Paul Thibado**, J. Mangum, T. Amin, S. Rahman, R. Kabir, A. Ashaduzzaman,* University of Arkansas*; G. Carichner, H. Do, D. Blaauw,* University of Michigan, Ann Arbor

Transparent, flexible, and electrically conductive graphene membranes hold great promise for multimodal energy harvesting. These sources include solar and ambient radiation, thermal, acoustic, and kinetic power. This poster reviews several graphene energy-harvesting avenues, then focuses specifically on the fabrication of graphene-based solar cells using mainstream semiconductor manufacturing methods. Our two-write maskless laser lithography process creates an array of graphene-based solar cells on a commercially available 100-mm silicon wafer topped with a 2-micron thick wet thermal oxide layer on top. The first pattern marks the wafer locations for etching the silicon dioxide down to the bare silicon substrate. The second pattern marks the wafer for gold traces and bonding pads. Once completed, the exposed silicon and graphene bonding pad are covered using a large-area graphene transfer method. The samples are then characterized using atomic force microscopy, optical microscopy, and photovoltaic measurements. We also used our energy harvester to charge a 3-volt rechargeable battery, which is simultaneously driving an ultralow power consuming custom temperature sensor system. This work was financially supported, in part, by a grant from the WoodNext Foundation, which is administered by the Greater Houston Community Foundation.

**RE-TuP-2 A Study on Robust $VO_2$ Protection Layer and Defect Inactivation in $BiVO_4$ Photoelectrodes through Photoelectrochemically Transition-Metal Engineering**, *H. Cho, **Kun Woong Lee,*** School of Advanced Materials Science & Engineering, Sungkyunkwan University (SKKU), Republic of Korea

Photoelectrochemical (PEC) cells for water splitting have garnered significant attention as a promising technology for solar-to-hydrogen energy conversion. Bismuth vanadate ($BiVO_4$), serving as the photoanode among photoelectrodes, stands out as a representative ternary oxide-semiconductor with several advantages. However, $BiVO_4$ photoanodes face controversial issues such as surface defects, performance limitations, and susceptibility to photo-corrosion instability. To address these challenges, we propose a groundbreaking protection layer. Based on deep understanding of the photo-corrosion mechanism regarding the dissolution of $V^{5+}$ ions on $BiVO_4$ surface, we introduce a surface photoelectrochemical oxidation approach. By strategically introducing $V^{5+}$ ions and $H_2O_2$ into the electrochemical electrolyte, we artificially modify photo-corrosion into advanced photo-oxidation. This induces a surface phase transition, leading to the formation of a novel vanadium oxide ($VO_2$) photoelectrochemical protection layer by transitioning the $V^{5+}$ ions to the electrochemically favorable $V^{4+}$ state. This layer is both conductive and ultrathin (~ 5 nm), while offering atomic-level controllability.

Characterizations of the $BiVO_4/VO_2$ photoanodes reveal enhanced carrier dynamics, with faster transport of interfacial charges (86%) and efficient transfer of photogenerated carriers through the $VO_2$ protection layer (95%). This innovative approach enables near-ideal performance, contributing to high stability and remarkable durability. Consequently, the $BiVO_4/VO_2/CoFeO_x$ photoanodes exhibit an impressive photocurrent density of 6.2 mA/cm$^2$ and an onset potential of 0.25 $V_{RHE}$. Additionally, they demonstrate an applied bias photon-to-current efficiency of 2.4% at 0.62 $V_{RHE}$ and stable operation without serious performance degradation for 100 hours, showcasing vigorous active oxygen evolution.

## Thin Films and Surface Modification
## Room Naupaka Salon 1-3 - Session TF-TuP
## Thin Films and Surface Modification Poster Session I

**TF-TuP-1 Effect of Ag Layer Thickness on the Transmittance and Conductivity of Transparent Antennas Fabricated Using ITO/Ag/ITO Structures**, ***Yoji Yasuda**, Y. Saitou,* Tokyo Polytechnic University, Japan*; F. Koshiji,* tokyo polytechnic university, Japan*; T. Uchida,* Tokyo Polytechnic University, Japan

In recent years, research and development efforts have focused on the Internet of Things and next-generation communication systems. In these systems, antennas are ideally placed on the surface of the chassis to improve communication characteristics. Hence, to maintain the appealing design features of these devices and systems, optically transparent antennas using transparent conductive films such as indium tin oxide (ITO) are attracting attention. However, there is a trade-off relationship between the optical transmittance and conductivity of transparent conductive films, and it has been challenging to achieve a good balance between the two. Nevertheless, it has been reported that multilayer composites with a dielectric-metal-dielectric (DMD) structure, in which a metallic thin film (e.g., Ag thin film) is introduced as an intermediate layer, can simultaneously achieve high transmittance and conductivity. In this study, we evaluated the transmittance and conductivity of a DMD structure composed of ITO/Ag/ITO with respect to changes in the thickness of Ag in the intermediate layer, and investigated the effects of the transmittance and conductivity on the antenna characteristics following annealing treatment.

ITO/Ag/ITO transparent conducting films were deposited by varying the thicknesses of the Ag and intermediate layers using a facing target sputtering system. The films were annealed at 200–500 °C in air, and their optical transmittance and electrical properties, such as sheet resistance and carrier density, were evaluated. In addition, a monopole antenna of 20 mm length and 5 mm width was fabricated and its radiation efficiency was measured. It was found that with an Ag layer thickness of 7.5 nm, the transmittance and conductivity of the ITO/Ag/ITO film were approximately 69.8% and 7.8 × $10^5$ S/m, respectively. When the transparent conducting film with an Ag film thickness of 7.5 nm was annealed at 200 °C, the transmittance and conductivity of the film increased to approximately 73.4% and 8.5 × $10^5$ S/m, respectively.

**TF-TuP-2 Extending the Lifetime of Plasma Torch Electrodes Using a Layer of Carbon Nanotubes**, ***Alexandr Ustimenko**, V. Messerle,* Affiliation, Kazakhstan

The lifetime of plasma torch electrodes is critical, however it is usually limited to 200 hours. Considered in this paper the long life direct current arc plasma torch has the cathode life significantly exceeded 200 hours. To ensure the electrodes' long life a process of hydrocarbon gas (propane/butane) dissociation in the electric arc discharge is used. In accordance to this method, atoms and ions of carbon from near-electrode plasma deposit on the active surface of the electrodes and form a carbon condensate in the form of carbon nanotubes. It operates as "actual" electrode. To realize aforesaid the construction of a plasma torch using air as the plasma forming gas has been developed and tested. Propane/butane mixture is supplied to the zone of the arc conjunction to the copper water-cooled electrodes (cathode and anode). As a result inside the cathode cavity and internal surface of the anode medium of carbonic gas is formed. Linked with the arc in series, the magnetic coils 3 guaranty stabilization of the discharge on the electrodes. The processes of propane/butane molecules dissociation and carbon atoms ionization start with the rise in temperature. Arisen from ionization positive carbon ions deposit onto the electrodes surface under the influence of near-cathode decline in potential and form coating of the electrode condensate. This coating is "actual" cathode, deterioration of which is compensated by the flow of carbon ions and atoms. The coating thickness depends mainly on ratio of the flows propane/butane and air and the arc current. It is found that when power of the plasma torch was in interval 76–132 kW and propane/butane flow in range of 0.4–0.7 LPM thermal efficiency of the plasma torch reached 90%. At that mass averaged temperature on the exit of the plasma torch increased to 5000 K. The electrode condensate was examined using scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. It is found that the electrode condensate is composite carbonic stuff made of carbon nano-clusters which consists mainly of single and multi-wall carbon nanotubes. The following parameters of the conducting nano carbon deposited at the cathode were determined: chemical composition, wt %: C 96.74–98.47, H 2.26–1.24, Cu 1–0.30; interplanar spacing, nm: 0.333 (100%), 0.207 (1%), 0.168 (5%); apparent density, 1.63 g/cm$^3$; and resistivity, <$10^{-8}$ Ohm·m.

**TF-TuP-3 Comparative Depth Analysis of Crystalline Phases in Copper Thin Films Using OrbiSims**, ***Jong Sung Jin**, J. Sung,* Korea Basic Science Institute (KBSI), Republic of Korea

Copper thin films with different crystallinities of poly and single crystal were formed on sapphire with excellent crystallinity. The latest OrbiSIMS equipment was used to analyze the depth from the surface to the interface where the sapphire substrate is exposed, and the three-dimensional structure of various ions was confirmed. Three thin films with different crystallinities, including copper foil, were analyzed. The internal oxygen showed a clear difference in the relative content and distribution pattern between poly and single crystal.In addition, the behavior of aluminum ions contained in sapphire was different. Naturally, the distribution of copper ions, which are the main raw material, was also different.From the results of this study, we were able to simultaneously confirm the distribution of oxygen that can control the oxidation of thin copper films, the correlation with the crystallinity of copper, and the behavioral changes of ions using OrbiSIMS. We are confident that these observations will provide basic data for the modification of solid surfaces, such as the prevention of oxidation of copper surfaces and the coating of ions of other metals in the future.

**TF-TuP-4 Surface Chemistry and Growth Characteristics of SiNx Films via Plasma-Enhanced Atomic Layer Deposition**, ***Ilkwon Oh,*** Ajou University, Republic of Korea

Recent advancements in semiconductor applications have emphasized the growing importance of $SiN_x$ due to its exceptional operational reliability.[1,2] In the scaling trends, the need to deposit gate spacers has underscored the significance of $SiN_x$ atomic layer deposition (ALD), which offers uniformity and conformality, andthickness control at the Angstrom level. [3, 4] However, the role of Si precursor chemistry in growth and electrical characteristics of $SiN_x$ films has not been fully explored. Understanding this relationship is crucial, as growth characteristics directly impact the electrical performance and leakage current behavior of $SiN_x$, which is vital for its effectiveness in electrical insulation applications. This study investigates the relationship between three different Si precursors and the electrical properties of $SiN_x$ films.Three alkyl amine precursors, bis(tertiarybutylamino)silane (BTBAS), bis(diethylamino)silane (BDEAS), and NSi-01 were used for this study. The deposition was done on the substrate temperature of 200 °C with 60 MHz very high frequency (VHF) $N_2$ plasma as a reactant. Density functional theory (DFT) calculations, Monte Carlo (MC) simulations, and ellipsometry were employed to analyze the growth characteristics during ALD process. Additionally, the film quality evaluation was done by using X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM). The correlation between electrical and growth characteristics was investigated by fabricating and evaluating metal-oxide-semiconductor (MOS) capacitors. This study provides key insights into optimizing precursor selection to enhance device performance, demonstrating how the choice of ligands can significantly impact the leakage characteristics and reliability of $SiN_x$-based devices.

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**TF-TuP-5 Enhanced Oxide versus Nitride Selectivity in Area-Selective Atomic Layer Deposition of SiO2 Thin Films Combining Small Molecule Inhibitors with Atomic Layer Etching**, ***Jiwoo Oh**, J. Lee, W. Kim,* Hanyang University, Korea

As the semiconductor industry advances towards complex multilayered devices with smaller features, area-selective atomic layer deposition (AS-ALD), a bottom-up method, has gained significant interest for its capability to enable precise and self-aligned deposition within specified areas, i.e., the growth areas. In this study, we primarily utilized small molecular inhibitors as vapor-phase deactivating agents to non-growth areas, due to their small size, high volatility, and ease of process integration into 3D structured devices. More particularly, this AS-ALD methodology is advantageous for manufacturing high aspect ratio $SiO_2$/SiN structures in V-NAND, where the reduction in tier size leads to cell-to-cell crosstalk between vertically downscaled $SiO_2$/SiN stacks. To mitigate this issue, it is essential to apply AS-ALD of $SiO_2$ thin films on $SiO_2$ surfaces while preventing deposition on SiN surfaces. For this purpose, we employed a vapor-dosing process using silane-based small molecule inhibitors that chemo-selectively adsorb on -NH terminated surface groups of the SiN surface. Moreover, to further improve deposition selectivity, we periodically introduced a post-atomic layer etching step with atomic scale fidelity after a certain number of ALD $SiO_2$ cycles, which effectively removed $SiO_2$ moieties from the SiN surfaces. Finally, we achieved a deposition selectivity greater than ~10 nm on blanket $SiO_2$ and SiN substrates. The approach we present here contributes to the advancement of the manufacturing process for next-generation bottom-up 3D nanofabrication.

**TF-TuP-6 Conductive Polymer Film Formation Using Plasma Process in Organic Solution According to Driving Power Condition**, ***Hyojun Jang**, J. Kim, H. Tae,* Kyungpook National University, Republic of Korea

Plasma material process in an organic solution uses the interaction between plasma and solution substances. Plasma generated in the solution occurs a strong discharge through an electrode structure designed for ease of ignition. Therefore, most plasma materials processes conducted in solution have been used to form metal or carbon nanoparticles by erosion of electrodes or carbonization of solutions. Recently, studies have been reported on igniting plasma that limits strong discharges in liquid phases and controlling chemical activity (oxidation, reduction) according to the driving waveform. As a result, this method succeeded in creating π-conjugated polymer film, as well as nanoparticles with the molecular structure of the starting solution.

In this study, we conducted research on controlling properties of conductive polymer films synthesized by the plasma process in organic solution. Plasma characteristics affect the chemical activity of the material and consequently change the properties of the polymer film. Therefore, this process is performed using various driving power conditions to control the plasma characteristics. The electrical and optical characteristics of plasma and the changes in solution are analyzed according to driving power conditions. Moreover, the differences in the properties of conductive polymer films are investigated in detail. Finally, it is confirmed that the conductive polymer synthesized in this method has stable electrical properties in room condition.

