

## Biomaterial Surfaces & Interfaces

### Room Naupaka Salon 4 - Session BI-MoM2

#### Biofunctional Surfaces and Coatings

Moderator: Buddy D. Ratner, University of Washington

#### 10:20am BI-MoM2-8 Structure in Lipid Films: From Biophysical Models to Drug Delivery, *Christine DeWolf*, Concordia University, Canada **INVITED**

Our understanding of the role of lipid membrane has evolved a long way from the Singer and Nicolson model of a fluid mosaic in which the bilayer served simply as a two-dimensional liquid providing a hydrophobic environment for membrane proteins. While inherently dynamic, membranes exhibit a wide polymorphism of co-existing structures that play important roles in cellular processes. Lipid films (monolayers and bilayers) are frequently used as models to understand and probe structural changes upon interaction with proteins, enzymes, drugs, drug delivery vehicles and foreign bodies such as pollutants and chemicals. Moreover, the understanding of such interactions and how they influence biomolecular conformation and structure, enables us to design lipid-based surface coatings that confer functionality (from simple biocompatibility to triggered drug delivery) to nanoparticles and other solid surfaces. Our work focuses on understanding the composition-structure-function relationships that govern such functionality using a surface analysis approach that encompasses lateral and vertical structure on both the molecular and meso-/microscopic scales and employs a combination of surface x-ray scattering (GIXD, GIXOS, X-ray reflectivity), imaging (AFM, Brewster angle microscopy and imaging ellipsometry) and spectroscopic (IRRAS) techniques. The power of these methods for elucidating the inter-relationships between the structure and organization of biomembranes and their functional properties will be shown using examples of Langmuir films as model membranes. A focus of the talk will be on lipid-nanoparticle interactions. On one hand, nanoparticles can be considered pollutants or contaminants as their impacts on cellular components, including the cell membrane itself, are not well established. This will be exemplified by examining the impact of inhaled nanomaterials on the functional properties of pulmonary surfactant membranes, a lipid-protein film coating the air-alveolar surface. On the other hand, nanocarriers which are comparable in size to many cellular components and easily internalized, cause unique interactions with cells and therefore offer an intriguing route for the encapsulation and delivery of difficult to deliver drugs. In this case the nanoparticle-lipid membrane interactions have to be tuned to minimize deleterious effects and in fact using a lipid coating can not only provide the necessary biocompatibility but also to enhance the delivery of drugs using nanocarriers via a carefully selected coating composition.

#### 11:00am BI-MoM2-10 Ways to Synthesize Silicone Nanobodies with Complex Shape and Their Applications as Coatings, *K. Chen, Stefan Seeger*, University of Zurich, Switzerland

One-dimensional (1-D) silicone micro- and/or nanostructures such as filaments, wires, fibers and tubes have attracted significant attention due to their remarkable application capabilities in a large range of material and surface science [1]. The chemical synthesis is surprisingly simple and based on the Droplet-Assisted-Growth and Shaping process (DAGS)[2]. Here, we demonstrate a novel, extraordinarily simple and efficient *dynamic* DAGS synthesis strategy allowing for the one-step synthesis and *in situ* control of the shape of nanostructures. We demonstrate bamboo-shaped silicone nanorods (SNRs) obtained by the repetitive dynamic regulation of growth conditions, concomitant with the periodic purging and injection of precursors. The new resulting nanostructures endow these newly designed SNRs with a specific number of segments and a highly regular arrangement. This approach allows the silicone micro- and/or nanorods to be customized with different heights and different segment numbers tailor-made to the requirements for various properties. With this method, various properties can be controlled, for example mechanical stiffness and water repellence. The obtained SNR coatings exhibit for example stable water-resistance under both static and dynamic wetting conditions, robust chemical and mechanical durability, and excellent performance in buoyancy promotion, self-cleaning and water harvesting. Notably, the properties are obtained by fluorine-free compounds, are very environmentally friendly, and are based on a very simple, solvent-free one-step procedure accomplishable at room temperature and normal pressure. The well-structured ultra-long rods can also be fabricated with an ultrahigh aspect ratio (~ 176), still standing straight upwards and regular even though they consist of flexible and soft silicone material [3]. Finally, the presentation will give insight in new applications which are accessible due to the precise control of the nanostructures' shape.

/1/ G. Artus, S. Jung, J. Zimmermann, H. P. Gautschi, K. Marquardt, S. Seeger, EP1644450A2 [<http://www.google.ch/patents/EP1644450A2?hl=de&cl=zh>](2003), *Adv. Mater.* (2006), 18, 2758, J. Zhang, S. Seeger, *Angew. Chem.* (2011) 50, 6652, Stojanovic, S. Oliveira, M. Fischer, S. Seeger, *Chem.Mat.*, 25, 2787(2013), X. Zhang, S. Seeger, *Small*, 15(34) 1901822 (2019)

/2/ G Artus, S Oliveira, D Patra, S Seeger, *Macromol.Rapid Comm.* 2017, 38, 1600558

/3/ K Chen, S Liu, Y Lau, S Seeger, *Small*, in press (2022)

#### 11:20am BI-MoM2-11 Isolation and Label-Free Detection of Circulating Tumour Cells by Fluidic Diffraction Chips with a Reflective Laser Beam System, *F. Lin*, National Taiwan University of Science and Technology, Taiwan; *H. Hsu*, National Defense Medical Center, Taiwan; *Jem-Kun Chen*, National Taiwan University of Science and Technology, Taiwan

A photonic crystal (PC) based line array of poly(methacrylic acid) (PMAA) brushes was grafted from a photoresist template using a trench array. The array was functionalised with anti-epithelial cell adhesion molecule antibodies (EpY). A laser beam was employed to analyse the two-dimensional (2D) and three-dimensional (3D) reflective signals of PCs at an incidence angle of 45°. The EpY-tailed PMAA PC possessed an optical feature with a characteristic diffraction effect along two laser input configurations including the SII configuration, in which the projection of the laser beam on the plane of the SPM chip was parallel to the strips, and the ST configuration, in which they were perpendicular. A fluidic diffraction chip based on the EpY-tailed PMAA PC with 1- $\mu$ m resolution was fabricated to examine the ability to detect circulating tumour cells (CTCs) along the ST configuration. The CTCs attached on the EpY-tailed PMAA PC, resulting in the change in the diffraction intensity. Dependence of change degree of the diffraction intensity exhibited a linear range of concentration of CTC from 0 to 64 cells and a limit of detection of 5 cells in 3 mL. CTC detection using both fluidic diffraction chips and a commercial IsoFlux system was carried out in clinical trials, including three healthy donors and 12 patients at various stages of colorectal cancer for comparison. Our platform provides a simple label-free method with high accuracy for rapid CTC counting, which has great potential in clinical treatment applications.

#### 11:40am BI-MoM2-12 Designer Silk: Plasma-Based Strategies to Customize Surface Properties of Silk Fibroin Films, *Morgan Hawker*, California State University, Fresno

Silk fibroin (silk) materials have promise for use in the biomedical space owing to their incredible mechanical properties. Compared to other naturally-derived polymers, silk exhibits remarkable tensile strength because of a unique antiparallel  $\beta$  sheet secondary structure. Additionally, silk is favorable for use in biological settings because it is non-immunogenic and degrades via enzymatic hydrolysis into non-toxic byproducts *in vivo*. Silk can be fabricated into a range of architectures to mimic biological settings, including films, porous networks, and microparticles. These aspects illustrate silk's utility in areas including biosensors, tissue engineering, and drug delivery. All biomedical applications, however, require silk to interact with biological species in specific ways. As with most polymers, silk lacks the necessary surface cues required to facilitate precise interactions with biological species. Thus, further modification is required to tailor silk materials' surface properties and enhance their efficacy as biomaterials.

Low-temperature plasma (LTP) modification represents a relatively unexplored but highly promising area for silk construct modification. LTP processing negates the use of solvents and high temperature conditions associated with wet chemical modification. Moreover, LTP treatment can be conducted with a range of precursors, translating to a myriad of attainable surface chemistries. In this talk, I will highlight three LTP approaches our group recently investigated to modulate silk film surface properties. For example, we utilized LTP strategies to enhance silk film hydrophilicity using N<sub>2</sub> and H<sub>2</sub>O(g) precursors. After N<sub>2</sub> and H<sub>2</sub>O(g) LTP treatments, water contact angles (WCAs) decreased by ~35° and ~50°, respectively. Notably, all LTP-modified constructs exhibited minimal hydrophobic recovery after 6 weeks of aging. In addition, we have developed plasma-enhanced chemical vapor deposition approaches to modulate silk film surface properties. We utilized LTP copolymerization, where feedgas composition was tuned using two unique precursors: acrylic acid (to produce thin films with polar functional groups on the silk surface) and pentane (to produce thin films with non-polar functional groups on the silk surface). WCA goniometry and x-ray photoelectron spectroscopy were utilized to evaluate wettability and changes in surface chemistry following

LTP treatment, respectively. We elucidated that surface properties depend on both feedgas composition and position of the film in the LTP reactor. In sum, LTP represents a promising avenue to customize silk surface properties for use in biomedical contexts.