**TF-TuP-7 UV Light Extinction Imaging Method for Monitoring Inkjet-Printed Organic Layer in Thin Film Encapsulation Process**, ***Jun Young Hwang**, J. Yu, H. Kang,* Korea Institute of Industrial Technology, Republic of Korea*; D. Lee, G. Yun,* LG Electronics, Republic of Korea*; S. Lee,* Poongsan System Co., Ltd., Republic of Korea

Organic thin layers are highlighted as crucial components of flexible and printed electronic products due to their ability to provide mechanical flexibility in various applications, such as flexible displays and wearable electronics. The thickness and uniformity of these layers are crucial factors that influence surface planarization, mechanical stress relief, and the enhancement of optical performance. Therefore, accurate measurement of their thickness distribution is essential. In this study, the two-dimensional thickness distributions of spin-coated and inkjet-printed organic microlayers on glass substrates, which are used in optically transparent resin for displays and thin film encapsulation for flexible OLEDs, were quantitatively and qualitatively measured using UV light extinction imaging method. Quantitatively, the organic materials tested absorbed 40 to 50% of light with a wavelength of 300 nm through a layer with a thickness of 3 to 4 µm. Consequently, a measurement error of less than a few nanometers could be achieved through image overlay and pixel binning. Qualitatively, this non-destructive, non-contact two-dimensional measurement method enables immediate and intuitive analysis of the thickness distribution or surface waviness of the coated layer.

**TF-TuP-8 Room–Temperature Ferromagnetism Observed in Graphene Oxide Fabricated by AFM Lithography**, *B. Park,* Department of Physics, Konkuk University, Republic of Korea*; **DaYea Oh**,* Deparment of Physcis, Konkuk University, Republic of Korea*; D. Lee,* Department of Physics, Konkuk University, Republic of Korea*; W. Kim,* Korea Research Institute of Standards and Science, Republic of Korea*; J. Choi,* Center for Spintronics, Korea Institute of Science and Technology, Republic of Korea

Graphene is typically considered to be a nonmagnetic material with long spin lifetime and transport distance. The potential to induce magnetic properties in graphene by various methods has generated significant interest since it would enable the development of novel spintronic devices where charge and spin manipulation could be combined. Recent works have predicted the formation of ferromagnetic order in graphene with point defects or functionalization. Ferromagnetic signals at room temperature have been observed for graphene or graphite with point-defects produced by various methods. However, there are debates on (1) the role of possible contamination and (2) the mechanism responsible for the strong interaction required for the formation of ferromagnetic order. According to a more recent report, point-defects in graphene only produce spinhalf paramagnetism, and the ferromagnetic order observed in previous studies was caused by the presence of small amounts of magnetic impurities. In the case of functionalized graphene, it has been reported that the ferromagnetic order is predicted for the oxidized graphene layer where C atoms have C–OH, C–O–C, or C=O bonds, and for the semi-hydrogenated graphene sheet. Although the existence of ferromagnetic order below 100 K in the n-doped graphene oxide layer has been experimentally confirmed with superconducting quantum interference device measurement, the possibility of magnetic contamination was not examined strictly.

Here, we investigate magnetic properties of graphene oxide flake that have been locally oxidized using atomic force microscopy (AFM) lithography. This approach reduces the possibility of magnetic contamination. Our Raman spectroscopy analysis reveals that the graphene oxide contains crystalline defects or disorders and differs from the pristine graphene in terms of its atomic structure. Using magnetic force microscopy measurements, we observe that the graphene oxide has a net magnetization pointing out of the surface plane. Furthermore, our magneto-optical Kerr effect data show small but clear hysteresis loops with non-zero remanent magnetization. We also conduct x-ray magnetic circular dichroism (XMCD) photoemission electron microscope measurements and identify remarkable asymmetry in carbon K edge spectra, which strongly suggests that the observed ferromagnetic order in the graphene oxide layer is intrinsic. A careful analysis of XMCD signals depending on the oxidized condition reveals the effects of chemical states of carbon atoms on the formation of ferromagnetic order in the graphene oxide.

**TF-TuP-9 Reactive Ion Etching of Contact Hole for LTPS Process Using Low Global Warming Potential Gas**, ***Jun Won Jeong**, J. Hong, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

The evolution of display technology has increased the demand for thinner, lighter, and higher-resolution panels in digital devices such as mobile phones, TVs, and laptops. In response to these demands, Thin Film Transistor (TFT) technology has emerged as a critical factor in determining display performance. In the early stages of display panel manufacturing, **a-Si (Amorphous Silicon) processes** were widely adopted due to their low cost and ease of mass production. However, the limitations of low electron mobility of a-Si processes limited the resolution and response speed of display panels. To overcome these limitation**, LTPS (Low-Temperature Polycrystalline Silicon)** technology was introduced. [1-2] LTPS TFT uses the excimer laser annealing (ELA) for crystallizing silicon at lower temperatures, therefore LTPS achieves significantly higher electron mobility than a-Si process. [3] Consequently, LTPS has become an essential technology for high-performance displays. In the context of next-generation electronic devices, optimizing the contact hole etching process for LTPS is critical. This requires the development of new etching gas mixtures that exhibit enhanced etching characteristics, including high etch rates, minimal sidewall and underlying layer damage, and anisotropic etch profiles. This study compares the Perfluorocarbon (PFC) gas A and low global warming potential hydrofluorocarbon (HFC) gas B, analyzing the etch characteristics and proposes optimization process to enhance the etching process in LTPS.

In gas A, as the flow rate increased, the etching rates of $SiO_x$, $SiN_x$, and a-Si all increased. The etch selectivity between $SiO_x$ and $SiN_x$ slightly decreased, while the selectivity between $SiO_x$ and a-Si showed minimal change. In contrast, in gas B, as the flow rate increased, the etching rates of $SiO_x$, $SiN_x$, and a-Si decreased slightly. The etch selectivity between $SiO_x$ and $SiN_x$ slightly decreased, while the selectivity between $SiO_x$ and a-Si showed a steep increase.

## Nano and 2D Materials
## Room Naupaka Salon 4 - Session NM1-TuE

### Synthesis and Manipulation

**Moderator: Sarah Burke**, University of British Columbia

6:00pm **NM1-TuE-2 Using a Zeolite Imidazolate Framework-8 Nanomaterial for Adsorption and Removal of Thymol from Water and Heparin Recovery**, ***Deepak Ganta,*** Texas A&M International University*; M. Karimi Abdolmaleki,* Texas A&M University-Corpus Christi*; S. Gonzalez Torres,* Texas A&M International University*; C. Velazquez,* Texas A &M International University

There is a strong demand for multiplex sensing and storage capabilities from nanomaterial-based biosensors. To address the limitations in the adsorption capacity of existing materials, porous zeolite imidazolate framework-8 (ZIF-8) 3D nanomaterial, with a larger surface area, was chosen to absorb and remove thymol from water. The experimental adsorption measurement results agree well with theoretical Langmuir and Freundlich isotherm models. The maximum adsorption capacity of thymol on ZIF-8 was determined to be 454.6 mg/g. Furthermore, we also demonstrated the potential of ZIF-8 in recovering heparin from porcine intestinal mucosa. A recovery of 37 mg/g of heparin was reported and verified through kinetic and thermodynamic adsorption models, along with the appropriate surface conditions for the adsorption of heparin molecules. All the characterization methods will be presented.

6:20pm **NM1-TuE-3 Interaction of Defects on Mxene Surfaces: Nonlinear and Anisotropic Effects**, ***Steven Goldy***, Colorado School of Mines, USA*; G. Tucker,* Baylor University*; C. Ciobanu,* Colorado School of Mines, USA

Defects in two-dimensional (2D) materials like hexagonal boron nitride (hBN) and MXene can drastically change mechanical, electronic, and optical properties. Furthermore, surface defects specifically affect the electrocatalytic performance of the material, and their understanding and control can lead to novel materials for catalysis, photocatalysis, and gas sensing. From a fundamental standpoint, understanding the surface-mediated interactions between defects provides insight into their spatial distribution and can serve as a way to control catalytic, sensing, and transport properties. Based on molecular statics simulations, we have developed an approach to extract the formation and interaction energy of vacancies on 2D (hBN) and quasi-2D (MXene, MoS2) materials. We have found that the interaction of defects on 2D and quasi-2D materials shows significant anisotropy, as well as marked departures from the well-used inverse cube distance-dependence associated with linear elasticity. The divergence from linear elasticity is more apparent in MXenes due to their complex, thickness-dependent scaling behaviors and out of plane displacement. Due to highly variable surface chemistries, understanding surface defects on MXenes is critical to their application. These scaling laws inform defect separation distributions that assist in design on 2D composites and catalytic applications.

6:40pm **NM1-TuE-4 Synthesis of Uniform Borophene: In Situ Spectroscopic Analysis and Ex Situ Macroscopic Transfer**, ***Marko Kralj**, S. Kamal, B. Radatovic, V. Jadrisko, D. Novko, N. Vujicic, M. Petrovic,* Center for Advanced Laser Techniques, Institute of Physics, Croatia

Borophene (Bo), a recently realized polymorphic monoelemental two-dimensional (2D) material, holds promise for diverse applications, including metal-ion batteries, supercapacitors, hydrogen storage, gas sensors, and freshwater production. We present a study of Bo fabricated via segregation-assisted chemical vapor deposition (CVD) epitaxy, where an Ir(111) substrate was exposed to borazine vapors in ultra-high vacuum (UHV) at elevated temperatures. This process yielded structurally uniform and high-coverage χ6 polymorph of Bo, as evidenced by electron diffraction and scanning probe microscopies. Such Bo samples were further subjected to extensive spectroscopic analysis and post-synthesis manipulation, both of which are scarce due to experimental challenges posed by sample inhomogeneity and significant chemical reactivity of epitaxial Bo systems.

In the first part of this talk, we characterize Bo on Ir(111) (Bo/Ir), focusing on electronic properties influenced by the nanoscopic modulation of the Bo sheet. X-ray photoelectron spectroscopy (XPS) and scanning tunneling spectroscopy (STS) data reveal inhomogeneous binding of Bo to Ir, creating a stripe-like structure. This structure acts as a one-dimensional (1D) grating, causing Umklapp scattering of photoelectrons detected in ARPES experiments [1]. Density functional theory (DFT) calculations support our findings, providing insights into the pristine electronic structure of Bo, unaffected by the Ir substrate.

In the second part, the challenges of developing large-area Bo applications are addressed. We demonstrate large-area growth followed by electrochemical transfer of macroscopic single-layer Bo sheets from the growth substrate to a target Si wafer [2]. Our results show that deterministic manipulation of Bo layers is feasible despite their inherent chemical and mechanical instability, advancing Bo research and utilization. Post-transfer Bo displayed minimal mechanical defects, such as cracks and holes, mostly inherited from the synthesis substrate. Successful Bo transfer was further confirmed by Raman spectroscopy, which showed very good overlap of Raman peaks before and after the transfer, indicating preservation of Bo's original crystal structure.

References:

[1] ACS Appl. Mater. Interfaces 14 (2022) 21727–21737

[2] ACS Appl. Mater. Interfaces 15 (2023) 57890–57900

7:00pm **NM1-TuE-5 Design at Nanoscale of Thermostable Hybrid Sol-Gel Bondlayer to Functionalize Aeronautical CFRP by Thermal Spray**, ***Sophie Senani-de Monredon,*** SAFRAN TECH, France*; L. Rozes,* Sorbonne Université, France*; G. Penvern,* SAFRAN TECH, Sorbonne Univ., France*; A. Joulia,* SAFRAN TECH, France*; S. Bonebeau,* SAFIR, France

Composite Fibers Reinforced Parts (CFRP) are widely used in aeronautic since more than 40 years to contribute to decrease the aircrafts environmental footprint. Indeed $CO_2$ and NOx emissions have been considerably decreased by lightweighting correlated to significate fuel consumption reduction (15% for last LEAP aircraft engines). Nevertheless to go further and reach the new ambitious target of 20% reduction for the next aircraft engine, functionalization and metallization of CFRP is mandatory to extend them to more aggressive use cases than fuselage, by resistance against high temperature, erosion or icing. To reach this goal, thermal spray coatings are widely studied, even if it remains very complex to implement.

Metallization of CFRP, especially by coldspray is favored by numerous teams [1,2,3], with interesting results but not sufficient to fit performance required for aeronautic qualification. Our approach aims to design a thermostable sol-gel hybrid bondcoat. We will discuss how we succeed to control of the chemical composition, the nanostructuration of this bondlayer and the nature of the substrate/bondlayer/topcoat interfaces to influence the thermomechanical bondcoat’s properties and thus the building and the thickness increase of the thermal sprayed topcoat layer linked to the adhesion of the stack. Understanding the relation between nanostructuration of the hybrid sol-gel layer and their mechanical and thermal properties is essential to optimize the whole system. Finally, this will widely open the variety of materials (from metals to oxydes) reachable to functionalize CFRP part and allow new use cases unthinkable up to now.

**References**

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3- CO3 Project– F. Delloro et al (https://www.projectco3.eu/fr/ )

## Nano and 2D Materials
## Room Naupaka Salon 4 - Session NM2-TuE

### 2D Materials Based on Carbon and Boron

**Moderator: Akitoshi Shiotari**, Fritz-Haber Institute

7:40pm **NM2-TuE-7 First-Principles Study of Adsorption and Reaction on the Hydrogen Boride Sheet**, ***Ikutaro Hamada,*** Osaka University, Japan **INVITED**

The hydrogen boride (HB) sheet [1] is a newly synthesized two-dimensional material composed of hydrogen and boron atoms with their ratio of 1:1. The HB sheet has been attracted increasing attention, not only because of its high gravimetric hydrogen content as a hydrogen storage material and its ability to release hydrogen through light [2] and electrochemical [3] means, but also due to its catalytic activities [4]. Furthermore, the HB sheet has been shown to be chemically stable against water [5], unlike many boron hydrides that undergo hydrolysis reactions. The stability is a fascinating considering the practical application of the HB sheet. However, the molecular and mechanistic details of the chemical processes occurring on the HB sheet have yet to be fully addressed. In this talk, I will discuss the electronic and structural properties of the HB sheet [5], as well as the adsorption and reaction on the HB sheet based on our density functional theory calculations. Special emphasis is placed on the interaction with water molecules, and the mechanism of the stability of the HB sheet against water will be discussed [6,7].