## Energy Harvesting & Storage

### Room Naupaka Salon 5-7 - Session EH-MoM2

#### Surfaces and Interfaces for Efficient Power Conversion and Batteries

Moderator: David Ginger, University of Washington

10:20am **EH-MoM2-8 Fabrication of Proton-conductive BaCeZrYO<sub>3-d</sub> Coatings by Solution Precursor Plasma Spray (SPPS) Method, Yen-Yu Chen, W. Zeng, C. Liu, G. Yao**, Chinese Culture University, Taiwan

Perovskite-type proton-conductive ceramic materials have high potentials for the application of sustainable energy fields, such as protonic ceramic fuel cell (PCFC), carbon dioxide conversion, ammonia fuel synthesis, etc. In this study, perovskite-type proton-conductive coatings, BaCeZrYO<sub>3-δ</sub> (BCZY), were deposited on NiO/BaZrYO<sub>3-δ</sub> (BZY) substrates by a solution precursor plasma spray (SPPS) method. The precursors consisted the BCZY species of the nitrate salts and dissolved into de-ionic water. The NiO/BZY substrates were prepared by a die-pressing method. Several properties of the coatings were analyzed, including crystal phases by X-ray diffraction (XRD), microstructures by scanning electron microscope (SEM), electrical properties by electrochemical impedance spectroscopy (EIS), etc. The results of XRD show the coatings after post-coating annealing over 600°C are mainly consisted of perovskite phases. The microstructure analysis of the BCZY coatings characterized by SEM show the coatings are mainly consisted of overlapped splats of BCZY materials and a few of surface pores can be found from the coating layers. The average thickness of the coating layers are about several microns. The formation mechanism of the BCZY coatings can be purposed as the BCZY precursor droplet breakup, liquid-phase evaporation, thermal pyrolysis of precursors, solid particles melting, and then the melting particles splatted and overlapped on the substrate to form the BCZY coatings. The details electrical property analysis of the BCZY coating samples are as mentioned in the following report.

10:40am **EH-MoM2-9 Metal Exsolution and Nanoparticle Self-Assembly Dynamics at Complex Oxide Surfaces, Moritz Lukas Weber**,

Forschungszentrum Juelich GmbH, Lawrence Berkeley National Laboratory, RWTH Aachen University, Juelich-Aachen Research Alliance; *B. Šmíd*, Charles University, Czech Republic; *H. Kersell*, Lawrence Berkeley National Laboratory (LBNL); *U. Breuer*, Forschungszentrum Jülich GmbH, Germany; *M. Rose*, Forschungszentrum Jülich GmbH, RWTH Aachen University, Juelich-Aachen Research Alliance (JARA-FIT, Germany); *N. Menzler*, Forschungszentrum Jülich GmbH, RWTH Aachen University, Germany; *R. Dittmann*, Forschungszentrum Jülich GmbH, Juelich-Aachen Research Alliance (JARA-FIT, Germany); *R. Waser*, Forschungszentrum Jülich GmbH, RWTH Aachen University, Juelich-Aachen Research Alliance (JARA-FIT), Germany; *O. Guillon*, Forschungszentrum Jülich GmbH, RWTH Aachen University, Juelich-Aachen Research Alliance (JARA-Energy), Germany; *C. Lenser*, Forschungszentrum Jülich GmbH, Germany; *S. Nemšák*, Lawrence Berkeley National Laboratory (LBNL); *F. Gunkel*, Forschungszentrum Jülich GmbH, Juelich-Aachen Research Alliance (JARA-FIT), Germany

Metal exsolution attracts much attention for the synthesis of nanostructured catalysts. Thermal reduction of doped perovskite parent oxides induces the migration of reducible cations from the oxide bulk to the surface and results in the self-assembly of metallic nanoparticles that serve as catalytic centers. Ideal exsolution-type catalysts therefore dynamically adapt with respect to the oxygen chemical potential. The parameters that influence the kinetics of nanoparticle exsolution, however remain an open question in the scientific community. Furthermore, little is known about the origin of stability limitations of exsolved nanoparticles that are typically anchored at the oxide support.

We employ epitaxial thin films model systems with atomically defined surfaces to investigate the exsolution response of Ni in SrTi<sub>0.9</sub>Nb<sub>0.05</sub>Ni<sub>0.05</sub>O<sub>3-δ</sub> and SrTi<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>3-δ</sub> of respective *n*-type and *p*-type defect chemistry. Here, we study the mass transfer of dopants towards the surface as well as the morphological evolution of the nanostructured catalysts. Our thin film approach enables to study differences in the exsolution behavior on the basis of well-defined (001) surfaces, eliminating uncertainties regarding the complex microstructure and anisotropy of ceramic oxides and the presence of secondary surface phases.

In order to assess the dynamic changes at the catalyst surface during metal exsolution, we conduct advanced *in-situ* spectroscopy and scattering analyses. In particular, we employ a recently developed technique that allows for the simultaneous analysis of the chemical and structural evolution of the solid-gas interface based on coupled *in-situ* ambient pressure X-ray photoelectron spectroscopy (AP-XPS) and *in-situ* ambient pressure grazing incidence X-ray scattering (AP-GIXS). Our investigations show that the defect chemistry of the near-surface region determines the dynamics of the exsolution response, where the formation of space charge regions at the perovskite surface plays a major role for the process.

We conclude that the mass transfer during metal exsolution and therefore the nanoparticle self-assembly at the perovskite surface is surface-controlled by interaction with the energy landscape of the complex oxide surface. Derived from our investigations, we propose a mechanistic model that describes how metal exsolution is mediated by the surface defect chemistry and we demonstrate surface engineering of the topmost atomic layers can be utilized as a novel strategy for the active control of the exsolution behavior. Moreover, our observations indicate that the different nature of the surface potential may influence the stability of exsolved nanoparticles.

11:00am **EH-MoM2-10 Characterization of Surfaces and Interfaces in Polymer Electrolyte Membrane Electrolyzers, Svitlana Pylypenko**, Colorado School of Mines

Polymer electrolyte membrane water electrolyzers (PEMWEs) are of significant importance towards enabling the large-scale utilization of renewable hydrogen. Fabrication and integration of components, advancement of scalable manufacturing techniques, elucidation of degradation mechanisms, and development of degradation mitigation strategies all require extensive characterization of materials, components, and devices. The complexity of the systems and problems combined with the multitude of relevant scales require multi-technique characterization and motivate further developments of characterization methods and novel approaches. This talk will discuss some of our recent studies on both catalyst layers (CLs) and porous transport layers (PTLs) for application in PEMWEs. Specifically, this presentation will highlight the complementary nature of electron and X-ray microscopy and spectroscopy methods for the investigation of surfaces, interfaces, and interactions within the CLs comparing results for Ir and IrO<sub>2</sub>-based CLs, and fresh and aged or tested CLs. Similarly, the characterization of PTLs requires advanced characterization to properly assess the elemental distribution and chemical speciation of PTLs and protective coatings.

11:20am **EH-MoM2-11 Design and Manufacture of Air-Silicon Batteries and the Impact of Plasma-Processed Silicon on the Efficiency of These Batteries, Marziyeh Gholami**, Shahid Beheshti University, Iran (Islamic Republic of)

Silicon, as the second most abundant material on earth, is a significant option as an anode material in air metal batteries, so the theoretical energy density is very high at about 8470 Wh kg<sup>-1</sup>. The discharge products of this battery are non-toxic and environmentally friendly. The final battery is light in weight and will be used in wet or very dry areas. Also, due to the lack of cathode in these batteries, less space will be occupied and the weight of the battery will be light. These advantages, along with the low cost, have made this battery one of the brightest prospects in the field of energy storage devices. In this primary battery, porous carbon, a catalyst, and a polymer as a cathode play an important role in the structure of the battery. An alkaline solution is used as the electrolyte. If plasma-untreated silicon is used in this battery, it has a lower OCV and a short discharge cycle. So, the research carried out in this project was the processing of silicon surface with plasma in order to increase the effective cross-section of silicon in contact with the electrolyte and increase the open-circuit voltage of the battery due to the increase in voltage that we will have at the sharp points. Surface roughness is also guaranteed by plasma etching.