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8:20pm **NM2-TuE-9 N-doped Graphene Synthesis through Nitrogen Ion Irradiation***, **Zbynek Novotny,*** Pacific Northwest National Laboratory*; B. Alupothe Gedara, P. Evans, Z. Dohnalek,* PNNL

Hydrogen ($H_2$) is one of the most promising clean and renewable energy sources. Nevertheless, the storage of hydrogen shows poor performance due to the low gravimetric and volumetric densities. Nitrogen-doped graphene (Gr) has been identified as a potential material for $H_2$ storage. We study the growth of Gr on a Ru(0001) surface by chemical vapor deposition (CVD) of pyridine ($H_5C_5N$) and N-doping through $N_2^+$ ion irradiation using scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). A high-quality Gr film with low N densities was obtained by pyridine CVD on Ru(0001) at 1100 K. Higher concentrations of N-dopants were introduced on the Gr/Ru(0001) through low-energy $N_2^+$ irradiation at 100 eV. Nitrogen can be embedded in the Gr lattice preferentially in two configurations, namely graphitic N (N substituted in the C lattice) and pyridinic N (substitutional N next to a C vacancy). Atomically-resolved STM images of graphitic and pyridinic-N defects demonstrate their preferential locations within the Gr Moiré. XPS shows that coverage of up to 3.9% of pyridinic-N and 2.3% of graphitic N can be embedded into the high-quality Gr film using $N_2^+$irradiation at room temperature, indicating a preferential formation of pyridinic N over graphitic N. Only graphitic N was observed upon annealing the ion-irradiated Gr/Ru(0001) to 1063 K, revealing higher thermal stability of graphitic N over pyridinic N. Our current efforts center on the adsorption studies of atomic hydrogen, its interactions with N dopants, and thermally induced diffusion.

8:40pm **NM2-TuE-10 Nanoscale Investigation of N-Heterocyclic Carbene Monolayers on Metal Surfaces***, **Francesco Tumino,*** Queen's University, Canada, Italy*; E. DesRoche, M. Aloisio, D. Nanan, A. McLean, C. Crudden,* Queen's University, Canada

Molecular monolayers on metal surfaces are two-dimensional (2D) systems of great interest for advanced applications in several fields, such as molecular electronics, photovoltaics and catalysis[1]. The physical and chemical properties of these systems critically depend on the choice of the molecular unit that constitutes the basic building block of the resulting 2D assembly[2].

Recently, N-heterocyclic carbenes (NHCs) have been proposed for the fabrication of robust molecular monolayers, based on their ability to form strong covalent bonds with transition metals[3]. Studies conducted on gold surfaces have shown that NHC-based monolayers can have greater thermal and chemical stability than alkanethiolate 2D layers[4], making them promising for applications in biosensing, surface patterning and corrosion protection[3].

The fabrication of NHC-based monolayers, however, requires a detailed understanding of how the NHC structure and the surface properties affect the molecular adsorption and self-assembly behavior on metals.

Therefore, we have conducted a nanoscale investigation of NHCs on single-crystal metal surfaces under ultra-high vacuum conditions (UHV). Our study includes NCHs with different backbones and N-substituents, deposited onto atomically clean surfaces using a vapor phase method (supplemental document, Fig.1). Low-temperature scanning tunneling microscopy (STM) was used to image in situ the resulting monolayers and obtain molecular-scale information on binding modes, adsorption geometries, and self-assembly patterns.

We observed different supramolecular assemblies (Fig. 2), in which the binding mode and lattice geometry vary depending on the N-substituents, the backbone structure, and the molecular density on the surface. Moreover, the metal surface properties play an important role, affecting the ability of NHCs to extract metal adatoms from the surface and form mobile NHC-metal complexes.

By discussing different factors which influence the NHC behavior on metals, our work contributes to a wider understanding of the coordination of these ligands to metal surfaces and the formation of 2D NHC-based layers.

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## Thin Films and Surface Modification
## Room Naupaka Salon 5 - Session TF1-TuE

### Thin Films - Bio- and Medical-related

**Moderator: Seo-Hyun Lee**, Hanyang University

5:40pm **TF1-TuE-1 Advanced Surface Engineering for Mass-Produced Medical Diagnostic Technology Addressing Tomorrow's Global Public Health Challenges***, **Christopher Muratore,** B. Robertson, M. Muratore,* University of Dayton*; N. Glavin,* Air Force Research Laboratory **INVITED**

Materials with high surface-to-volume ratios demonstrate exquisite sensitivity and detection limits in diverse molecular sensing applications.Integration of nanowires, nanotubes, and two-dimensional (2D) semiconductors into sensing devices, however, presents challenges inhibiting product development.For example, thousands of trials are required to obtain US government approval for point of care diagnostics, yet producing a suitable number of 2D devices via conventional synthesis and fabrication techniques to meet this testing requirement is not currently feasible. To realize commercial applications of 2D transducers in ubiquitous low-cost diagnostic devices, new synthesis and fabrication approaches were developed. Processes for high-rate (>$10^6$ per day) mass-production of low-cost two-dimensional electronic medical diagnostic devices with limits of detection rivalling polymerase chain reaction (PCR) based techniques (<10 fg/mL) with response times of <2 minutes will be presented. Rapid and inexpensive sensor chip fabrication relies upon sputter deposition, laser pattering, and laser annealing processes in a roll-to-roll physical vapor deposition system. Moreover, naturally abundant and recyclable materials were selected for use in these scaled processes for reduced waste stream impact in anticipation of large numbers of devices are consumed daily.An automated high-speed Raman spectroscopy system was developed for quality control of mass-produced materials during fabrication.Fundamental studies employing this system to measure point defect densities in 2D semiconducting transducer materials will be shown to correlate synthesis and fabrication process parameters, 2D materials structure, and diagnostic device performance.

6:20pm **TF1-TuE-3 Development of Stretchable Plasma Patch using Kirigami Technique for Biomedical Applications***, **Sunghoon Jung**, J. Kim,* Korea Institute of Materials Science, Republic of Korea

Plasma technology has recently been widely utilized in the biomedical field. Reactive oxygen and nitrogen species generated by plasma have been increasingly reported to sterilize pathogens and improve skin conditions. Traditional biomedical plasma devices include jet-type plasma sources and flexible patch-type plasmas. However, jet-type plasma is not suitable for large-area skin applications, and flexible plasma patches are not ideal for use on the stretchable surfaces of the human body. In this study, we employed the kirigami technique to impart stretchability to the existing plasma patch structure and applied it to pathogen removal.

The primary objective of this research is to develop plasma patches that naturally create discharge spaces and possess mechanical stretchability through the kirigami technique. This allows for effective plasma discharge and ozone generation without the need for additional spacers, even when deformed.

Plasma patches with 30%, 50%, and 100% stretchability were fabricated using screen printing and laser cutting technique. The discharge characteristics and ozone generation properties were evaluated in both non-attached states (large discharge space), where the patches were suspended in open space, and attached states(very small discharge space), simulating skin attachment.

In the non-attached state, where the patches were suspended in open space, the kirigami patches exhibited similar discharge characteristics to non-stretchable patches. However, when attached to a substrate, non-stretchable patches failed to generate plasma due to the lack of discharge space. In contrast, the kirigami patches, when stretched, caused the electrodes to rotate diagonally, creating discharge spaces and enabling plasma generation. This demonstrates that kirigami patches can achieve effective plasma discharge without additional spacers. Furthermore, antibacterial experiments confirmed the efficacy of the patches in eliminating Escherichia coli and Staphylococcus aureus.

The kirigami-based stretchable plasma patches offer significant advantages for biomedical applications, particularly in skin treatments. The ability to generate plasma without the need for additional spacers and the successful elimination of bacteria highlight the high potential of these patches. Future work will focus on optimizing the design and exploring further biomedical applications.

6:40pm **TF1-TuE-4 Silver-Copper Coatings: Combating Microbes on Surfaces and in Air Filtration***, L. Reyes-Carmona,* UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO, CU, Mexico*; V. Perez-Bucio, A. Almaguer-Flores,* UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO*; O. Sepulveda-Robles,* Instituto Mexicano del Seguro Social, Mexico*; **Sandra E Rodil,*** UNIVERSIDAD NACIONAL AUTONOMA DE MEXICO **INVITED**

The significant risk posed to healthcare workers by the transmission of bacteria and respiratory viruses through expelled saliva microdroplets and aerosols, underscored by the SARS-CoV-2 pandemic, has driven researchers to develop nanomaterials with antimicrobial properties for respiratory protection equipment like facemasks, respirators, and air filtration systems. Beyond medical doctors, odontologists are continually exposed to bioaerosols that may contain viruses or bacteria. This study introduces SakCu®, a silver and copper nanolayer applied to one side of spun-bond polypropylene fabric using the magnetron sputtering technique. The antibacterial and antiviral properties of the AgCu nanolayer were tested against droplets landing on the material and aerosols passing through it.

The effectiveness of the nanolayer was rigorously assessed through viability assays using respiratory surrogate viruses, ssRNA Leviviridae, and ssDNA Microviridae as representatives of non-enveloped viruses. Colony-forming unit (CFU) determinations were used to evaluate the survival of four aerobic and four anaerobic bacteria, as well as multiple species present in subgingival biofilm samples taken from patients with periodontitis.

Viability assays with surrogate viruses showed significant reductions in viral replication within 2-4 hours of contact. A simulated viral filtration system demonstrated inhibition of viral replication ranging from 39% to 64%. PhiX174 viability assays showed a 2-log reduction in viral replication after 24 hours of contact and a 16.31% inhibition in viral filtration assays. Bacterial growth inhibition varied by species, with reductions ranging from 70% to 92% for aerobic bacteria and over 90% for anaerobic strains. Regarding the viability of microorganisms from the subgingival biofilm samples, a 57.8 ± 9.7% reduction was observed when the samples were in contact with the AgCu nanolayer.

In conclusion, the AgCu nanolayer demonstrated robust bactericidal and antiviral activity under both contact and aerosol conditions. These findings suggest that the nanolayer has significant potential for incorporation into personal protective equipment, effectively reducing and preventing the transmission of aerosol-borne pathogenic bacteria and respiratory viruses in real-world settings.

## Thin Films and Surface Modification
## Room Naupaka Salon 5 - Session TF2-TuE

### Thin Films - Processing

**Moderator: Christopher Muratore**, University of Dayton

7:40pm **TF2-TuE-7 Guided Combinatorial Synthesis, High-Throughput Materials Characterization and Machine Learning Methods Expedite the Discovery of Improved Pt-Au Thin Films***, **David Adams**, T. Shilt, R. Kothari, K. Dorman, C. Martinez, C. Sobczak, S. Addamane, M. Jain, F. DelRio, M. Rodriguez, B. Boyce, R. Dingreville,* Sandia National Laboratories

Sputter-deposited Pt-Au thin films have been reported to develop a stable, nanocrystalline structure that exhibits high hardness and exceptional resistance to fatigue damage, yet little is known about how these characteristics vary with PtxAu1-x composition and processconditions. Toward this end, we describe an extensive combinatorial Pt-Au thin film library

which spans large ranges of binary stoichiometry and deposition atomistics.

Our approach to combinatorial material synthesis implements confocal magnetron sputtering of two elemental sputter targets. Kinematic Monte Carlo SIMTRA simulations helped guide efficient experiments that achieved a broad range of composition of PtxAu1-x (from x ~ 0.02 to0.93) in relatively few (i.e., 3) depositions. The produced films were subsequently characterized using high-throughput, ex-situ methods to further accelerate materials discovery. Automated nano-indentation, X-ray reflectivity, X-ray diffraction, Atomic Force Microscopy, surface profilometry, four-point probe sheet resistance techniques, and Wavelength Dispersive Spectroscopy determined how hardness, modulus, density, surface roughness, structure, and

resistivity vary with film stoichiometry and process parameters.

Combinatorial Pt-Au films displayed an assortment of properties with the hardness of some films exceeding values reported previously for this material system. High hardness, high modulus, and low resistivity were generally attained when using increased deposition energy and reduced angle-of-incidence processes. Finally, we discuss a machine learning approach trained on this complex combinatorial space, which offers new insights into our understanding of these films. An unsupervised clustering algorithm based on variational inference was implemented to encode the different modalities into a shared latent representation. Through analysis of this representation, we identified distinct mechanistic regimes with correlations across modalities. Overall, these efforts help pinpoint promising, new PtxAu1-x compositions for

future study and reveal strategies for improved deposition.

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8:00pm **TF2-TuE-8 Dynamic Fracture of Copper/silica interfaces***, **Cristian Ciobanu,*** Colorado School of Mines and NIST*; F. Bobaru,* University of Nebraska-Lincoln, USA*; G. Stan,* National Institute of Standard and Technology, Gaithersburg, Maryland 20899 USA

Within the real of recent efforts to address new challenges in semiconductor packaging, the hybrid bonding between a dielectric (e.g. silica) and a metal (usually copper) occupies a special place. This direct bond interconnect holds the key to superior functionality, high-density packaging, and low-power operation of future semiconductor devices. However, as the dimensions of the copper interconnects decrease, preparing high quality hybrid bonding that withstands further processing or packaging becomes a challenge. At micron or submicron dimensions, the copper pads or bumps may debond from the silica matrix, which can compromise at least the mechanical integrity of the packaging. In this work, we present a study of dynamic fracture in a heterogeneous system consisting of a copper pad embedded in a silica matrix using peridynamics simulations based on the Fast Convolution-Based Method (FCBM) for spatial discretization and an explicit time marching scheme. Depending on the interface bonding energy, we show different cracking scenarios encountered when a crack initiated in the matrix propagates towards and through the metal inclusion. Crack propagation around the inclusion is consistent with low bonding energy, and we use the simulations to map out the acceptable bonding ranges for different loadings, i.e. those for which cracks propagate through (rather than around) the interface. These results may provide guidance in understanding the cracking of single or multiple pads, and can help estimate acceptable ranges of bonding energy, pad dimensions, and packing density (pads per area).

8:20pm **TF2-TuE-9 Maskless Localized Atomic Layer Deposition Applied to Surface Functionalization***, T. Souvignet, J. Carlotti, V. Salles, M. Maillard,* ***Catherine Marichy,*** Laboratoire des Multimatériaux et Interfaces - Universite Claude Bernard Lyon 1, France

Nowadays, interest in surface engineering is strongly expanded in many domains like nanoelectronics, energy, transportation, medicine, and the environment. Especially, precise (micro-) surface functionalization patterning are sought after for many devices and applications such as self-cleaning surfaces, microfluidic devices, moisture harvesting and anti-fogging coatings as well as bio-sensor, bio-microarray, and efficient water management in fuel cell.