# Monday Morning, December 12, 2022

11:40am **EH-MoM2-12 Insights into the Interfacial Reactions of High Voltage  $MgV_2O_4$  Cathodes for Rechargeable Magnesium Batteries**, D. Nguyen, V. Prabhakaran, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research (JCESR); V. Shutthanandan, Pacific Northwest National Laboratory; J. Hu, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research; G. Alexander, J. Cabana-Jimenez, University of Illinois at Chicago, Joint Center for Energy Storage Research; K. Mueller, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research; Vijayakumar Murugesan, Pacific Northwest National Laboratory, Joint Center for Energy Storage Research

Interfacial reactions driven by charge transfer occurring at the electrode – electrolyte interface contribute to the formation of complex interphasial layers that govern the performance of energy storage devices. These interfacial reactions are influenced by various factors such as surface chemistry of electrode, electrochemical properties of the electrolyte solution, and the working potential of the device. Precise capturing of critical interfacial reactions and subsequent evolution of solid-electrolyte interphase components is extremely challenging due to the complexity and heterogeneity of the interphasial reactive components, the reaction dynamics under variable potentials, and the smaller dimensions of interphase region. Probing complex interfacial processes requires the integration of advanced spectroscopies within an electrochemical device to monitor interfacial reactions and structural changes during operation. In this study, we investigated the interphasial evolution of  $MgV_2O_4$  cathodes for rechargeable magnesium batteries using both *in situ* and *ex situ* X-ray photoelectron spectroscopy while also probing structural transformation of interphasial chemical species using *operando* Raman spectroscopy. Our study revealed that the solid electrolyte interphase layer on  $MgV_2O_4$  was formed mainly by the decomposition of electrolyte anions that occurred at a very early stage of the initial charging process. The interphase layer also thickened with increased cell potential as well as repeated cycling. Post surface analysis of the  $MgV_2O_4$  cathode after 20 cycles also confirmed surface conditioning processes that is well supported by its electrochemical performance in early cycles. Our study revealed insights into the surface evolution of  $MgV_2O_4$ , which provides crucial information for development of an oxide cathode for rechargeable magnesium batteries as well as other battery chemistries that involve sodium and lithium ions.

## Thin Films

### Room Naupaka Salon 4 - Session TF-MoM1

#### Innovations in the Development of Multifunctional Thin Films/Nanostructural and Surface Morphological Evolution: Experiment and Theory

Moderator: Jolanta Klemberg-Sapieha, Polytechnique Montréal, Canada

8:00am **TF-MoM1-1 Hybrid Technologies to achieve Multifunctional Properties**, Pierre Collignon, PD2-1, France; A. Schuetze, ACT

Author :Dr Pierre Collignon , PD2-1

Co-Author: Dr. Andreas Schuetze

Duplex Coatings involving a nitriding - and subsequent coating process are already used for forming tools to improve the carrying pressure load. We have worked to broaden this hybrid technology to applications requiring higher temperatures like Aluminum die casting or hot forming. These applications require high thermal fatigue resistance which can be obtained through a dedicated nitriding process and multifunctional coatings to achieve the appropriate properties required at the surface of the dies; i.e. heat and oxidation resistance, hot hardness, and low thermal conductivity.

This paper reports our developments and the investigations to achieve the aforementioned properties to achieve hot hardness and oxidation resistance of different coatings. First, we investigated properties like hot hardness and oxidation resistance on the basis of ALTiN, AlCrN, and CrN coatings. Secondly, to improve the properties we have studied the influence of elements like W, B, and Si as doping or alloying elements.

We found, that CrWAIN coating keep the highest hardness after annealing in air at 750 °C. In case of ALTiSiN the best results have been achieved using a multilayer of ALTiBN/TiSiN with 25% Si producing a high content of Si<sub>3</sub>N<sub>4</sub>. For hot applications requiring thick coatings (6 to 8 μm), the morphology and structure has been investigated using cross section SEM and residual stress measurements.

8:20am **TF-MoM1-2 Multifunctional Hybrid Optical Coatings for Flexible Substrates**, Ludvik Martinu, J. Klemberg-Sapieha, O. Zabeida, Polytechnique Montréal, Canada

Optical coating (OC) applications represent a multibillion dollar market worldwide; they range from antireflective coatings (ARC) found in most optical components and devices to complex optical interference filters (OIFs). Specifically, there has been considerable effort to develop optical films with multifunctional characteristics suitable for applications in ARCs and OIFs on plastic and flexible substrates. This includes a necessity to control and optimize the mechanical and thermal properties (hardness, Young's modulus, adhesion, thermal expansion coefficient), surface energy (hydrophobicity), and possibly provide complementary functionalities (color, electrical conductivity, etc.), while allowing one to well adjust the refractive index.

In this context, we focus our work on the hybrid organic-inorganic materials (such as SiOCH) that are shown to combine high mechanical resistance of ceramics with high elasticity of polymers. We demonstrate, that using the scalable ion beam assisted chemical vapor deposition (IBA-CVD) process the refractive index (n) of such films can vary from ultra-low (n less than 1.38@550nm) to low (1.47-1.53), while the extinction coefficient is kept below 10<sup>-4</sup>. At the same time, the hardness-to-Young's modulus ratio, H/E, is substantially increased (to 0.16) compared to 0.08 for pure SiO<sub>2</sub>, a result that is well correlated with the increased resistance to crack formation and propagation. This is also confirmed by the value of the crack onset strain (COS) of 4% for the hybrid films compared to 1% for inorganic SiO<sub>2</sub>. Such hybrid layers, incorporated in multilayer structures on plastic substrates, provide significantly enhanced optical and mechanical stability in environments involving large temperature and humidity excursions.

We discuss the optical, chemical, morphological, and mechanical properties of the deposited films in relation to the discharge current and oxygen gas ratio during deposition, while showing that these main parameters provide an opportunity to manipulate the functional coating properties within a wide range.

8:40am **TF-MoM1-3 High-Sensitivity UV Photoemission Spectroscopy Using Low Energy Photon to Probe the Electronic Structures of Semiconductors, Insulators and Biomolecules**, Hisao Ishii, Chiba University, Japan

INVITED

The information on electronic structure such as density-of-states (DOS), ionization energy, and energy level alignment at the interfaces of various materials is a key factor to understand and improve their functions. Photoemission spectroscopy (PES) has been, so far, widely applied to many materials. The detection limit is enough to investigate valence states, but not to probe weak density of states which is practically important to device performance as trap etc. By using well-monochromatized light source, minimum detection limit of PES has been recently much improved [1]. Our group have also developed high-sensitivity UV photoemission spectroscopy (HS-UPS) and photoelectron yield spectroscopy (PYS) using tunable low energy light source, achieving the detection of very low DOS less than 10<sup>15</sup> cm<sup>-3</sup>eV<sup>-1</sup> level[2]. Our technique has additional advantage: this method is tough for sample charging problem, opening chance to measure various insulating films. In this talk, I will report on its application to organic and inorganic semiconductors and insulators. First topic is the observation of density-of-states including both valence top region and band tail structures for polymers[3,4], perovskite[5], and transparent oxide semiconductor[6]. Second topic is the detection of negative carrier states in organic semiconductor films and devices using *operando*-PYS[7]. Finally, I will talk about our recent trial to measure the electronic structure of protein films[8,9].

[1] F. Bussolotti, J. Electron Spectrosc. Relat. Phenom. 204, 29 (2015).

[2] T. Sato and H. Ishii et al., Appl. Phys. Express 10, 011602-1 (2017)

[3] T. Sato and H. Ishii et al., Appl. Phys. Lett. 110, 111102-1 (2017)

[4] Y. Yamaguchi and H. Ishii et al., IEICE Trans. on Elect., E102.C 168 (2018).

[5] I. Levine and H. Ishii et al., J. Phys. Chem. C, 125, 9, 5217 (2021)

[6] R. Nakazawa and H. Ishii et al., Appl. Phys. Express,14, 071004 (2021).

[7] Y. Tanaka and H. Ishii et al., Appl. Phys. Express 11, 081601 (2018).

[8] D. Sano and H. Ishii et al., *Molecular Crystals and Liquid Crystals*, vol.687, No.1, 34-39 (2019).

[9] Z. Futera and H. Ishii et al., *The Journal of Physical Chemistry Letters*, 11, 9766-9774(2020).

9:20am **TF-MoM1-5 Stress Corrosion Cracking Simulation of FCC Type High Entropy Alloy via Reactive Molecular Dynamics Method, Jo Watanabe**, Institute for Materials Research, Tohoku University, Japan; Q. Chen, New Industry Creation Hatchery Center, Tohoku University, Japan; Y. Asano, Institute for Materials Research, Tohoku University, Japan; Y. Ootani, Institute for Materials Research, Tohoku University, Japan; N. Ozawa, New Industry Creation Hatchery Center, Tohoku University, Japan; M. Kubo, Institute for Materials Research, Tohoku University, Japan

Recently, FeNiCrCoMn-based high-entropy alloys (HEA) are expected to be used in extreme environments because of the superior properties that not found in conventional alloys. However, stress corrosion cracking (SCC) is a problem for HEA used in high-temperature and high-pressure water environments. SCC is the phenomena resulting from corrosion and tensile stress, and thus it is difficult to analyze detailed mechanism by experiments. Molecular dynamics (MD) method using reactive force field (ReaxFF) is suitable for analyzing phenomena involving chemical reactions. Recently, we showed that ReaxFF is useful to investigate the SCC of HEA (Fig.1). However, ReaxFF parameter set for FeNiCrCoMn HEA under the water environment has not been established because it shows complex mechanical and chemical phenomena. In this study, we develop ReaxFF parameters for FCC-type FeNiCrCoMn HEA using recently proposed Hybrid Real-Coded Genetic Algorithm (HIRCGA)<sup>[1]</sup>. Then tensile simulation of FeNiCrCoMn HEA was performed in vacuum and high-temperature water to elucidate its SCC.