Maskless fabrication approaches are highly attractive as they enable rapid prototyping of surface functionalities. Based on self-limiting surface reactions, Spatial Atomic Layer Deposition (SALD) technique has recently enabled localized deposition with a control of the film thickness at the atomic scale.*(1–4)*

Using a modified open-air SALD head, we successfully demonstrated the maskless deposition of uniform and homogenous oxide thin films with a lateral resolution tuned from millimeters to hundred micrometers range while keeping a film thickness in the range of a few to hundreds of nanometers with a control at the nanoscale.*(4)*

Herein, surface functionalization using of this maskless SALD approach is introduced. From alkyl silane, it is indeed possible to locally modify the surface properties (hydrophilic/hydrophobic character, etc.) by grafting monolayers, without change of surface topography. Tuning the functionalization degree/saturation of the grafting sites is achieved to modulate the hydrophobic character of the patterns. Contact angles and surface energies are determined before and after functionalization. On patterns, gradient of composition occurs that induces a controllable gradient of hydrophobicity, as demonstrated by the presence of a wetting hysteresis. Imprinted gradients in wettability are particularly interesting for controlling the dropwise condensation of vapor and drop displacement.

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8:40pm **TF2-TuE-10 Advanced Atomic Level Patterning Process by Area Selective Atomic Layer Deposition Integrating Atomic Layer Etching***,* ***Seo-Hyun Lee****, J. Lee, J. Oh, W. Kim,* Hanyang University, Korea

As semiconductor devices continue to be miniaturized, the reduction in the width of their components has become significant, prompting increased research into 3D structured patterns. Traditional optical lithography-based patterning methods, though commonly utilized, face challenges such as complex processing steps, escalating costs, and difficulties in achieving patterns below 10 nm. To overcome these limitations, we have explored the use of area-selective atomic layer deposition (AS-ALD), a bottom-up thin film deposition technique, which enables selective growth of thin films in specified regions. A malonate-based inhibitor was introduced in the gas phase to deactivate non-growth regions, *i.e.*, SiN substrates, allowing $SiO_2$ thin films to grow selectively via ALD only on growth regions, *i.e.*, $SiO_2$ substrates. However, the AS-ALD process often results in unintended deposition of ALD films in non-growth regions, thereby compromising the selectivity between growth and non-growth regions. To address this issue, a post-etching process using atomic layer etching (ALE) was implemented to remove the undesired $SiO_2$ films deposited on the SiN substrates. Through a repeated sequence of inhibitor exposure, $SiO_2$ film deposition, and post-etching, we precisely achieved deposition selectivity of 10 nm-thick $SiO_2$ films, confined exclusively to the $SiO_2$ substrates.Furthermore, this deposition selectivity was also achieved when applying the sequences to a patterned $SiO_2$/SiN substrate, demonstrating its suitability for versatile use in upcoming semiconductor devices. This methodology can be leveraged for application in 3D NAND fabrication processes, particularly utilizing the results obtained on $SiO_2$ and SiN substrates.

## Nano and 2D Materials
## Room Naupaka Salon 4 - Session NM1-WeM
## Surface Engineering and Characterization

**Moderator: Gregory S. Herman**, Argonne National Laboratory

8:20am **NM1-WeM-2 Synthesis, Doping, and Encapsulation of 2D Transition Metal Dichalcogenides*, Yu-Chuan Lin,*** National Yang Ming Chiao Tung University (NYCU), Taiwan **INVITED**

Two-dimensional (2D) transition metal dichalcogenides (TMDC), such as $MoS_2$ and $WSe_2$, exhibit useful material properties and versatile material chemistry for optoelectronic devices, quantum information, and energy missions. To realize these applications, we need to make them in large areas and be able to control their impurity concentrations. First, I will introduce our metalorganic chemical vapor deposition (MOCVD) process for deposition of TMDC epitaxial monolayers and the approach for growth of epitaxial TMDC multilayers on sapphire. Next, I will discuss how we introduced Re or V dopants into the cation sites of TMDC by MOCVD and their impact on the quality and properties of TMDC films.[3] In addition to cation substitutional doping, we can create Janus TMDC with an intrinsic dipole moment by replacing the elements at the anion sites (i.e., S and Se). I will present our result [4,5]of the conversion of 2D $WS_2$ and $MoS_2$ into 2D Janus WSSe and MoSSe by pulsed laser deposition and explain how we confirmed the presence of a dipole moment in 2D Janus TMDC optically. To improve the interface quality between TMDC and oxide dielectric materials for electronic applications, we developed thermal atomic layer deposition (ALD) of amorphous boron nitride (aBN) on both traditional and van der Waals surfaces. In the end, I will talk about nucleation and growth of aBN on $MoS_2$ surface in our thermal ALD and aBN/$MoS_2$ integration for improve field-effect transistor performance and quantum well fabrication.[6]

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9:00am **NM1-WeM-4 Small Clusters of Molecular Anions: Locally Probing a Model Hubbard System*, Sarah Burke,*** University of British Columbia, Canada **INVITED**

Electronic correlations drive many important phenomena in materials that cannot be described by a single-electron picture. The Hubbard model captures a remarkable range of this behaviour by introducing an on-site interaction – the “Hubbard U” – that competes with the kinetic energy of the electrons, or delocalization through wavefunction overlap – described by the hopping parameter t. While Hubbard models are not generically analytically or even exaclty solvable, model systems such as clusters often are and can lend insights into more complex extended structures. The success of such models in describing correlated electron phenomena like Mott-insulator transitions, charge density waves, magnetically ordered states, and superconductivity[1], is typically assessed by comparing to macroscopic quantities. However, as a model that captures the local character of electron-electron interactions, local tools provide a unique perspective. Noncontact atomic force microscopy (ncAFM) offers a particularly intriguing view through the ability to probe charge states and electrostatic interactions locally.

We used clusters of PTCDA molecules adsorbed on NaCl bilayer films on silver as an experimental prototype of a 4-site Hubbard model in a regime where U>>t. PTCDA clusters have weak in-plane hybridization (t small), and isolated moelcules have a Hubbard U in gas phase of ~3eV, reduced to ~1.4eV by screening of the nearby silver[2]. The large electron affinity of PTCDA leads to electron transfer from the silver substrate, so that isolated molecules carry a charge of -1. Thus, these clusters represent a half-filled Hubbard model where localization is expected, connected to a reservoir of charge. We used STM, STS, ncAFM and electrostatic force spectroscopy to probe the structures, charge states, and charging energies of two different geometries of 4-moelcule clusters as well as isolated PTCDA- molecules. Equilibrium charge distributions of asymmetric clusters show charge segregation, while symmetric clusters show uniform charge. A 4-site extended Hubbard model was mapped onto the experimental results to identify the necessary interactions required to describe the ground state and charge excitations of the system. Once above a threshold where U/t drives localization, intersite energy differences and repulsion compete with hopping, driving the observed charge segregation and unexpected correlated behaviour.

1. M. Qin, et al., Annu. Rev. Condens. Matter Phys. 13, 1–28 (2021).
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9:40am **NM1-WeM-6 Tunable Areal Density and Defined Morphology Regimes of Langmuir Monolayers of PEGylated Gold Nanoparticles***, H. Cameron, I. Curtis, R. Takai,* Mount Allison University, Canada*; M. Radford,* Simon Fraser University, Canada*; A. Williams,* Mount Allison University, Canada*; B. Gates,* Simon Fraser University, Canada*; **M.-Vicki Meli,*** Mount Allison University, Canada

The interfacial behaviour and control of nanoparticles has important consequences on their assembly into thin films, superstructures and subsequent materials suitable as metamaterials and nanophotonics applications. Our investigations into the interfacial self-assembly of nanoparticles coated with polyethylene glycol (PEG) and tetradecane thiols as a function of ligand shell and subphase composition will be presented. Methyl- and carboxylic acid-terminated PEG thiols are compared as a function of subphase pH. Film morphology is demonstrated as a function of ligand composition, transitioning from island-forming to isolated individual nanoparticles with controllable areal density. Transmission electron microscopy of the self-assembled films will be presented with corresponding surface pressure vs. area compression isotherms.Insights into NP film purity and (in)stability as it relates to the mentioned parameters will also be discussed. Compression-expansion isotherms with exceptionally large onset areas were measured. The effect of added tetradecanethiol into the ligand shell is shown to improve the stability and maintain the separation of the nanoparticles in the films.

## Nano and 2D Materials
## Room Naupaka Salon 4 - Session NM2-WeM
## Properties of 2D Materials

**Moderator: Zbynek Novotny**, Pacific Northwest National Laboratory

10:20am **NM2-WeM-8 Atomic-Scale Control of Plasmon-Driven Single-Molecular Switch*, Akitoshi Shiotari,*** Fritz-Haber Institute, Germany**INVITED**

Localized surface plasmons provide effective molecule–light interactions that are highly motivating for the realization of advanced molecule-based optoelectronic devices [1]; however, innovative precision in plasmon control is still required to induce local selective reactions at the single- or sub-molecule level. Scanning tunneling microscopy (STM) using a plasmonic metal tip not only creates a local photochemical reaction field, but also enahnces Raman signals from molecules within the STM junction, namely tip-enhanced Raman spectroscopy (TERS). Low-temperature STM-TERS is a powerful tool to evaluate the structure and photoreactivity of single molecules, even on a semiconductor silicon surface [2].

In this talk I will mainly report on a plasmon-induced single-molecule switch in a Ag-tip–anhydride-molecule–Si-surface junction characterized and controlled by low-tempearture STM-TERS [3]. The localized surface plasmon at the tip can dissociates of the O–Si bonds between the molecule and the Si(111)-7x7 surface, resulting in the conductance switching between OFF (tunnelling) and ON (point-contact) states of the tip–adsorbate junction. Sub-angstrom scale positioning of the plasmonic tip over the target molecular can tune the switching rate. We also demonstrated that the switching ability can be changed by the single-atom-level substitution of the molecular structure; imide/Si(111) is inert against the tip plasmon. Our demonstrations of the tip-plasmon control and the chemical tailoring for the single-molecule switch pave the way to the fusion of single-molecule electronics and plasmonics, towards ultimate minitualization of optoelectronics, namely "pico-optoelectronics."

Reference:

1. Xiaona Xu, Chunyan Gao, Ramya Emusani, Chuancheng Jia, and Dong Xiang, *Adv. Sci.* 2400877 (2024) DOI: 10.1002/advs.202400877
2. Borja Cirera, Shuyi Liu, Youngwook Park, Ikutaro Hamada, Martin Wolf, Akitoshi Shiotari, and Takashi Kumagai, *Phys. Chem. Chem. Phys.* (2024) DOI: 10.1039/d4cp01803f.
3. Youngwook Park, Ikutaro Hamada, Adnan Hammud, Takashi Kumagai, Martin Wolf, and Akitoshi Shiotari, *Nat. Commun.* (2024) DOI: 10.1038/s41467-024-51000-w.

11:00am **NM2-WeM-10 Tunable Metasurface with Gap and Collective Surface Plasmon Modes***, **Anatoliy Pinchuk**,* University of Colorado at Colorado Springs

We investigate a tunable metasurface composed of a monolayer of gold nanoparticles on a glass substrate in close proximity to a thin aluminum film, both numerically and experimentally. The extinction spectra of the metasurface exhibit three angle- and polarization-dependent peaks. Using the finite-difference time-domain (FDTD) method, we confirm the positions of both the collective surface plasmon and gap modes. Altering the polarization of the incident light causes a shift in the wavelength of these peaks.

A recent study reported strong coupling between the gap and collective surface plasmon polariton modes in a system consisting of a monolayer of gold nanoparticles supported on a glass substrate, separated from a thin aluminum film by a shellac polymer spacer film of varying thickness [1,2]. Two optical extinction bands were identified: a long-wavelength gap mode and a short-wavelength collective surface plasmon mode. The position and amplitude of both modes were found to depend strongly on the thickness of the shellac dielectric spacer. Varying the spacer thickness causes a shift in the two modes and their degeneration into a single mode as the thickness increases. These findings reveal a complex interplay between the gap and collective surface plasmon polariton modes.

Despite detailed numerical and experimental studies on various geometries of plasmonic metasurfaces, all such studies have been conducted with the probing light beam incident normally. There have been no reports on the polarization dependence of the extinction spectra for monolayers of gold nanoparticles in close proximity to a thin metal film. Our study addresses this gap by exploring the effects of polarization on the optical properties of these metasurfaces, providing new insights into their tunable characteristics and potential applications in nanophotonic devices.

References

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11:20am **NM2-WeM-11 Probing Inherent Optical Anisotropy in Transition Metal Dichalcogenide Substrates via Mie Scattering-Induced Surface Analysis (MISA)***, H. Woo,* Korea Research Institute of Standards and Science, Republic of Korea*; J. Han, S. Ji, B. Shin,* Sungkyunkwan University (SKKU), Republic of Korea*; S. Lee,* Nanyang Technological University, Singapore*; **Young Jae Song**,* Sungkyunkwan University (SKKU), Republic of Korea

We present a novel approach to investigate the optical anisotropy of transition metal dichalcogenide (TMD) substrates using Mie scattering-induced surface analysis (MISA). By employing scattering-type scanning near-field optical microscopy (s-SNOM) and finite-difference time-domain (FDTD) simulations, we systematically studied and directly visualized the Mie scattering patterns of superspherical gold nanoparticles (s-AuNPs) at the nanoscale.

Our research revealed distinct differences in the optical properties of molybdenum disulfide (MoS2) and rhenium disulfide (ReS2) substrates. While MoS2 exhibited optical isotropy, ReS2 demonstrated significant anisotropic behavior, particularly in the near-infrared energy range. This anisotropy was manifested through more pronounced spectral and angular responses in the satellite peaks of Mie scattering patterns.

We observed that the distances between satellite peaks in the Mie scattering patterns varied with the incident angle of light for ReS2, but remained constant for MoS2. This angular dependence in ReS2 was consistently observed across different excitation energies, providing strong evidence of its inherent optical anisotropy.

Our findings highlight the potential of MISA as a powerful, non-destructive tool for probing the intrinsic dielectric properties of substrates at the nanoscale. This technique offers superior visualization of nanoscale anisotropies and enables a more nuanced approach to substrate characterization compared to traditional spectroscopic methods.

The insights gained from this study not only advance our understanding of light-matter interactions at the nanoscale but also have significant implications for the development of advanced nanophotonic devices and the field of optical metrology.

Keywords: superspherical-AuNP, scattering-type scanning near-field optical microscope, Mie scattering, anisotropy, substrate

11:40am **NM2-WeM-12 Enhancement of Photocatalytic Water Splitting Upon Induced Structural Evolution and Increase of Phase Polarity of Two-Dimensional Covalent Organic Frameworks***, **Jrjeng Ruan**,* National Cheng Kung University (NCKU), Taiwan

The evolution of smectic liquid crystals of newly designed two-dimensional covalent organic frameworks (COFs) has been disclosed for the first time. With obtained changes of phase morphology, selected-area electron diffraction patterns, and Young’s modulus via compressive testing, this smectic phase is realized to transfer to nematic phases upon the ph. changes of surrounding solutions. Furthermore, the coordination of selected metal ions for the preparation of M-COFs is also stimulated by conducted ph. changes, which is surprisingly found able to greatly adjust the out-of-plan phase polarity and thus the piezoelectric responses of evolved liquid crystals of synthesized M-COFs. The controlled adjustment of phase polarity has been clarified able to modify energy bandgap, enhance absorption of visible lights, and increase the efficiency of stimulated electron transition to metal active centers upon the absorption of visible lights. As a result, the coordination of metal ions and accompanied elevation of phase polarity significantly promote the photocatalytic water splitting via synthesized M-COF as photocatalysts. Hence, with the coordination of metal ions on evolved COF liquid crystals, this research has investigated the availability of various levels of phase polarity of M-COF liquid crystals, and comprehensively studies achievable impacts and contributions of phase polarity on photocatalytic water splitting.

## Nano and 2D Materials
## Room Naupaka Salon 1-3 - Session NM-WeP
## Nano and 2D Materials Poster Session

**NM-WeP-1 Introduction to Measurement Uncertainty Evaluation Method and Results of Silicon Nitride Thin Film Layer Thickness and Complex Dielectric Constant***, Yong Jai Cho*, *W. Chegal,* Korea Research Institute of Standards and Science, Republic of Korea

SE (Spectroscopic Ellipsometer) has excellent measurement resolution, but measurement quality control of SE requires careful attention because measurement uncertainty can be easily affected by small changes in the device. For SE measurement quality control, thin film layer thickness certified reference materials are mainly used. SE has the advantages of being non-destructive, ultra-fast, and non-contact, but also has excellent high-precision characteristics that can detect a single atomic layer even before it is completely grown, so demand is increasing as a core measurement equipment for the semiconductor device manufacturing process. As semiconductor device manufacturing technology has recently developed due to the complexity of semiconductor device structures, the introduction of atomic layer-level processes, and the introduction of new materials, there is a need to improve quality control of TTTM (Tool-To-Tool Matching) related to measurement uncertainty. Therefore, in order to improve the measurement quality control level of SE equipment for semiconductor processing, it is necessary to develop higher quality thin film layer thickness certified reference materials. As a first research step, our research team developed a unified uncertainty evaluation method for the measurands of various types of rotating-element spectroscopic ellipsometers with excellent real-time measurement performance[1]. This method allows the measurement uncertainty of ellipsometric transfer quantities (e.g. Psi and Delta) to be calculated directly from observed ellipsometric transfer quantities, so there is no need for the analysis results of unknown optical properties of the sample required to calculate the measurement uncertainty. As a second research step, we developed a method for assessing uncertainty in the values of unknown optical properties of the sample, obtained using a nonlinear least-squares fit from the spectra of the observed ellipsometric transfer quantities[2]. The implicit function theorem was adopted to describe the propagation of uncertainty for nonlinear least-squares calculations[3]. We would like to introduce the method and results of applying the developed uncertainty evaluation method to the uncertainty evaluation of the thin film layer thickness and complex dielectric constant of silicon nitride thin film sample obtained through SE.

**References**

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**NM-WeP-2 A New Tool for Single Ion Implantation and Nanoscale Materials Engineering: System Design and Source Development***, **Paul Blenkinsopp**,* Ionoptika Ltd., UK*; K. McHardy,* Ionoptika, Ltd., UK*; G. Aresta,* Ionoptika Ltd., UK

Quantum computing is the next great frontier of science. It has the potential to revolutionize many aspects of modern technology, including digital communications, “quantum-safe” cryptography, and incredibly accurate time measurements.

Single impurity atoms in semiconductors are receiving attention as potential quantum technologies, and proof-of-concept devices have shown promise. However, such devices are incredibly challenging to manufacture, as single atoms must be placed within ~ 20 nm of each other within a pure $^{28}$Si matrix.

All working devices thus far have been fabricated using hydrogen lithography with an STM followed by atomic layer deposition. This is labour-intensive and requires several days of meticulous preparation to create just a single quantum bit (qubit). Real-world devices will require arrays of hundreds or thousands of impurity atoms, highlighting the requirement for a scalable method of positioning single atoms with nanometer precision.

We report on a new commercial instrument for the fabrication of quantum materials and devices via single ion implantation.

The instrument features a high-resolution mass-filtered focused ion beam (FIB), a high-sensitivity deterministic implantation system, 6-inch wafer handling, and a high-precision stage. The deterministic implantation system allows single ion implantation with confidence levels as high as 98%.

The ion dose delivered to the sample can be adjusted across a wide range, providing many nanoscale materials engineering capabilities in a single tool, from single ion implantation to direct-write capabilities such as isotopic enrichment and targeted ion-implantation of nanomaterials.

The liquid metal alloy ion sources, coupled with and mass filtered column will enable for the implantation of many different elements with isotopic resolution. Available sources include silicon, erbium, gold, and bismuth, while many others of technological interest are in development. We will report on the LMIG source development carried out at Ionoptika in collaboration with our partners.

**NM-WeP-3 Graphene-Incorporated Dielectric Composites by Varying the Mixing Method and Degree of Oxidation of Graphene***, S. Jun,* ***Kwangsin John Ahn****, S. Yu,* Hankuk University of Foreign Studies, Republic of Korea

Graphene-incorporated dielectric composites by varying the mixing method and degree of oxidation of graphene

So-Yeon Jun, Kwangsin John Ahn, and SeGi Yu

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To obtain high-performance dielectric properties of dielectric composites, graphene and barium titanate ($BaTiO_3$, BTO) fillers were mixed in the polymer matrix, by varying the degree of reduction of graphene and the mixing method. Two kinds of graphene materials, i.e., graphene oxide (GO) and reduced graphene oxide (rGO); and two kinds of mixing methods for graphene and BTO, i.e., encapsulation of BTO in graphene and subsequent mixing, and simple mixing of BTO and graphene in the polymer matrix. This yielded to four kinds of graphene-incorporated samples, which was compared with the reference sample, i.e., a sample with only BTO fillers in the polymer matrix without graphene. Encapsulation process was performed by the self-assembly of positively functionalized BTO and negatively functionalized GO. After the encapsulation, GO-encapsulated BTO fillers were chemically reduced to become rGO-encapsulated BTO fillers [1,2]. All the four graphene-incorporated samples exhibited better dielectric constant values, i.e., 1.5 to 2.2 times higher than the reference sample. It was thoughted to be caused by the presence of graphene via the interfacial polarization or micro-capacitor effects [1]. However, the increase in dielectric loss, which had frequently occurred for the simple mixing cases of conducting nano-fillers, was successfully suppressed for the encapsulated samples. Here, the dielectric loss was controlled under lower 20%, which was caused by removal of free graphene platelets during the chemical process of the encapsulation [2]. The best performance one is the encapsulation method for rGO material. The next one is GO encapsulation case. The highest enhancement of 120% in the dielectric constant and moderate dielectric loss was obtained for rGO-encapsulation case. Therefore, we can say that encapsulation of BTO in graphene is very promising mixing method for high-performance polymer-based dielectric composite materials.

References:

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**NM-WeP-4 Deep Learning-Based Prediction of Adsorption Energies for $MoO_2Cl_2$ Precursor on $SiO_2$ Surface Using Density Functional Theory***, **Do-Hyun Kwon**, J. Lee,* Korea University of Technology and Education, Republic of Korea*; J. Kim,* Pohang University of Science and Technology (POSTECH), Republic of Korea*; Y. Kim,* Korea University of Technology and Education, Republic of Korea

A search for appropriate adsorption geometries of a $MoO_2Cl_2$ precursor on an -OH terminated β-$SiO_2$ surface was conducted using a deep-learning approach. The adsorption geometries were configured by translating and rotating the precursor located near the surface. A deep-learning model was developed to learn important properties of the adsorption geometries; the model consists of three main units to learn positional features of the precursor atoms, to learn distance features among the precursor and surface atoms, and to predict the corresponding adsorption energy. A dataset of adsorption geometry and the adsorption energy pairs was collected by grid search. Using this dataset, the model was trained to predict the adsorption energies with minimal error and optimized to achieve a root mean square error (RMSE) of less than 0.011%. Energetically more favorable adsorption geometries were found using the trained model. By inputting arbitrary adsorption structures into the trained model and obtaining the predicted adsorption energies, recommendations for energetically stable adsorption structures were received. Through actual calculations, it was confirmed that the model could identify energetically stable adsorption structures that were not included in the dataset. The proposed method is applicable to finding appropriate adsorption geometries of other types of precursors and surfaces.

**NM-WeP-5 Induced Self-Assembly of Small (3 - 5 nm) Nanoparticles Into Flexible Nanofilms at Air- and Oil-Water Interfaces***, H. Cameron, Y. Zhang, K. Leslie, B. Scott, I. Curtis, L. Gamble,* ***M.-Vicki Meli,*** Mount Allison University, Canada

Thin-film assemblies of gold nanoparticles (AuNPs) at the liquid interfaces have been an exciting research area over the past decade due to their promising applications in optics, sensors, shape-shifting and meta-materials, and catalysis. Autonomous self-assembly at such interfaces is an attractive method of synthesizing these superstructures, however this is a complex process that has proven to be difficult to control. Small AuNPs with core sizes <10 nm pose greater difficulties than larger AuNPs because they have a small free energy of adsorption that is comparable to their thermal energy. Therefore, there are few published examples of the self-assembly of such AuNPs at the liquid-liquid interface. The present research analyzes the effects of various experimental parameters on the adsorption of ~3 nm AuNPs to the oil–water interface, including ligand shell composition, alcohol additive structure and amount, oil phase composition and the phase of NP introduction. Film quality is qualitatively assessed and compared with a recent thermodynamic model to elucidate the primary driving forces of adsorption. Films with tunable optical density ranging from lightly coloured to gold and lustrous, are obtained with variation over a single parameter. Determining approaches that promote the adsorption of 3 nm AuNPs to an aqueous interface and furthering the understanding of its thermodynamic mechanism is necessary to gain precise control and to work towards the industrial use of such thin films.

**NM-WeP-6 Molecular Structure and Vapor Pressure of Molybdenum Pentachloride Using Ab-Initio Thermodynamics***, N. Lee,* Korea University of Technology and Educaiton, Republic of Korea*; S. Kim, J. Kim,* ***Yeong-Cheol Kim,*** Korea University of Technology and Education, Republic of Korea

This study aims to elucidate the molecular structure and vapor pressure of molybdenum pentachloride in the gas phase using ab-initio thermodynamics. Molybdenum pentachloride can exist as $MoCl_5$ (monomer) and/or $Mo_2Cl_{10}$ (dimer). The monomer is thermodynamically favored above 215 K, but Cl-Cl bond breakage is required to dissociate a dimer into two monomers. This suggests that the dimer is kinetically favorable even above 215 K, and the calculated dimer vapor pressure agrees well with the experimental data.

**NM-WeP-7 Isotropic Atomic Layer Control of 2d $Ws_2$ Using Organic Solvent Vapor***,* ***Hye Won Han****, J. Kang, J. Kim, G. Yeom,* Sungkyunkwan University, Republic of Korea

Two-dimensional transition metal dichalcogenides (TMDs) exhibit diverse electronic and optoelectronic properties depending on their thickness, making precise layer control essential for their integration into advanced materials and devices. Atomic layer etching (ALE) techniques are crucial for achieving such precise thickness control and can be performed using either plasma or thermal methods. Previous studies have primarily focused on radical adsorption and ion desorption processes to enable anisotropic etching. However, with the evolution of device structures into three-dimensional configurations, isotropic etching has become increasingly important. In this study, we introduce isotropic thermal ALE of $WS_2$ using organic solvent vapors. The ALE process consists of the adsorption of reactive radicals generated by oxygen plasma, followed by exposure to organic solvent vapors for desorption. This approach not only enables isotropic etching but also allows for damage-free processing, offering a significant improvement over conventional etching techniques. Additionally, we compare the etching performance based on organic vapors' chemical structures and process temperatures, highlighting their differences in reactivity and volatility during the etching process. By providing precise layer control of $WS_2$, this study advances the integration of TMDs into next-generation material and device technologies, marking a significant advancement in the field of advanced materials research.

**NM-WeP-8 Uniform Vertical Doping of TMDC Materials via** ***, Jimin Kim****, J. Kang, H. Han, G. Yeom,* Sungkyunkwan University, Republic of Korea

Two-dimensional (2D) semiconductors, with their electrical and optical properties varying depending on thickness, are gaining recognition as key materials for future semiconductor technologies. To improve the properties of 2D materials Researchers are focusing on precise thickness control, large-scale production, and doping techniques. Doping, in particular, is an effective technique for adjusting the electrical behavior of 2D semiconductors, but conventional doping methods like ion implantation often damage the delicate and thin 2D semiconductors. To address this problem, alternative surface treatments such as plasma-based radical adsorption, liquid solution spin coating, and immersion techniques have been explored [1]. However, these approaches primarily modify the surface and become less effective as the material's thickness increases. To overcome the challenge of achieving uniform vertical doping, this research introduces an innovative cyclic doping technique utilizing a specialized transfer process. This method enhances the consistency of doping across multiple layers while preserving the distinct layered structure of $MoS_2$. The cyclic doping technique presents a promising solution to current challenges in doping efficiency and uniformity, marking a significant advancement in the precise manipulation of 2D materials for semiconductor applications.