First, we optimized the parameters for Mn-Mn interaction to reproduce the energy change of  $\alpha$ -Mn and  $\beta$ -Mn crystals with respect to the change in lattice constant obtained by density functional theory (DFT). Fig.2 shows a comparison of the energy change with respect to the change in lattice constant fraction of  $\alpha$ -Mn and  $\beta$ -Mn obtained by DFT and MD calculations with optimized ReaxFF parameters. As shown in Fig.2 the optimized parameters reproduce the DFT results with good accuracy. Subsequently, we optimized the parameters for Mn-Fe, Mn-Ni, Mn-Cr, and Mn-Co interactions by using  $\text{Fe}_{0.5}\text{Mn}_{0.5}$ ,  $\text{Ni}_{0.5}\text{Mn}_{0.5}$ ,  $\text{Co}_{0.25}\text{Mn}_{0.75}$ , and  $\text{Cr}_{0.4}\text{Mn}_{0.6}$  crystals with similar manner.

After the optimization of the ReaxFF parameters between Mn-Mn, Mn-Fe, Mn-Ni, Mn-Cr, and Mn-Co interactions by HIRCGA, we combined these parameters and re-optimize the combined parameters to reproduce the  $\text{Fe}_{20}\text{Ni}_{20}\text{Co}_{20}\text{Cr}_{20}\text{Mn}_{20}$  crystal structure. The crystal structure analysis showed that the optimized parameter can reproduce the experimentally obtained crystal structure. The details of the tensile simulation of FeNiCrCoMn-based HEA with the optimized ReaxFF parameters will be reported at the conference.

[1] Song, H., Wang, J., Song, L., et al. Improvement and application of hybrid real-coded genetic algorithm. *Applied Intelligence*, 2022, <https://doi.org/10.1007/s10489-021-03048-0>.

# Monday Evening, December 12, 2022

## Charles S. Fadley Memorial Session

### Room Naupaka Salon 4 - Session CF-MoE1

#### Charles S. Fadley Memorial Session I: Advances in X-ray Spectroscopy and Analysis

Moderators: Gregory S. Herman, Oregon State University, Boris Sinkovic, University of Connecticut

5:40pm **CF-MoE1-1 Pursuing Chuck Fadley's Ideas a Scientific Lifetime: Photoelectron Recording with Maximum Parallelization, Gerd Schönhense**, Institut für Physik, Johannes Gutenberg-Universität, Germany  
**INVITED**

In 1988-89 the author had the great pleasure of doing postdoctoral work in the Fadley group. Experiencing the impressive work with an electron spectrometer with a multi-channel detector (VG ESCALAB5) [1] initiated decades of thinking about a further parallelization of photoelectron recording techniques. Today we find powerful implementations that extrapolate those early ideas that have resulted in orders of magnitude increased recording efficiency.

Thanks to the excellent time structure of modern photon sources such as lasers, HHG sources, Synchrotrons and FELs, time-of-flight (ToF) detectors can record a wide energy band in parallel. Additional full-field imaging of ( $k_x, k_y$ ) momentum patterns has led to a novel ARPES technique, termed ToF momentum microscopy (ToF-MM). A fast delay-line detector records ( $x, y$ ) position and ToF for each electron with count rates up to  $8 \times 10^6$  cps. ToF-MM enabled new types of experiments, such as fast tomographic-like Fermi surface and -velocity mapping [2].

The developments had a dramatic impact on experiments with very low signal intensities. In particular, spin-resolved experiments suffer from the low figure-of-merit of spin detectors. Significant advances have been made with the advent of multichannel spin recording [3]. Bulk-sensitive photoemission using hard X-ray excitation suffers from low cross sections and enhanced phonon scattering. The ToF-MM approach was extended to energies  $>7$ keV and an order of magnitude higher ( $E_B, k_x, k_y$ ) phase-space acceptance. This led to new types of (H)ARPES [4] and X-ray photoelectron diffraction (XPD) experiments [5]. The large k-field-of-view provides 4D bulk spectral functions  $\rho(E_B, \mathbf{k})$  in a single measurement without scanning the photon energy.

In fs time-resolved photoemission (tr-ARPES), weak signals of transient excited states are recorded with high efficiency, both for FELs [6] and HHG sources [7]. In parallel to the tracking of the electronic structure, rapid changes in the geometric structure can be observed using tr-XPD. Resolving the intrinsic time scale of ultrafast processes and further parameters like pump-laser fluence coined the term "multidimensional photoemission" for such experiments. For further reading, see current reviews [4,5,7].

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6:20pm **CF-MoE1-3 The State of Interpretation for Multiplet Splitting and Shake-Up Satellites in Transition Metal Compound XPS: Fe<sub>2</sub>O<sub>3</sub> and NiO**, Christopher R. Brundle, C. R. Brundle and Associates; B. Crist, XPS Library; P. Bagus, University of North Texas

We discuss the understanding of multiplet splitting and shake-up satellite structure for transition metal compounds. Chuck Fadley was an early pioneer for the former (1).

Gupta and Sen (2) expanded atomic multiplet splitting theory to include spin orbit coupling, providing predictions for the 2p XPS splitting features for TM cations. Such calculations do not include ligand-field or bonding effects in solids. Later semi-empirical approaches attempted to include such effects by scaling parameters and by invoking a charge transfer model to describe shake-up satellites. A free program, CTM4XAS (3), incorporates all this to simulate the cation 2p XPS spectrum.

Though CTM4XAS may roughly describe the BE spread in the cation 2p XPS, it completely disagrees with the description obtained from our full ab initio cluster calculations (Fe<sub>2</sub>O<sub>3</sub> and NiO) of the electronic characteristics of the major features. The strong experimental satellite intensity for the Fe2p spectrum of Fe<sub>2</sub>O<sub>3</sub> and other high spin Fe(III) compounds, at  $\sim 8.5$  eV, has long been assigned to shake-up; and has been used to verify the presence of Fe(III) (4). Similarly, in the Ni2p spectrum of NiO, the satellite at  $\sim 6.5$ eV is

used to verify the presence of Ni(II). Our calculations confirm that these satellites do have a large amount of shake character, and that the leading edge of the "main" peak (lowest BE) is essentially "normal", ie it has no shake involvement (5, 6). CTM4XAS reverses these assignments, claiming that main peak is a shake state (charge transfer in their parlance) and the intense satellite represents the "normal" transition. Furthermore, our calculations show that once shake excitation is included, the intensity distribution of all structure in the 2p spectrum is highly modified, and there is no region, except the leading edge of the main 2p<sub>3/2</sub> peak, that is 100% "normal" (5). Everywhere else there is significant mixing of "normal" and shake. We expect this mixing to hold for other TM compounds.

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6:40pm **CF-MoE1-4 Zinc and Cadmium: Chemical State Determination Through XPS Analyses of Standard Samples**, Jeffrey D. Henderson, S. Buchanan, L. Grey, M. Biesinger, Surface Science Western, Canada

Zinc, cadmium, and their related compounds have a myriad of applications, including, but not limited to, automotive manufacturing, batteries, photovoltaic devices, corrosion protection, and pigments. From a research perspective, the ability to accurately speciate different compounds is critical to understanding how surface chemistry can influence material properties. This ability allows for the advancement of our mechanistic understanding. It has been repeatedly demonstrated that X-ray photoelectron spectroscopy (XPS) is a powerful analytical tool for the study of changes in surface chemistry. Typically, speciation is achieved through the careful analysis of photoelectrons, and occasionally, Auger electrons. Since the main photoelectron binding energies of many zinc and cadmium compounds overlap, the modified Auger parameter must also be utilized to reliably detect chemical shifts. While the binding energies and Auger parameter data can be found in the literature for some zinc and cadmium compounds, in most cases, the available data lacks consistency, certainty, and reproducibility. Notably, Auger parameter data is often underreported in the existing literature, despite its proven utility. Additionally, many of these sources do not provide the variety of compounds needed to perform accurate chemical state analyses.

In this presentation, recent work to extend upon previously published XPS reference data and curve-fitting procedures will be detailed for a wide range of high-purity zinc- and cadmium-containing compounds. This will include a summary of literature data, carefully excluding those which contain issues related to reliability. Lastly, the applicability of peak fitting Auger lines will be explored for the analyses of mixed species systems.