## Thin Films and Surface Modification
## Room Naupaka Salon 1-3 - Session TF-WeP
## Thin Films and Surface Modification Poster Session II

**TF-WeP-1 Annealing Temperature Effects on Liquid Crystal Behavior and Electro-Optical Properties in Inorganic Alignment Films***, H. Lee, J. Sim,* Ulsan National Institute of Science and Technology, Republic of Korea*;* ***Hong-Gyu Park,*** Changwon National University, Republic of Korea

Aligning liquid crystal molecules in a single direction is essential for achieving a uniform and clear display. Additionally, research on the application of new alignment films and methods to enhance the optical, thermal, mechanical, and chemical stability of liquid crystal alignment is ongoing. In this study, we observed the changes in liquid crystal behavior and the resulting electro-optical properties in high-k inorganic alignment films depending on the annealing temperature. While conventional polyimide alignment films are typically annealed at 230°C, we examined how the characteristics of the inorganic films used in this study changed with annealing temperatures of 100°C, 150°C, and 200°C. This allowed us to explore the feasibility of low-temperature processing with inorganic alignment films and to assess their potential as a replacement for traditional polyimide alignment films.

**TF-WeP-3 Synaptic Characteristics of Memristive Au/$LiNbO_3$/Pt Device Based on Schottky Barrier Modulation***,* ***Sejoon Lee****, Y. Lee, D. Kim,* Dongguk University, Republic of Korea

The (113) $LiNbO_3$ layers were grown onto the (111) Pt/$SiO_2$/Si substrates at 180 – 320 °C by radio-frequency magnetron sputtering. The samples grown at 250 °C displayed the improved crystallinity as well as the smooth surface morphology without any hillocks and pits. The memristive devices, fabricated in the form of the top-to-bottom Au/$LiNbO_3$/Pt two-terminal device scheme, clearly exhibited the external electric field polarity-dependent asymmetric memristive hysteresis loops in their current-voltage characteristic curves. When repeating the current-voltage sweep at an appropriate program voltage range, the on-state current was gradually increased with increasing sweep number. Through analyzing the transport mechanism in Au/$LiNbO_3$/Pt, such a behavior was confirmed to be attributable to the Schottky barrier modulation, arising from the ionic migration of oxygen vacancies inside the $LiNbO_3$ layer. In other words, the electro-migrated oxygen vacancies in $LiNbO_3$ lead to the Schottky barrier modulation particularly at the $LiNbO_3$/Pt side; and it eventually gives rise to the switchable diode effect in the Au/$LiNbO_3$/Pt device. Since the degree of the switchable diode effect relies on the pulse parameters of the applied voltage stresses, the memristive characteristics (e.g., data storage speed, multiple resistance states, data retention, etc.) could be effectively controlled by changing the pulse magnitude and the pulse duration of the program/erase voltages. Using these unique features, various synaptic functions such as a short-term memory, long-term potentiation/depression, and spike-timing dependent plasticity were effectively demonstrated. The results suggest that the $LiNbO_3$ based memristors hold great promise for the future neuromorphic applications.

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**TF-WeP-4 X-Ray Photoelectron Spectroscopy and X-Ray Emission Spectroscopy Data Fitting Using a Genetic Algorithm***, **Alaina Humiston**, J. Terry,* Illinois Institute of Technology

The ever-growing problem in modern science is that data is being collected at a rate faster than analysis can be performed by characterization experts. The analysis that is done for many recently published x-ray photoelectron spectroscopy (XPS) and x-ray emission spectroscopy (XES) data, is often incorrect/irreproducible and leads to a cycle of incorrect fits in this spectroscopy data. In this work, a genetic algorithm (GA) is being constructed to potentially minimize this human error. This GA code known as XPS Neo/XES Neo, is based on the Neo package which exists for EXAFS (EXAFS Neo) and Nanoindentation (Nano Neo) data. GAs are based on biological methods and depend on parameters such as populations size, number of generations, genes, crossover, and mutation. The GA takes in a certain population size and constructs individual vectors each with their own unique genes i.e the fitting parameters we are trying to optimize. It then performs crossover and mutation to these individual vectors to progress toward a lower global minimum. This GA allows for a variety of mutation options including, Random Perturbations, Rechenberg, Metropolis mutation, and Self Adapting Differential Evolution. The methods of how a GA works in relation to XPS and XES datasets are discussed. The difficulties in making this work for XPS data arise from complicated backgrounds due to many effects such as plasmon loss, Auger peaks, and satellite peaks. XPS and XES data can also have many peaks that are difficult to distinguish from one another. Currently, the algorithm is only able to fit simplistic XPS spectra such C, O, N, and Si and is being worked on with the hopes of it becoming applicable for more difficult data. The goal is to make the algorithm applicable to all XPS data, with a greater focus given to the actinides, specifically for the use of fitting plutonium data as analysis of this spectra is highly sought after and difficult to fit. Through proper use of an informed GA, and collaboration with the XPS/XES database website XPSOasis.org, theoretically correct fitting of this data is hoped to be achieved.

**TF-WeP-5 Synaptic Characteristics of Au/$Hf_xZr_{1-x}O_2$/Pt Memristors Based on Double-Barrier Schottky Junctions***, **Youngmin Lee**, S. Lee, D. Kim,* Dongguk University, Republic of Korea

The $Hf_xZr_{1-x}O_2$ layers were grown onto the (111) Pt substrates at 450 °C by radio-frequency magnetron sputtering, and were annealed at 600 – 800°C. The 700°C-annealed samples showed a smooth surface and an improved orthorhombic lattice phase. The $Hf_xZr_{1-x}O_2$ layers exhibited the nonlinear lossy-type ferroelectric characteristics, by which the degree of ferroelectric polarization and its appropriate data retention can be gradually adjustable. The memristive devices, comprising the top-to-bottom Au/$Hf_xZr_{1-x}O_2$/Pt two-terminal device scheme, clearly displayed the ferroelectric polarization-dependent asymmetric hysteresis behaviors in their resistive switching characteristics. When repeating the current-voltage sweep at a certain and moderate voltage range, the on-state current was gradually increased with increasing sweep number. This could be attributed to the Schottky barrier modulation at the $Hf_xZr_{1-x}O_2$/Pt side. Since the repeated voltage stresses at the Au/$Hf_xZr_{1-x}O_2$ biased region would tenaciously increase the ferroelectric polarization field inside the $Hf_xZr_{1-x}O_2$ layer, the increased potential gradient along the Au-$Hf_xZr_{1-x}O_2$-Pt direction could also increase. Then, the effective Schottky barrier height at the grounded $Hf_xZr_{1-x}O_2$/Pt side will eventually decrease upon increasing the ferroelectric polarization field inside the $Hf_xZr_{1-x}O_2$ layer. Since the ferroelectric polarization strongly depends on both the magnitude and the duration of the applied voltage pulses, gradual Schottky barrier modulation could be easily accomplished by controlling the pulse parameters. Furthermore, due to the ferroelectric nature in $Hf_xZr_{1-x}O_2$/Pt, the Schottky emission rate could be retained at every modulated Schottky barrier heights. This eventually enabled the fine and precise control of the multiple memristive resistance states. Using these unique characteristics, we successfully demonstrated various synaptic functions such as excitatory post-synaptic current, paired pulse facilitation, long-term potentiation/depression, and spike-timing dependent plasticity. The results depict that the present memristive device scheme of the ferroelectric $Hf_xZr_{1-x}O_2$-based double-barrier Schottky junction holds substantial promise for the future neuromorphic applications.

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**TF-WeP-6 Isotope Labeling Study of CO2 Formation Pathways in CO-H2O Ice Films under Ultraviolet Irradiation***, **Koichiro Yamakawa**, A. Hirayama, I. Arakawa,* Japan Atomic Energy Agency, Japan

Molecular clouds are composed of gases and interstellar dust grains. The dust grains are covered with ice mantles predominantly composed of $H_2O$ [1]. When the densities of the clouds increase up to $10^4$ $cm^{-3}$ or more and their temperatures drop below 20 K, CO is condensed on $H_2O$-rich ice. The ice mantles are exposed to ultraviolet (UV) radiation, which causes a variety of photochemical reactions. $CO_2$ is one of the abundant molecules in the ice mantles, and the following two formation channels have been discussed [2]: (1) reaction of two CO molecules, one of which is electronically excited by UV light; (2) reaction of CO with the OH radical which is a dissociation product of $H_2O$. We focused on the fact that these two channels can be distinguished from each other by isotope labeling, i.e., by employing $H_2{}^{18}O$ instead of $H_2{}^{16}O$. In the present study, we investigated the UV photolysis of CO-$H_2O$ ice and determined the effective rates of the $CO_2$ formation channels with use of isotope labeling and infrared spectroscopy [3].

A CO gas and an $H_2{}^{18}O$ vapor were mixed in a gas handling system. The mixing ratio was changed in the range of CO/$H_2{}^{18}O$ = 1000-0.1. The gaseous mixture was introduced into an ultrahigh vacuum chamber and was condensed on a gold substrate cooled down to 10 K. After the condensation, the CO-$H_2{}^{18}O$ ice was irradiated with UV light from a deuterium lamp for 120 min. Reflection-absorption infrared spectra were recorded during the condensation and UV-irradiation.

After the UV irradiation of any sample, we detected infrared absorption bands of $C^{16}O_2$ (2346 $cm^{-1}$) and $C^{18}O^{16}O$ (2328 $cm^{-1}$), which were generated through the CO–CO and CO–$H_2O$ reactions, respectively. The absorption band of $C^{18}O_2$ was also detected at 2308 $cm^{-1}$ when the mixing ratio was in the range of CO/$H_2{}^{18}O$ = 100-0.1. This indicates that the photodissociation and regeneration of $CO_2$ took place in ice. We analyzed the irradiation-time dependence of the $C^{16}O_2$ and $C^{18}O^{16}O$ column densities to determine the effective cross sections of the $CO_2$ formation through the CO–CO and CO–$H_2O$ reactions simultaneously.

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**TF-WeP-10 Synthesis and Characterization of Mo and W Compounds for Disulfide Materials***, **Sunyoung Shin**, C. Kim, T. Chung, B. Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Two-dimensional transition metal dichalcogenides (TMDs), particularly $MoS_2$ and $WS_2$, are regarded as potential substitutes for graphene in electronic devices due to their semiconducting properties, exhibiting both indirect and direct band gaps depending on the layer. Various methods have been employed in the synthesis of $MoS_2$ and $WS_2$ thin films. In chemical vapor deposition (CVD) and atomic layer deposition (ALD) processes, metal precursors are typically used in conjunction with a sulfur source, such as hydrogen sulfide ($H_2S$), sulfur powder, and so forth. In the majority of cases, the synthesis of crystalline $MoS_2$ has been achieved at elevated deposition temperatures, with the subsequent treatment at high temperatures being necessary for the attainment of crystallinity. In this study, precursors suitable for the deposition of $MoS_2$ and $WS_2$ were synthesized, characterized, and even $MoS_2$ deposition studies with molybdenum precursors were conducted at relatively low temperatures without any post-treatment process. Precursors ($Mo(NtBu)_2(StBu)_2$ (**1**), $W(NtBu)_2(StBu)_2$ (**2**)) suitable for the deposition of $MoS_2$ and $WS_2$ were synthesized and characterized. The molecular structures of **1** and **2** exhibit a tetrahedral geometry according to single-crystal x-ray crystallography. Thermogravimetric analyses of **1** and **2** showed two-step weight loss. The residues from each step of **1** were $MoS_3$ and $MoS_2$, and these results were consistent with the subsequent deposition results of **1**. We successfully established a PEALD-$MoS_2$ process using **1** and $H_2S$ plasma as the precursor and reactant, respectively, at relatively low temperatures of 150–300 ºC without any post-sulfurization process. A temperature-dependent selective deposition of $MoS_x$ phases was observed with the growth of amorphous MoS3 films (150–200 ºC), and crystalline $MoS_2$ films (250–350 ºC).

**TF-WeP-11 Creating Multiple Catalytic Sites for Enhanced $CO_2$ Photoreduction Activity Through Synergistic Catalysis of MIL-$TiO_2$-PI Hybrids***, **Lipei Ren**, H. Wang,* Deakin University, Australia, China*; M. Laghaei,* Deakin University, Australia, Iran (Islamic Republic of)*; S. zhao, L. Kong,* Deakin University, Australia

Excessive burning of fossil fuels and changes in land use have led to rising atmospheric concentrations of carbon dioxide ($CO_2$), resulting in dramatic and potentially irreversible changes in the world's climate. Nanoscale metal-organic framework (MOF) MIL-101(Cr) with high porosity and large specific surface area is an excellent porous nanomaterial for catalytic reduction of $CO_2$. However, its applications have been typically restricted by nanoscale size. Herein, we assembled MIL-101(Cr) nanocrystals on $TiO_2$-coated polyimide (PI) substrates via atomic layer deposition (ALD) for high-efficient photocatalytic $CO_2$ conversion. The high $CO_2$ capturing capability of MIL-101(Cr) is combined with the unique property of inorganic semiconductor nanoparticles ($TiO_2$) to generate photoexcited electrons. Carbon monoxide (CO), methanol ($CH_4$), and hydrogen ($H_2$) were the main products of $CO_2$ photoreduction. The prepared MIL-$TiO_2$-PI felts with 1000 cycles of $TiO_2$ deposition exhibited the best photocatalytic performance, with high CO, $CH_4$, and $H_2$ yields of 158.6, 83.1, and 22.9 μmol $g^{-1}$, respectively. This work opens new routes for $CO_2$ reduction using MOF-based membrane hybrids prepared by ALD technology.

**TF-WeP-12 Synthesis of Novel Yttrium and Lanthanide Precursors and Fabrication of $La_2O_3$ Thin Films Through High-Temperature ALD***, **Yongmin GO**, B. Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; T. Park,* Hanyang University, Korea

Yttrium and lanthanide metal oxides are known for their high permittivity and wide band gaps, making them ideal materials for metal-oxide semiconductor field-effect transistors (MOSFETs) and dynamic random-access memory (DRAM). Although various thin film deposition techniques are used to make these metal oxide films, atomic layer deposition (ALD) is a useful method because it produces high quality films, allows self-limited growth, and allows precise control of film thickness.

Achieving the desired crystal structure and crystallinity during ALD requires forming crystallization seeds during the deposition process. To improve the crystal structure and crystallinity of the thin films, deposition must occur at high temperatures. Therefore, developing new precursors with excellent thermal stability, which can withstand high temperatures without decomposing, is critical for the ALD process.