7:00pm **CF-MoE1-5 X-Ray Spectroscopic Identification of Strain and Structure-Based Resonances in a Series of Saturated Carbon-Cage Molecules: Adamantane, Twistane, Octahedrane, and Cubane**, Trevor Willey, J. Lee, Lawrence Livermore National Laboratory; D. Brehmer, O. Paredes Mellone, SLAC National Accelerator Laboratory; L. Landt, Lawrence Livermore National Laboratory; P. Schriener, A. Fokin, B. Tkachenko, Institute of Organic Chemistry, Justus Liebig University, Germany; A. de Meijere, S. Kozhushkov, Institute for Organic and Biomolecular Chemistry, Georg-August-University, Germany; T. van Buuren, Lawrence Livermore National Laboratory

Novel nanocarbons such as fullerenes, nanotubes, graphene, and nanodiamond reside at the cutting edge of nanoscience and technology. Along with chemical functionalization, geometrical constraints (such as extreme curvature in nanotubes, or defects within or at the surfaces of diamond nanoparticles) significantly alter the electronic states of the nanocarbon material. Understanding the effects of steric strain on electronic structure is critical to developing nanoelectronic applications based on these materials. This paper presents a fundamental study of how strain affects electronic structure in a benchmark series of some

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fundamental saturated carbon cage compounds. Adamantane, C<sub>10</sub>H<sub>16</sub>, the smallest diamondoid, and arguably the smallest nanodiamond crystallite, has carbon atoms essentially commensurate with diamond lattice positions and possesses by far the least bond strain of this series. Twistane also is a C<sub>10</sub>H<sub>16</sub> isomer but the fixed cyclohexane twist conformation of the central ring introduces some strain into the cage. Octahedrane, (CH)<sub>12</sub>, and cubane, (CH)<sub>8</sub>, are considerably much more strained, culminating in cubane where carbon-carbon bonds lie either parallel, or orthogonal to one another. Using gas-phase near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to probe the unoccupied electronic states, we observe two major progressions across this series. First, a broad C-C  $\sigma^*$  resonance in the absorption splits into two more narrow and intense resonances with increasing strain. Second, the first manifold of states previously associated with tertiary C-H  $\sigma^*$  in the diamondoid series appears to broaden and shift to lower energy. This feature is more than twice as intense in cubane as in octahedrane, even though these two molecules have only tertiary carbons, with chemical formula (CH)<sub>x</sub>. The spectral differences are entirely due to the shape of the molecules; in particular, in cubane, the features arise from a high degree of p-p interaction between parallel C-C bonds. In contrast to the conventional wisdom that near-edge X-ray absorption is primarily an atomically localized spectroscopy, molecular shape and associated bond strain lead to the dominant features in spectra acquired from this fundamental series of carbon cage structures.

## Charles S. Fadley Memorial Session Room Naupaka Salon 4 - Session CF-MoE2

### Charles S. Fadley Memorial Session II: Ambient-Pressure X-ray Photoelectron Spectroscopy

Moderators: Christopher R. Brundle, C.R. Brundle and Associates, Alexander Gray, Temple University

#### 7:40pm CF-MoE2-7 Catching a Wave: From Quantum Materials to Liquid Chemistry, Slavomir Nemsak, Lawrence Berkeley National Laboratory, USA

INVITED

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

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#### 8:20pm CF-MoE2-9 High Pressure Hard X-ray XPS Studies of Operando Catalytic Reactions for CO<sub>2</sub> and N<sub>2</sub> Reduction, Anders Nilsson, Stockholm University, Sweden

Charles Fadley was a pioneer in the field of x-ray photoelectron spectroscopy (XPS) for over 5 decades and I had the pleasure to interact with him frequently since my time at Uppsala University in the 1980s. In the last part of his scientific life he brought forward hard x-ray XPS as an important tool to investigate interfaces. In the following contribution, I would like to honor him with a new direction of hard x-ray XPS that can play an important role for the development of a sustainable society to address climate change and in particular to mitigate CO<sub>2</sub> emissions.

Some of the most essential catalytic reactions for our energy society is to reduce CO<sub>2</sub> to hydrocarbons and alcohols to be used as fuels and base chemicals for the chemical industry. In order to convert a fossil dependent chemical industry and instead use sustainable hydrogen as a feedstock we

need to develop new catalysts. Furthermore, the catalytic reduction of N<sub>2</sub> to ammonia has been considered as one of the most important discoveries during the 20<sup>th</sup> century to produce fertilizers for a growing population. Despite an enormous effort in studying these catalytic reactions we are still lacking experimental information about the chemical state of the catalytic surface and the adsorbates existing as the reaction is turning over.

X-ray photoelectron spectroscopy (XPS) is a powerful surface sensitive technique that can provide almost all essential chemical information and it has been developed to operate also in a few mbar of pressure with great success for probing oxidation catalytic reactions. Unfortunately, this pressure regime is too low for the hydrogenation reactions to turn over. However, utilizing the hard x-ray XPS technique can bring the pressure up by many orders of magnitude in a unique instrumentation<sup>1</sup>.

Here I will present how Fischer-Tropsch, methanol and ammonia synthesis reactions on single crystal metal surfaces have been probed during operando conditions in the pressure range 100 mbar-1 bar using the new XPS system built at Stockholm University<sup>1</sup> and permanently located at the PETRA III synchrotron in Hamburg. The instrument can vary the incidence angle of the X-rays allowing it to be either surface or bulk sensitive.

<sup>1</sup>P. Amann, D. Degerman, M. T. Lee, J. D. Alexander, M. Shipilin, H. Y. Wang, F. Cavalca, M. Weston, J. Gladh, M. Blom, M. Björkhage, P. Löfgren, C. Schlueter, P. Loemker, K. Ederer, W. Drube, H. Noei, J. Zehetner, H. Wentzel, J. Ålund and A. Nilsson, *Rev. Sci. Instrum.* **90**, 103102 (2019).

#### 8:40pm CF-MoE2-10 Initial Oxidation of Ternary Amorphous Metal Alloy Surfaces Under Ambient Oxygen Pressures, Gregory Herman, Oregon State University; P. Alzaga, HP Inc.; T. Diulus, R. Addou, Oregon State University; W. Stickle, HP Inc.; J. Jenkins, R. Elzein, Oregon State University

The oxidation of complex alloys is governed by both thermodynamics and kinetics. The formation of a surface oxide influences a range of surface properties, including catalysis, corrosion resistance, tribology, and others. Further, the structure of ternary alloys can influence oxidation properties, where grain boundaries in polycrystalline samples can provide fast diffusional pathways for oxygen or metal ions/atoms. Amorphous metal thin films (AMTFs) do not have grain boundaries and as a result can have both unique mechanical properties and chemical stability. AMTFs are typically structurally unstable at high temperatures, where they are found to crystallize. Recent studies have developed AMTFs with high thermal stability, including Ta<sub>54</sub>W<sub>27</sub>Si<sub>19</sub>. The present research is focused on the characterization of the chemical stability of Ta<sub>54</sub>W<sub>27</sub>Si<sub>19</sub>, a ternary AMTF, using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). AP-XPS allows the surface composition and oxidation states of the growing oxide layer to be measured in situ as the AMTFs are heated over a range of temperatures and O<sub>2</sub> partial pressures. Typical experiments were performed at 1 mbar O<sub>2</sub> partial pressure with temperatures ranging from 25 to 300° C. AP-XPS data was obtained with relatively short time intervals and the spectra were modeled using the Simulation of Electron Spectra for Surface Analysis (SESSA) software package. This analysis made it possible to determine the rate of oxide growth for the conditions studied, as well as the oxide film composition. Spectral analysis of the AP-XPS data indicated that Ta in Ta<sub>54</sub>W<sub>27</sub>Si<sub>19</sub> films was preferentially oxidized, thus forming primarily a tantalum pentoxide (Ta<sub>2</sub>O<sub>5</sub>) layer on the surface. Experiments were also performed on elemental Ta, W, and Si samples, and the results were compared to Ta<sub>54</sub>W<sub>27</sub>Si<sub>19</sub>. Analysis of the data indicated that the apparent activation energies for the formation of Ta<sub>2</sub>O<sub>5</sub> films on polycrystalline Ta and amorphous Ta<sub>54</sub>W<sub>27</sub>Si<sub>19</sub> films were very similar. However, we found that the oxidation of polycrystalline W and amorphous Ta<sub>54</sub>W<sub>27</sub>Si<sub>19</sub> films were distinctly different. We will discuss these results based on thermodynamic considerations and competitive reactions in the ternary alloys.

## Biomaterial Surfaces & Interfaces

### Room Naupaka Salon 4 - Session BI-TuM2

#### Novel Biomaterials

**Moderator: Michael Grunze**, Max Planck Institute for Medical Research

#### 10:20am BI-TuM2-8 Moving Towards Intracellular and Enzyme Catalyzed Molecule Synthesis with Mesoporous Materials, *Brian Trewyn*, Colorado School of Mines

As we think about advanced medicine and new biomolecule synthesis, we need to turn to cells and biological systems where drugs and precursors to new consumer goods can be synthesized. We are investigating mesoporous silica nanomaterials (MSN), functionalized with a series of catalytic active sites (inorganic and biological) that are physisorbed and covalently tethered to the pore surface and external surface of the MSN. Because catalytic active sites can be cytotoxic to viable cells, we are investigating pore properties that can be tuned and modified so single site, nanoparticle, and enzymatic catalytic sites can be active in the pores and not interfere with the health of the cell.