In this study, we developed new yttrium and lanthanide precursors and evaluated their suitability as high-temperature ALD precursors. Various analytical techniques, including NMR, EA, TGA, and vapor pressure measurements, were used to confirm the characteristics of the newly synthesized precursors. Additionally, we proposed an ALD process for $La_2O_3$ using the new lanthanum precursor and compared it to the commonly used $La(iPrCp)_3$ precursor. By processing at high temperatures with the new lanthanum precursor, we successfully obtained $La_2O_3$ thin films with excellent crystallinity, higher density, and improved leakage current characteristics. These findings suggest that the new precursors are promising candidates for high-temperature growth of yttrium and lanthanide-based thin films via ALD.

**TF-WeP-13 X-Ray Photoelectron Spectroscopy Analysis of Gallium Nitride Thin Film Prepared by Atomic Layer Deposition***, Y. Choi, H. Yoo, H. Kim, W. Lee, **Sun Jae Kim**,* Sejong University, Republic of Korea

Gallium nitride (GaN) is a wide direct bandgap semiconductor with high electron mobility and thermal conductivity. It is widely used in power electronics, RF amplifiers, and optoelectronics such as light-emitting diodes (LEDs). Low-temperature deposition is essential for depositing high-quality GaN thin films on temperature-sensitive substrates or devices. Atomic layer deposition (ALD) is the most suitable technique for this purpose. However, nitride films deposited at low temperatures tend to be nitrogen-deficient, and quantitative compositional analyses of ALD GaN thin films are scarce. X-ray photoelectron spectroscopy (XPS) using an Al Kα source makes the quantitative analysis difficult due to overlapping Ga KLL and N 1s peaks. Although the overlap can be avoided by using a non-monochromatic Mg Kα source, low resolution and many satellite peaks are problems. Auger electron spectroscopy lacks chemical shifts, which limits chemical bond analysis, and its relatively low peak intensity limits quantitative analysis. In this study, we performed XPS analyses of the ALD films prepared at 225 ˚C or lower. To overcome the problem of overlapping N 1s and Ga LMM peaks, we calculated the ratio of Ga to N using the Ga 2p and N KLL peaks. The GaN wafer was used as a reference, and the sensitivity factors were obtained. We also performed deconvolution of the Ga 3d peak to analyze the chemical states of Ga. This method was then used to investigate the effect of process temperature on the composition of GaN thin films.

## Thin Films and Surface Modification
## Room Naupaka Salon 4 - Session TF1-WeE

### Thin Films - Properties

**Moderator: Tetsuhide Shimizu**, Tokyo Metropolitan University

5:40pm **TF1-WeE-1 Superlubricity: Toward Design of Zero-Friction and Zero-Wear Materials***, **Diana Berman**,* University of North Texas **INVITED**

Friction and wear-related failures remain the greatest problems in today's moving mechanical components, from microelectromechanical devices to automotive assemblies and to biological systems. The critical need to reduce and eliminate the tribological failures constitutes the necessity for continuous search of novel materials and lubrication solutions. In this presentation, we overview recent advances in establishing the fundamental understanding of materials interactions at sliding interfaces and use this knowledge as a guide to developing nanomaterials solutions that enhance reliability and efficiency of tribological systems. We evaluate tribological performance of 2D materials, including graphene, molybdenum disulfide, and MXene, and demonstrate realization of superlubricity regime at macroscale. To extend the lifetime of the tribological materials, we demonstrate tribochemically-driven self-replenishment of materials inside the contact interfaces, thus enabling a zero-wear sliding regime.

Overall, the findings have not only allowed us to solve some long-standing puzzles, but could also open a new avenue for the development of new concepts and design strategies for next generation of tribologically efficient materials systems.

6:20pm **TF1-WeE-3 Langmuir Monolayer Studies of First-Generation Photoswitchable DASA Surfactants***, H. Kaur,* University of Saskatchewan, Canada*; S. Sumat, S. Murphy,* University of Regina, Canada*; **Matthew Paige**,* University of Saskatchewan, Canada

Donor-Acceptor Stenhouse Adducts (DASAs) are photochromic molecules that can be isomerized with visible light between a coloured, linear triene form to a colourless cyclic form.These compounds have garnered considerable interest for a variety of light-based applications in the field of photopharmacology and related fields.In this work, we have synthesized several first-generation DASAs with a barbituric acid-based acceptor and a dialkyl amine donor, and investigated how the chemical structure of the DASA affects fundamental structural properties of Langmuir films they form.The DASAs form stable monolayer films at the air-water interface and exhibit a classical LE-LC phase transition at room temperature.Photoillumination leads to a significant alteration in film packing, along with spectroscopic changes consistent with successful isomerization between triene and cyclic form.Film morphology at the air-water interface is also significantly impacted by the photoisomerization process, as assessed by *in situ* Brewster Angle Microscopy.We have also explored the ability to deposit films as both monolayers and multilayers onto solid substrates and characterized the deposition process efficiency and resulting film structures using a variety of techniques.Time allowing, the structure and orientation of the DASA headgroup at the air-water interface will be discussed in context of appropriate molecular modeling calculations.

6:40pm **TF1-WeE-4 Precise Synthesis of Covalent Organic Framework Thin Films***, **Dong Wang**,* Institute of Chemistry, Chinese Academy of Sciences, China

The exotic properties associated with graphene and other 2D layered inorganic materials have attracted great interests from a variety of research fields. Two-dimensional covalent organic frameworks (2D COFs), which are covalently constructed from planar aromatic building blocks based on the principles of reticular chemistry, are a class of porous crystalline material with the highly ordered porous architectures and pre-designable electronic skeletons. 2D COFs feature the extended conjugation within a 2D layer and periodically columnar arrays aligned with an atomic precision in vertical direction, which is hardly achievable in other molecular architectures. In this context, high crystallinity and closely eclipsed stacking alignment of aromatic moieties render 2D COF as an ideal plat-form for charge carrier transport. With the improved crystallinity and controllable orientation, substrate supported 2D COF film would enable fabrication of advanced architectures for electronic devices, which however remains unexplored so far.

Herein, we report the on surface synthesis of high quality 2D COF thin film. We have developed a general method for constructing COF monolayers and thin films on substrate surfaces based on gas-solid and liquid-solid interfacial reactions. We proposed a method to improve 2D polymer orderliness by remotely modulating the molecular conformation through the effect of steric hindrance. We developed a chemical vapor deposition method, and prepared highly ordered 2D polymer films with controllable number of layers by modulating the kinetic process of the reaction. We further demonstrate that it is possible to fabricate COF thin film for optoelectric device. Two types of field-effect transistors with horizontal and vertical structures were constructed by directly growing COF films on the surfaces of hexagonal phase boron nitride and monolayer graphene, respectively, and their in-plane transverse charge transport properties and electronic properties in the π-π stacking direction were investigated. We have constructed COF-based electrochromic devices, and the highly ordered structure of COF significantly enhances their performance such as response speed.

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## Thin Films and Surface Modification
## Room Naupaka Salon 4 - Session TF2-WeE

### Thin Films - Materials II

**Moderator: Diana Berman**, University of North Texas

7:40pm **TF2-WeE-7 On the Growth of Cubic Boron Nitride Thin Films Using High-Power Impulse Magnetron Sputtering**, ***Tetsuhide Shimizu**, H. Nagakura,* Tokyo Metropolitan University, Japan*; Y. Tokuta,* Tokyo Metropolitan Industrial Technology Research Institute, Japan*; I. Fernandez,* Nano4Energy, Spain*; R. Boyd,* Linköping University, Japan*; D. Lundin, U. Helmersson,* Linköping University, Sweden **INVITED**

To realize the growth of cubic boron nitride (c-BN) towards a full-scale industrial application of this coating materials, this work has been aimed to understand the discharge physics and growth kinetics in reactive high-power impulse magnetron sputtering (HiPIMS) of $B_4C$ target in $Ar/N_2$ gas mixtures. Besides the developments of hard transition metal nitride coatings, c-BN coatings have been attracted because of its extremely high hardness, high thermal conductivity, high temperature resistance above 1000°C, and inertness to steel materials. Although a wide variety of deposition processes have been studied since 1990s, it has not yet been commercialized. One of the major challenges is the significant degradation of film adhesion due to the high residual stresses during the cubic phase formation. While the key to nucleation of the c-BN phase is the formation of "nano-arches" by ion bombardment on the turbostratic BN phase (t-BN), the bombardment by the gas ions, such as $Ar^+$ ions, leads to the entrapment of the gas atoms into the crystal lattice, causing the increase in residual stress.On the other hand, the time-transient discharge of HiPIMS makes the time separation of ion arrivals to the substrate and it enables the tuning of the incident ions and the independent control of their kinetic energy by using the synchronized pulsed substrate bias technology. This would realize the selective ion bombardment of film forming species, which is expected to result in efficient momentum transfer without introducing film stress through the rare gas incorporation. In addition, this great feature of the HiPIMS discharge allows us to systematically isolate the influencing factors and will dramatically advance the understanding of the nucleation physics of c-BN. In this study, the effects of ion acceleration schemes, including DC bias, synchronized pulsed bias and bipolar pulse configurations and their process parameters, such as the pulse duration, delay time and the substrate bias potential are thoroughly investigated, based on the mass-spectroscopy study of reactive HiPIMS discharge of $B_4C$ target in $Ar/N_2$ gas mixture. In addition to the great importance of the bias potential, the obtained results clearly show the effect of the synchronized pulse duration and the time delay on the chemical bonding states of B-C-N films and its mechanical properties, due to the time domain of accelerated ions during film growth. By focusing on the average momentum transfer per deposited atom at each biasing condition, the role of the mass and flux of the incident ions on the formation of c-BN bonding state is discussed.

8:20pm **TF2-WeE-9 Physical Properties of Pure Vanadium Nitrides Thin Films***, **Marjorie Cavarroc**, J. Neyrat,* Safran, France*; D. Marquez, D. Michau, A. Poulon-Quintin,* ICMCB, France

Transition metal nitrides coatings are widely studied because of their good optical, mechanical, thermal... properties. Depending on the microstructure, coatings present different properties. For vanadium nitride (VN), stable and metastable phases can be deposited as coatings. In this study, their physical and adherence properties on 316L stainless steel and AlN substrates depending on the microstructure and the thin film PVD technique used, are compared. Both Reactive High Power Impulse Magnetron Sputtering (R-HiPIMS) and Reactive RadioFrequency Magnetron Sputtering (RF-MS) were selected. Characterisations of structures and films microstructures were realised by *Grazing* Incidence X-Ray diffraction and Electron Microscopies (SEM and TEM). Scratch tests and nanohardness measurements were used to compare adherence and mechanical properties. OPtical properties were explored with a four-point probe.

The correlation between microstructure, process and physical properties is discussed. The aim of this study is to show the interest for specific applications of VN thanks to the quantification of its physical properties and/or tuning its microstructures.

8:40pm **TF2-WeE-10 Sputter Depth Profile Study of Zrn as a Barrier to Silver Migration in Triso Fuels Using the XPS Neo Artificial Intelligence Fitting Package***, **Jeff Terry**,* Illinois Institute of Technology

We have measured simulated TRISO Fuel model structures of SiC and ZrN with and without a 2 nm carbon capping layer. We have used both Sputter Depth Profiling with conventional X-ray Photoemission (XPS) and Ambient Pressure X-ray Photoemission Spectroscopy (APXPS) to explore the reactivity of these layers with both Ag and $H_2O$. One set of the samples that were depth profiled were measured at room temperature. Another set was annexed to 500 °C and then cooled to room temperature before profiling. The samples measured with APXPS were exposed to 1 mbar of $H_2O$ exposure and annealing up to 500 °C. The exposure was done in a near ambient pressure cell within the XPS system. High resolution scans of the Ag 3d, Zr 3d, O 1s, Si 2p, C 1s and N 1s region were collected and the peaks were fit to identify the chemical species as it is being exposed and annealed. The deconvolution was performed using our Artificial Intelligence analysis package XPS Neo. This study shows that materials used in TRISO fuel (SiC and ZrN) have a strong reaction to water and high temperature and having a barrier layer of carbon to can effectively prevent oxidation of the materials. The Ag is effectively stopped by the ZrN layer. Adding a layer of ZrN may prevent exposure to workers during shutdowns.

# Thursday Morning, December 12, 2024

## Nano and 2D Materials
## Room Naupaka Salon 5 - Session NM1-ThM

### Nanomaterials - Properties and Applications I

**Moderator: Santosh KC**, San Diego State University

8:40am **NM1-ThM-3 Different Directions In Layered Materials*, Joshua Goldberger,*** The Ohio State University **INVITED**

Layered and 2D materials are currently one of the most well-studied classes of solid- state compounds, due to the plethora of unique physical phenomena found in these anisotropic materials. Here we will describe our recent work in the synthesis, properties, and applications of layered materials that exhibit either n-type or p-type conduction behavior depending on the crystallographic direction, a phenomenon we refer to as "goniopolarity". We will establish the origin of this exotic behavior and the band structure design principles for identifying new goniopolar materials.[1] This has led to a significant expansion in the number of compounds that we have experimentally demonstrated to exhibit this effect, such as $NaSn_2As_2$, NaSnAs, $WSi_2$ and $PdSe_2$.[2-5] Finally, considering that most modern electronic devices require the integration of p-type and n-type regions for functionality, we will show how the unique charge separation in goniopolarmaterials have the potential to create new efficient energy-harvesting and electronics technologies.

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9:20am **NM1-ThM-5 Evaluation of Vapor Pressure of $MoO_2Cl_2$ and Its Initial Chemical Reaction on a $SiO_2$ Surface by Ab Initio Thermodynamics***, H. Kim, N. Lee,* ***Yeong-Cheol Kim,*** Korea University of Technology and Education, Republic of Korea

The vapor pressure of $MoO_2Cl_2$ and its initial chemical reaction on a $SiO_2$ surface were evaluated and analyzed using *ab initio* thermodynamics. The vapor pressure of $MoO_2Cl_2$ was calculated using the Gibbs free energy, while considering the zero-point energy, temperature-dependent enthalpy change, and entropy. The initial surface reaction was also studied as a function of temperature and partial pressure. The calculated sublimation temperature of $MoO_2Cl_2$ was 410 K, and its vapor pressure at 350 K was 8.2 torr. The partial pressure calculated for $MoO_2Cl_2$ agreed reasonably well with the experimentally measured value. The surface reaction energy barrier between $MoO_2Cl_2$ and $SiO_2$ was 0.8 eV.