Our initial effort into this grand plan has been a tandem system initially using two independent metal nanoparticles to catalyze the oxidative esterification of allyl alcohol. Using separate gold nanoparticle (Au NP) and palladium nanoparticle (Pd NP) catalysts we studied the initial oxidation of the alcohol followed by ester formation to allyl acrylate. Our next generation tandem system finds us replacing the first step of the reaction (Pd NP catalyzed oxidation of allyl alcohol) with an enzyme, alcohol dehydrogenase and conducting the tandem reaction in aqueous buffer at ambient conditions. Future directions of including tethered organometallic catalysts in syntheses conducted in biological and biological simulated environments will be shared.

#### 10:40am BI-TuM2-9 QCM-D Characterization of Competitive Plasma Protein Adsorption on Low-Fouling Fluoropolymers for Thromboresistant Biomaterials, *Sherry Liu, B. Ratner*, University of Washington

Blood-contacting medical devices have classically suffered from endogenous protein fouling that initiate coagulation and inflammation pathways, often leading to fatal thromboembolic complications. The temporal turnover of adsorbed plasma proteins forms the basis for materials-induced thrombosis: human serum albumin (HSA), a platelet-inert and mobile protein, forms an initial passivating layer but is rapidly displaced by fibrinogen (Fg), which is surface-activated to mediate platelet recruitment and initiate fibrin clot formation. Herein, we employ quartz crystal microbalance with dissipation (QCM-D) to monitor competitive HSA:Fg adsorption on a selected panel of superhydrophobic low-fouling fluoropolymers (FPs): poly(vinylidene difluoride) (PVDF), poly(vinylidene difluoride)-co-poly(hexafluoropropylene) (PVDF-HFP), and our custom plasma-polymerized C<sub>3</sub>F<sub>6</sub> (ppC<sub>3</sub>F<sub>6</sub>). Across all FPs, ppC<sub>3</sub>F<sub>6</sub> demonstrates the greatest HSA:Fg adsorption affinity ratio. Comparing Sauerbrey vs. Voigt mass models, ppC<sub>3</sub>F<sub>6</sub> exhibits an uncharacteristic viscoelasticity for the HSA adlayer attributed to hydrophobic-induced reorganization and partial coupling of the hydration layer at the protein-bulk fluid interface. Additionally, binary protein exposure reduced the equilibrium areal mass ( $R_{max}$ ) compared to the pure Fg condition across all FPs, indicating that HSA competes with Fg for nonspecific binding spots and is retained on the surface at different equilibrium coverages for prolonged periods. Finally, longer HSA residence time on the surface reduces total Fg adsorption upon sequential exposure, suggesting that time-dependent denaturation and packing of HSA on a surface following adsorption increases resistance to Fg displacement. Ultimately, our observations for ppC<sub>3</sub>F<sub>6</sub> are attributed to its unique fluorochemistries and superhydrophobic properties created through the plasma polymerization process, while the hydration shells are subject to further study due to existing evidence that they deter cellular adhesion. With QCM-D-enabled characterization of protein adlayers, we hope to identify the optimal FP surface modifications that encourage favorable protein surface compositions and mitigate downstream thrombus formation.

#### 11:00am BI-TuM2-10 Hierarchical Surface Restructuring for Next Generation Implantable Neural Interfacing Applications, *Shahram Amini*, University of Connecticut, Pulse Technologies Inc.; *S. Shahbazmohamadi*, University of Connecticut

Selective and targeted stimulation of neurons in close proximity to implantable electrodes is an essential prerequisite for successful application of neural interfacing devices. Additionally, the trajectory for further refinement of neural interfacing devices is in large part predicated on increased miniaturization of electrodes that enables higher spatial

resolution, precision, and reliability. To achieve miniaturization, the geometric surface area of the electrodes must be reduced while the electrochemical surface area is increased. Therefore, availability of highly electroactive electrode materials or surfaces capable of improving the electrodes' electrochemical performance is paramount as it ensures delivery of enough charge across the electrode/tissue interface for stimulation as well as low impedance at the interface for sensing and recording purposes. In the past two decades, several surface treatment technologies e.g. coatings, thin films, nanomaterials, and also physical and electrochemical techniques have been vastly investigated. Despite varying degrees of improvement in electrochemical performance, most of these techniques are still facing several challenges and shortcomings, e.g. poor performance and durability, manufacturing, scalability and commercialization challenges. In this research, we introduce, for the first time, an innovative, tunable, scalable and commercially viable electrode surface treatment technology known as hierarchical surface restructuring targeted for use in next generation neural interfacing applications. In this work, we demonstrate how ultra-short pulse lasers are utilized to hierarchically restructure the surface of electrodes to create ultra-high-surface-area electrodes. In-vitro electrochemical studies such as cyclic voltammetry and electrochemical impedance spectroscopy were used to show unprecedented improvement in electrochemical performance of these electrodes compared to their untreated electrode counterparts.

#### 11:20am BI-TuM2-11 Blood Compatibility Assessment of Biomaterial Surface Chemistries to Reduce the Intrinsic Coagulation Pathway Activation, *Kyung-Hoon Kim, B. Ratner*, University of Washington

Implantable biomedical devices play critical roles for patients in need of sustainable treatment. However, surface thrombus formation is still a significant complication for blood-contacting surfaces, as it can cause lethal problems. Countless attempts have been made over the past decades to overcome this challenge. However, there is still no perfect blood compatible surface yet. One efficient approach to resolve this issue is to propose different strategies depending on the hemodynamic shear rates. A single mechanism does not govern the blood coagulation of high and low shear hemodynamic flow. The low shear condition is governed by an intrinsic pathway triggered by Factor XII adsorption and activation at the surface. On the other hand, high shear is dominantly affected by an extrinsic pathway initiated by platelet aggregation. We have investigated the blood compatibility regarding an intrinsic pathway by studying diverse biomaterial groups to understand better how each molecular event of clotting varies over different surface chemistries. Two promising categories of biomaterial surface have been tested based on two different hypotheses. The zwitterionic carboxybetaine surface is one of the popular blood-compatible surfaces due to its ultralow protein fouling properties. Fluoropolymer, a popular class of biomaterial used in vascular graft, is another historical surface for improved blood compatibility. The RFGD plasma polymerized hexafluoropropylene (ppC3F6) surface has demonstrated unique properties for preferential albumin tight binding since albumin is hypothesized as a benign protein to reduce the surface blood coagulation. The tight binding of albumin can reduce the factor XII adsorption, resulting in less activation of the intrinsic coagulation pathway.

The zwitterionic polymer outperformed all the surface groups tested, demonstrating low thrombin generation, extended clotting time, low factor XII adsorption, and low factor XIIa activity. Besides, ppC3F6 also demonstrated second-best performance in reducing the intrinsic pathway activation compared to commercial fluoropolymers and other medical polymers. We will further investigate the various ppC3F6 surfaces with varying fluorocarbon ratios, including the CF<sub>2</sub>:CF<sub>3</sub> portion, to discover the potential rules that can contribute to the mitigation of intrinsic pathway activation and improve the understanding of how fluorocarbon chemistry can affect the surface-blood interaction. The result of this study will offer varying strategies for reducing the factor XII-triggered surface thrombus formation, aiming to enhance the blood compatibility at the low shear hemodynamic flow condition.

#### 11:40am BI-TuM2-12 Innate Immune Response an Integral Part of Acorn Barnacle Surface Adhesion, *Kenan Fears, J. Schultzhaus*, US Naval Research Laboratory

Understanding the adhesion mechanisms of marine hard foulers (e.g., barnacles and tubeworms) is of critical importance to the global maritime community due to the pervasiveness of these organisms, coupled with the desire to transition away from toxic antifouling paints that have a deleterious ecological impact. Often, the biochemical processes that are crucial for the attachment and survival of hard foulers occur at buried

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interfaces, which further complicates analysis. We use confocal laser scanning microscopy protocols for imaging the adhesive interface of a model hard fouler, acorn barnacles (*Amphibalanus (=Balanus) amphitrite*), using multiple fluorescent probes to simultaneously label up to four different biochemistries. Time lapse imaging reveals cellular and extracellular processes related to cuticle development, biomineralization, and surface adhesion. More importantly, the presence of a lipidaceous secretion that phase-separates once it is exposed to seawater. This secretion oxidizes and detaches surface-adhered biofilms ahead of barnacle growth and cement deposition, and also facilitates the remodeling of the cement matrix to fill voids that may exist between the base of the barnacle and the underlying substrate. Enzymes present in this secretion generate hypochlorite ions (i.e., bleach) to oxidize organic matter at the adhesive interface and defend against microbial attack. Protein sequence analysis reveals that peroxidase enzymes found in cement collections are highly conserved across the barnacle tree of life, which includes stalked, calcareous-based, and membranous-based barnacles. However, we did not observe this surface-cleaning secretion in two membranous barnacles, *Chthamalus fragilis* and *Elminius modestus*, suggesting it is a more recent evolutionary trait.