9:40am **NM1-ThM-6 Development of TiAl Alloys: A Future Light-Weight Material for Extreme Condition*, Seong-Woong Kim,*** Korea Institute of Materials Science, Republic of Korea

Research on developing new TiAl alloys for high temperature (> 900$^o$C) applications is introduced. TiAl alloys have been gained interest for automobile and aerospace applications due to their low density, good oxidation resistance and high temperature strength. However, lack of room temperature ductility and the limitation of operating temperature hindered the practical applications of TiAl alloys. At KIMS, we have developed new TiAl alloys which have excellent room temperature and high temperature properties. Expecially, the alloy #16 showed excellent oxidation resistance in the temperature range from 900 to 1000$^o$C by forming stable $Al_2O_3$ oxidation layer. Moreover, alloy #16 exhibit room temperature ductility up to 0.78% solely by casting.

In addition, we introduced some in-situ transmission electron microscopy experiments in order to understand an underlying mechanism on room temperature ductility of TiAl alloys. Also, molecular dynamics simulation was conducted to calculate the stacking fault energy of TiAl alloys and to show which deformation mode is dominant. The difference in deformation mode was explained by stacking fault energy of the TiAl alloys which was calculated by molecular dynamics. Furthermore, the role of lamellar orientation of tensile direction on deformation behavior was examined using Schmid factor of each orientation. Finally, we proposed the important microstructural factors to have room temperature ductility of TiAl alloys.

## Nano and 2D Materials
## Room Naupaka Salon 5 - Session NM2-ThM

### Nanomaterials - Properties and Applications II

**Moderator: Yu-Chuan Lin**, National Yang Ming Chiao Tung University (NYCU)

10:20am **NM2-ThM-8 2D Metal Carbides (MXenes) for Catalysis*, Yue Wu,*** Iowa State University

MXenes, a new group of 2D transition metal carbides, are of considerable interest in catalysis due to their rich surface chemistry, tunable electronic structures, and thermal stability. In this presentation, we will discuss our latest discovery on utilization of metal-support interactions between noble metal and 2D metal carbides to enhance the catalytic reactions, such as alkane dehydrogenation, methane coupling, and electrochemical catalytic reactions. In addition, the nature of active sites in the MXene-based catalysts will be discussed.

10:40am **NM2-ThM-9 Investigating 2D-Materials Using Correlative Spectroscopy & Microscopy*, James Lallo,*** *L. Ping, T. Nunney, P. Mack, R. Simpson, H. Tseng,* Thermo Fisher Scientific

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

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

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

11:00am **NM2-ThM-10 Electronic, and Optical Properties of 2D Metal Chalcogenophosphates***, H. Chiu,* ***Santosh KC,*** San Diego State University

Recently, there have been significant research activities on two-dimensional (2D) materials for their potential use in electronic and optical devices. The structure, electronic, and optical properties of 2D metal chalcogenophosphates are investigated based on the Density Functional Theory. The lattice dynamics, surface, and interface properties with metal and oxides are investigated. Moreover, the electronic properties are tuned with substitutional impurities for metals and chalcogens. Our results indicate that the electronic and optical properties of metal chalcogenophosphates exhibit them as an emerging candidate material for devices.

## Thin Films and Surface Modification
## Room Naupaka Salon 4 - Session TF1-ThM

### Thin Films - Plasma and Etching-related

**Moderator: Gregory S. Herman**, Argonne National Laboratory

8:40am **TF1-ThM-3 Reactive Ion Etching of InGaZnO using HFC-based Gas and Chamber Cleaning*, Sang Jin Lee,*** *J. Hong,* Sungkyunkwan University, Republic of Korea*; Y. Jeong, H. Cho, D. Jung, Y. Yeo,* Samsung Display, Republic of Korea*; D. Kim, G. Yeom,* Sungkyunkwan University, Republic of Korea

Indium gallium zinc oxide (IGZO) is one of the most important active layer semiconductor materials for next-generation semiconductor and display devices. In this study, IGZO was etched with various hydrofluorocarbon (HFC)-type gases composed of $CH_xF_y$ and $C_3H_xF_y$ in an inductively coupled plasma (ICP) etcher and, the etch characteristics and its cleaning characteristics have been investigated. The results showed that, among HFC gases used in the experiment, IGZO was etched faster with $C_3H_xF_y$ compared to $CH_xF_y$ and, especially, HFC gases with lower F in the gas chemistry showed the better etch characteristics in addition to a low GWP. In addition, the etch by-products including dissociated HFC gases accumulated on the chamber wall could be in-situ cleaned using a $H_2$/Ar plasma. X-ray photoelectron spectroscopy (XPS), quadrupole mass spectrometer (QMS), and optical emission spectroscopy (OES) were used to understand the IGZO etch mechanism and chamber cleaning mechanism.

9:00am **TF1-ThM-4 Eco-Friendly Dry-Cleaning of Silicon Dioxide Deposition Chambers using a Cylinder-Type Remote Plasma Source with $NF_3/N_2$ Mixtures*, Won Kyun Yeom,*** *H. Gil,* Sungkyunkwan University, Republic of Korea*; G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Silicon dioxide ($SiO_2$) chamber cleaning is critical in semiconductor manufacturing, but traditional methods using perfluorocarbon gases like $NF_3$ raise environmental concerns due to their high global warming potential. This study presents a novel, eco-friendly approach utilizing a cylinder-type inductively coupled plasma remote plasma source (ICP RPS) with $NF_3/N_2$ gas mixtures for enhanced $SiO_2$ removal.The addition of a small amount of $N_2$ to $NF_3$ (1:9 ratio) was found to significantly improve cleaning efficiency and uniformity. Comprehensive plasma diagnostics, including quadrupole mass spectrometry (QMS), optical emission spectroscopy (OES), and Langmuir probe measurements, revealed that $N_2$ addition increases electron density and temperature, leading to enhanced generation and consumption of highly reactive fluorine radicals responsible for $SiO_2$ etching.This innovative process offers a promising pathway to reduce $NF_3$ consumption in $SiO_2$ chamber cleaning, mitigating environmental impact while maintaining high cleaning performance. The results of this study contribute valuable insights into the optimization of plasma-based cleaning processes for the semiconductor industry.

9:20am **TF1-ThM-5 Innovative Fluorite-Based High-Entropy Oxide: A Novel Electrocatalyst for All-Vanadium Redox Flow Batteries*, Chen-Hao Wang,*** National Taiwan University of Science and Technology, Taiwan **INVITED**

Vanadium Redox Flow Batteries (VRFBs) are emerging as a promising solution for large-scale energy storage, offering advantages such as high capacity, long lifespan, and scalability. This study introduces a novel approach using fluorite high-entropy oxides (HEO) nanoparticles as catalytic materials for VRFBs, synthesized through a surfactant-assisted hydrothermal method followed by calcination.

The research focuses on HEO compounds, which incorporate multiple metal cations into a single-phase crystal structure, resulting in unique properties. Among the samples tested, the HEO calcined at 750°C (HEO-750) demonstrated superior electrocatalytic performance for both $V^{3+}/V^{2+}$ and $VO_2^{+}/VO^{2+}$ redox couples.

Key findings include:

1. Excellent efficiency: VRFBs using HEO-750 achieved high coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) at various current densities.
2. Durability: No significant degradation was observed after 500 charge-discharge cycles.
3. Enhanced performance: The improved results are attributed to the forming of a single-phase fluorite structure during calcination, facilitating vanadium redox reactions.
4. Beneficial properties: High surface area, good wettability, and abundant oxygen vacancies improve electrochemical performance and stability.

The study concludes that HEO catalysts show great potential as next-generation electrode materials for VRFBs, potentially leading to the development of high-performance, cost-effective energy storage systems for various applications.

## Thin Films and Surface Modification
## Room Naupaka Salon 4 - Session TF2-ThM

### Thin Films - Surface Modifications

**Moderator: Hyo-Chang Lee**, Korea Aerospace University

10:20am **TF2-ThM-8 Wafer-Level Glassblowing Process for Fabrication of 3d Micro-Resonators and Associated Imperfections Due to Surface Modifications and Change in Material Composition*, Andrei Shkel,*** University of California Irvine

Glassblowing is an art that dates back over 2000 years. Today, glass blowing is used in a wide array of applications, including scientific glassware, optical components, consumer glass containers, and visual arts.

We introduced a fabrication process where glass micro-structures are blown on a wafer level, allowing thousands of 3D glass parts to be bult simultaneously. We reported, for the first time, a fabrication process for building atomically smooth, symmetric 3D wineglass and spherical shell structures, using low internal loss materials, fused quartz (FQ) and ultra low expansion titania silicate glass (ULE TSG).

In order to minimize surface losses in resonant and optical applications highly smooth surfaces are required. Characterization of the glassblown samples before glassblowing and after revealed a two-fold improvement in surface roughness, from 04 nm Sa down to 0.23 nm Sa. Such improvements in surface roughness are attributed to viscous flow of the glass layer and the associated surface tension forces. The glassblowing creates an effect analogous to “stretching out” the angstrom-level wrinkles on the surface, lowering the surface roughness.

We found that glassblowing temperature and the rate of cooling are the most important parameters that affect the quality of the FQ and TSG layer after glassblowing. With slow cooling (~8 hours from 1700 C to room temperature), recrystallization and micro-cracks were observed on the surface. In contrast, when glassblowing followed rapid cooling by bringing temperature from 1700 C to 200 C within a minute, no recrystallization and micro-cracks were observed. The electron dispersive spectroscopy (EDS) was used to confirm that in the later case a homogeneous SiO2 and TiO2 distribution was the underlying reason. We concluded, the absence of recrystallization makes rapid cooling and essential step in glassblowing of micro-structures.

The technology for fabricating high-Q resonators includes mechanical grinding (utilized for removing the flaw-rich surface layer) and polishing, followed by (or alternated with) chemical cleaning and etching. Such treatment activates numerous physical-chemical processes on the glass surface. Our study included a comprehensive look into the surface effects and derived the technological approaches for chemical and thermal surface treatments.

A strong correlation between surface and thermal treatments and increase in the quality factor of 3D shell resonators have been established. We experimentally demonstrated that the method of fabrication leads to an unprecedented mechanical quality factor of such resonators, with the quality factor of over 3,000,000.

10:40am **TF2-ThM-9 Relationship between the Uniformity of the r- and S-plane nanofaceted Substrate and the Nuclei Formation for Molecular Beam Epitaxial Layer of ZnTe on Sapphire*, Shumpei Tanaka,*** *M. Kobayashi,* Waseda university, Japan

Annealing of a sapphire m-plane (1-100) substrate produces a nano-meter-scale faceted structure with alternating r- and S- planes [1]. It has been confirmed that (111)- oriented ZnTe layers with a single domain were grown by molecular beam epitaxy on sapphire S-plane (1-10-1) substrate, which was confirmed by the X-ray diffraction pole figure measurement. One domain ZnTe(111)/S-plane sapphire aligned layer structure was also confirmed from the layer grown on the r- and S- nanofaceted sapphire substrate (Fig.1(a)). With a 17.66° off of the r- and S-nanofacet substrates, (110)-oriented ZnTe thin films were grown on the substrate [2]. (111)-

oriented ZnTe layers were preferentially grown on the S-plane of the nanofacet structure, but the diffraction peaks from twinned (-1-1-1) ZnTe were also confirmed (Fig.1(b)). The off-angle of the substrate caused the reduction of the surface area ratio of the S-plane surface and increased the r-plane, resulting in an increase in the number of growth nuclei on the r-plane.

The annealing duration of the substrate affects the height and size uniformity of the nanofaceted structure. The existence of large height nanofacet structures would result in the preferential formation of nuclei on the large area r-plane and result in the twin formation. Extending the annealing time has shown to improve the uniformity of the nanofacet heights. Therefore, the uniform structure of the nanofacets could lead to reduce the number of nuclei on the r-nanofacet surface. The nuclei and r- and S- plane nanofaceted structures on the substrate surface were analyzed by atomic force microscope (AFM). Figure 2 shows the AFM observation result of the surface right after the nuclei formation. The substrate was annealed at 1400°C for 20h and 1400°C for 40h, respectively. The non-uniform nano facet structure was confirmed only from the sample annealed for 20h. The sample annealed at 1400°C for 40h has nuclei formed on the S-plane rather than r-plane, while the sample annealed at 1400°C for 20h has many nuclei formed on the r-plane with few formations on the S-plane. The sample with the high uniformity of nanofacet structure was considered to have preferential formation of growth nuclei on the S-plane.

This work was supported in part by a Waseda University Grant for Special Research Projects and was partly carried out at the Joint Research Center for Environmentally Conscious Technologies in Materials Science at ZAIKEN, Waseda University.

[1] S. Curiotto, and D. Chatain, *Surf. Sci.* 603, 2688 (2009).

[2] T. Nakasu, T. Aiba, S. Yamashita, S. Hattori, T. Kizu, W. Sun, K. Taguri, F. Kazami, Y. Hashimoto, S. Ozaki, M. Kobayashi, and T. Asahi, *J. Electron. Mater.* 45, 4742 (2016).

11:00am **TF2-ThM-10 Atomic Force Microscope-Based Surface Investigation of Low-Dimensional Materials and Fabrication of the Microscale Probes***, **Sangmin An**,* Jeonbuk National University, Republic of Korea **INVITED**

The atomic force microscope (AFM) is a crucial tool for investigating the surface properties of low-dimensional materials, such as zero-dimensional (0D) [1] and two-dimensional (2D) [2] nanomaterials. It offers exceptional high-resolution topographical imaging capabilities. This research aims to provide an overview of recent advancements in AFM techniques, focusing on the exploration of both 0D and 2D materials and their applications in 3D printing, guided by AFM. A novel approach is presented by integrating a nanopipette with a quartz tuning fork-based AFM [3], enhancing the utility and precision of AFM in these fields. Additionally, the research examines the current progress in microscale cantilever fabrication, highlighting significant developments in this area. This comprehensive review of advanced AFM techniques and their applications sheds light on the latest innovations in the field, setting the stage for future discoveries and technological advancements.

[1] S. Kim et al., *Phys. Rev. X* 8 (2018) 041046

[2] H. Kim et al., *Nanoscale Adv.* 5 (2023) 2271-2279

[3] C. Kim et al., *Nano-Micro Lett.* 14 (2022) 13

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