## Charles S. Fadley Memorial Session

### Room Naupaka Salon 5-7 - Session CF-TuM1

#### Charles S. Fadley Memorial Session III: Hard X-ray Photoelectron Spectroscopy

**Moderators:** Gerd Schönhense, Johannes Gutenberg-Universität, Trevor Willey, Lawrence Livermore Laboratory

8:00am **CF-TuM1-1 Probing Quantum Materials Interfaces with HAXPES at the GALAXIES Beamline, SOLEIL Synchrotron, Jean-Pascal Rueff, Synchrotron SOLEIL, France** **INVITED**

We will review recent HAXPES results obtained at the GALAXIES beamline, SOLEIL Synchrotron [1] regarding interfacial properties of metal oxides specially when combined to standing waves. This approach started at GALAXIES in collaboration with C.S. Fadley in CCMO [2] and continues today in different systems including CMO / YCO superlattices [3]. The functionality of novel quantum materials derives from the competition between the internal degrees of freedom (electrons, spin, orbital, topology, spin-orbit coupling) most notably observed at interfaces. An intense research activity has been set off for fabricating and manipulating interfacial properties of quantum materials leading to a frenzy of scientific discoveries including 2DEG, interfacial superconductivity, etc. HAXPES appears as a major probe of electronic interfacial behavior due to its superior probing depth and sensitivity to the local atomic properties. Extension of this work to investigating materials properties in operando conditions or characterizing ultrafast charge dynamics as recently obtained in GeSe [4] will be discussed. These results will be put in the context of the 4<sup>th</sup> generation (DLSR) synchrotron sources with much reduced H source size which offer new possibilities for in-depth interfacial characterization.

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8:40am **CF-TuM1-3 Hard X-ray Photoemission Spectroscopy (HAXPES) at the Advanced Photon Source: A Legacy of Charles S. Fadley, Jeff Terry, Illinois Institute of Technology**

Over my career few scientists have helped me as much as Charles S. (Chuck) Fadley. He was always willing to provide advice, analysis code, and a pep talk when needed. Unfortunately, we were only able to put together one document out of all of our shared interests. This document, "**Study of Complex Materials and Nanostructures Using Hard X-ray Photoemission Spectroscopy**," has played an important role at the Advanced Photon Source (APS). The APS had no hard x-ray photoemission facilities dedicated to photoemission measurements prior to our writing this document. The APS now has 3 HAXPES instruments and one intermediate energy PES system of which 3 of are used primarily of photoemission, one is utilized more for detection of x-ray standing wave measurements. In this talk, I will

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highlight some of the measurements performed using HAXPES at the APS and discuss how Chuck's passion and dedication to the development of HAXPES within the US will continue to shape the future of photoemission for the foreseeable future.

9:00am **CF-TuM1-4 Bulk Sensitive PhotoElectron Spectroscopy on Metal Hydrides**, G. Panaccione, IOM- Consiglio Nazionale delle Ricerche (CNR), Italy; **Curran Kalha**, A. Regoutz, University College London, UK; L. Ratcliff, University of Bristol, UK; F. Offi, Università Roma III, Italy; C. Schlueter, A. Glaskovskii, DESY, Germany; J. Osterwalder, University of Zurich, Switzerland; G. Colombi, Technical University of Delft - TU Delft, Netherlands

Efficient hydrogen storage is a key process for energy, transport and electrochemistry technology and metal hydrides have demonstrated high capacity of reversible storage, tuneable diffusion rate, and thermodynamic stability [1]. In terms of electronic structure, the identification of the electronic character vs. thickness and the hybridization between hydrogen and the metal host are fundamental values to be known, and a number of Photoelectron Spectroscopy works captured many relevant characteristics of the metal-hydrides properties, such as i) the high reactivity of the surface and formation of more or less stable intrinsic oxides (influencing catalytic properties), and ii) the changes in the electronic character of the extended valence states upon formation of the hydrides (influencing the (semi)-metallic or semiconducting behaviour) [2-6]. Though, these results have been mainly obtained with a strong surface sensitivity in the VUV or soft X-ray region. As the hydrides are extremely reactive and their surfaces easily oxidize under ambient conditions, a precise determination of H-related features was difficult, leaving significant uncertainties in the understanding of hydrides both experimentally and theoretically

In this work, we exploit the bulk-sensitivity of Hard X-ray PhotoElectron Spectroscopy (HAXPES) to probe the electronic structure of metal-hydrogen states of two technologically relevant metal hydrides titanium (TiH<sub>x</sub>) and yttrium hydride (YH<sub>x</sub>). By means of energy dependent core level peak analysis we are able to disentangle the hydride, the main oxide and hydroxide spectral line shapes, and precisely determine their thicknesses and their chemical shifts (related to their valence oxidation number) (Fig.1). Analysis of valence band spectra and comparison with model calculations allow to attribute the metal-hydrogen states, as well as to identify the d vs sp contribution in the electronic states near the Fermi level, thus providing estimate of the charge-transfer between the metal and H, a value strongly affecting the conductivity of the system.

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9:20am **CF-TuM1-5 Synergies between Synchrotron and Lab-Based X-Ray Techniques for the Studies of Complex Materials and Interfaces, Alexander Gray, Temple University** **INVITED**

X-ray photoelectron spectroscopy, or photoemission, is a powerful and well-established experimental technique for probing the electronic structure and chemical composition of matter. Since the pioneering measurements in the 1950s, to the most recent angle-, spin-, and time-resolved studies, photoemission had and continues to have major impacts on condensed-matter physics in emerging fields, such as the studies of topological phenomena, strong electronic correlations, high-temperature superconductivity, and 2D materials. In this talk, I will describe several new directions in the field of photoemission that were pioneered by the Fadley Group, with a particular focus on the enhancement and control of the depth sensitivity and selectivity of the measurements through high-energy excitation and the use of standing waves. I will further discuss some of the latest studies that utilize hard x-ray and standing-wave photoemission in synergy with complementary synchrotron and lab-based x-ray spectroscopic and electron imaging techniques.



## 10:20am CF-TuM1-8 In Situ Observation of Electrochemical Lithiation and Delithiation in Silicon Electrodes in All-solid-state Battery Configuration, *Takuya Masuda*, National Institute for Materials Science, Japan

We have developed an in-situ/operando XPS apparatus equipped with a bias application system and investigated electrochemical lithiation/delithiation reactions of a silicon electrode in contact with a solid electrolyte in an all-solid-state battery configuration. Not only lithium silicides but also lithium oxides, lithium silicates and lithium carbonates are formed due to the lithiation of silicon and native oxide, followed by undesired side reactions with residual oxygen and carbon dioxide in the chamber. Lithium silicides reversibly respond to the successive lithiation/delithiation cycles. However, lithium oxides, lithium silicates and lithium carbonates are remained at the surface as irreversible species. The lithium silicide peak drastically shifts during the successive delithiation after preceding lithiation up to certain level. This is attributed to the phase transition of a crystalline lithium silicide to an amorphous phase. The effect of this phase transition on the cycle performance will be discussed on the basis of nanomechanical aspect.

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## 10:40am CF-TuM1-9 Structural Investigation of Ruthenium Silicide Si 2p Core Level Surface States Using X-Ray Photoelectron Diffraction, *Jonathan Denlinger*, Lawrence Berkeley National Laboratory

The Si 2p core-level photoemission spectra of  $\text{URu}_2\text{Si}_2$ , a heavy-fermion superconductor with a famous unexplained 'hidden'-order transition at 17.5K, provides a distinct signature of the (001) cleaved-surface termination, which is important for the interpretation of valence band electronic structure studies. The Si-terminated surface, in particular, exhibits multiple distinct Si 2p peaks shifted to lower binding energy than the bulk component. Density functional theory calculations of the core-level spectra predict an unexpected structural site assignment and energy ordering of the top surface dangling bond surface state relative to a sub-surface Si site. Structural investigation with these surface states is explored using photon- and angle-dependent measurements of the Si 2p x-ray photoelectron diffraction intensities in comparison to EDAC scattering simulations.

## Plasma Processing

### Room Naupaka Salon 4 - Session PS-TuM1

#### Plasma Modification of Surfaces and Materials

Moderator: *Morgan Hawker*, California State University, Fresno

## 8:20am PS-TuM1-2 Development of Novel High-Entropy-Alloy Powders and Their Plasma-Sprayed Coatings, *Shih-Hsun Chen*, National Taiwan University of Science and Technology, Taiwan

With our experience in the research and development of metal materials, we will continue to develop various multi-principal high-entropy alloy powder materials and establish their technical capabilities for additive manufacturing. The alloy powders prepared by gas atomization method can ideally present the characteristics of homogeneous high-entropy alloy through the rapid solidification process, and achieve the most suitable process technology for high-entropy alloy products. Combined with the selected additive manufacturing technologies, including plasma spraying and selective laser melting processes, it hopes to implement the application and promotion of high-entropy alloys. The above-mentioned two processes are common and important process technologies in the industry. Although material research continues to innovate, there are not many researchers engaged in the development of thermal spray process technology. In addition, metal 3D printing technology is sprouting and looking for key applications in the current industry. Therefore, this project

will rely the established high-entropy alloy powder manufacturing technology, and the development experience of thermal spraying process, focusing on the development of new high-performance  $\text{AlCrFeNiSi+Y}$  high-entropy alloy powder products and their applications via additive manufacturing technology. Starting from the high-entropy stainless steel alloy ( $\text{AlCrFeNi}$ ), the new elements (silicon and yttrium) are going to be added to improve the quality of the material. It is expected to be developed and built to be suitable for high-temperature environments, with oxidation, corrosion and abrasion resistance. The goal is to develop industrially applicable products and promote them to the industry.

## 8:40am PS-TuM1-3 Surface Fenicral Medium-Entropy-Alloy Coating to Enhance High-Temperature Air-Oxidation Resistance of a Plain Carbon Steel, *W. Kai, I. Yang*, National Taiwan Ocean University, Taiwan; *C. Chu*, National Taiwan Ocean University, Taiwan; *S. Chen*, National Taiwan University of Science and Technology, Taiwan; *J. Kai*, City University of Hong Kong

The effect of thermal spraying  $\text{FeNiCrAl}$  coating (~150 micron thick) on a low carbon steel to enhance oxidation resistance was investigated at 700–900 °C in dry air. The oxidation kinetics of both the steel with and without coating followed the parabolic-rate law, and the oxidation rate constants ( $k_p$  values) steadily increased with increasing temperature. It was found that the  $k_p$  values of the coating alloy were at least 3 orders of magnitude lower than those of the uncoated carbon steel. The scales formed on the carbon steel consisted of iron oxides ( $\text{FeO/Fe}_3\text{O}_4$ ), while an exclusive layer  $\alpha\text{-Al}_2\text{O}_3$  formed on the coating alloy. The formation of slow-growing  $\alpha\text{-Al}_2\text{O}_3$  is responsible for the significant reduction of oxidation rates for the coating alloy.

## 9:00am PS-TuM1-4 Synthesis of Carbon-Based Thin Films by PECVD and Their Nanostructure Control, *Shinsuke Mori, F. Bohlooli, N. Nedjad, A. ANAGRI*, Tokyo Institute of Technology, Japan

In this study, catalyst-free growth of carbon nanomaterials was performed by plasma-enhanced chemical vapor deposition using CO as a carbon source gas. Microwave discharge system was utilized for this study. The pressure of the discharge was between 20 to 250 Pa and the input power was between 60 to 120 W. The effect of CO: H<sub>2</sub> and CO: O<sub>2</sub> ratio on the morphology of carbon films is investigated. In the microwave discharge system, without an addition of hydrogen, vertically aligned CNFs were synthesized. At lower H<sub>2</sub>: CO ratio carbon nanowalls were synthesized, while polycrystalline diamond films were deposited with much higher H<sub>2</sub>: CO ratio. We have also synthesized carbon nanowalls from CH<sub>4</sub> and CO<sub>2</sub> gas mixtures and compared their structure, crystallinity, and growth rate with those synthesized by CO and H<sub>2</sub> gas mixtures. The optical emission spectroscopy of the CO/H<sub>2</sub> and CH<sub>4</sub>/CO<sub>2</sub> plasma was performed to discuss the reaction mechanism. Scanning electron microscopes and transmission electron microscopes were utilized to examine their nanostructures. Raman spectroscopy and X-ray photoelectron spectroscopy were performed to analyze crystallinity, chemical composition and the bonding state of the film. We have also investigated the effect of electric field on the structure of carbon nanomaterials and the well-parallelized carbon nanowalls were successfully synthesized by the addition of strong electric field near the substrate. The possible mechanism for their growth and control of the nanostructure of carbon nanomaterials is discussed.

## 9:20am PS-TuM1-5 Tunable Photoluminescence from Carbon-Based Nanostructures, *Frank Güell*, Universitat de Barcelona, Spain

Carbon nanostructures such as graphene nanowalls (GNWs) or vertically aligned carbon nanotubes (VACNTs) show an intense and very broad emission band in the visible range from 350 to 850 nm, which also exhibits a tunable luminescence from 450 to 600 nm. The origin of these visible contributions change as a function of the growth conditions and the nanostructures obtained. GNWs were grown by inductively coupled plasma chemical vapor deposition (ICP-CVD) at low-pressure into a tubular reactor under pure methane. VACNTs were obtained by plasma-enhanced CVD (PECVD) and water-assisted CVD. Incorporation of oxygen and nitrogen functional groups by oxygen-plasma, water-plasma and nitrogen-plasma changes the photoluminescence properties of the carbon nanostructures. The understanding of these processes provides additional criteria for designing nanomaterials based on carbon, which is environmentally friendly for optoelectronics applications.

# Tuesday Morning, December 13, 2022

9:40am **PS-TuM1-6 Cold Plasma and Artificial Intelligence Synergistic Effects on Future Domestic Food Security: A Prospective Study**, *M. Bakhshi*, Department of Cellular and Molecular Biology, Faculty of Advanced Science and Technology, Tehran Medical Sciences, Islamic Azad University, Iran (Islamic Republic of); *F. Ostovarpour*, **Mohammad Sadegh Abbassi Shanbehbazari**, Laser and Plasma Research Institute (LAPRI), Shahid Beheshti University, Iran (Islamic Republic of); *A. Bakhshi*, School of Physics, Institute for Research in Fundamental Sciences (IPM), Iran (Islamic Republic of)

Plant diseases affect the yield and appearance of plants which can be detected using machine learning. Image processing techniques and computer vision can detect the differentiated spots on leaves, stems, petals and roots. In this research, we try to suggest the artificial neural networks (ANNs) as a promising feedback of plant diseases to control atmospheric cold plasma activated water (PAW). Carefully introducing the reactive species can treat the plants and seeds which result enhanced features like the disease/stress resistance, metabolism boosting, surface modifications and growth enhancements. Induction of plant's immune system and inactivation of pathogens is possible with PAW as a green method and the amount of reactive species/treatment time can be controlled by ANNs. Thus, the severity and type of diseases can determine cold plasma parameters which leads us to an automated and smart agriculture for domestic/personal food security enhancing. Combining the PAW part, plant pot and ANNs satisfies primary needs of plant care from germination state. Furthermore, amount of nitrogen fixation in soil-based agriculture can be adjusted using a database or simultaneous monitoring of the plant. In soilless agriculture like hydroponics and aeroponics, using the assembled device has emerging applications in space colonization and saving the species.

## Biomaterial Surfaces & Interfaces

### Room Naupaka Salon 1-3 - Session BI-TuP

#### Biomaterial Interfaces Poster Session

**BI-TuP-1 Cell-Mimetic Biosensors for Detecting Avian Influenza Virus Through the Viral-Fusion Mechanism, Jong-Woo Lim**, College of Veterinary Medicine, Research Institute for Veterinary Science, Seoul National University, Republic of Korea; *G. Park, C. Park*, Department of Chemical and Biomolecular Engineering, Yonsei University, Republic of Korea; *M. Yeom*, College of Veterinary Medicine, Research Institute for Veterinary Science, Seoul National University, Republic of Korea; *S. Lee*, Department of Chemical and Biomolecular Engineering, Yonsei University, Republic of Korea; *K. Lyoo*, College of Veterinary Medicine, Jeonbuk National University, Republic of Korea; *S. Haam*, Department of Chemical and Biomolecular Engineering, Yonsei University, Republic of Korea; *D. Song*, College of Veterinary Medicine, Research Institute for Veterinary Science, Seoul National University, Republic of Korea

Avian influenza virus (AIV) is a major respiratory disease of poultry, especially High pathogenic AIV (HPAIV) presents high morbidity and mortality. To control the spread of HPAIV, it is very important to detect HPAIV at the early stages for taking timely countermeasures such as quarantine and isolation. In this study, we developed cell mimicking nanoparticles (CMPs) for rapid detection of HPAIV as well as low pathogenic AIV (LPAIV) via a viral fusion mechanism. CMPs were polymeric nanoparticles constructed with sialic acid and FRET dye pairs, exposing FRET off signal responding to membrane fusion with AIV activated by enzymatic cleavage at endosomal condition. CMPs exhibited highly sensitive detection of various types of LPAIVs and HPAIVs in the biological environment. The developed detection system utilizing the viral infection pathway can be a potent diagnostic assay for LPAIV and HPAIV, contributing to minimizing the economic loss of the viral outbreaks.

**BI-TuP-2 Using Cinnamaldehyde Plasma Treatment to Develop an Antioxidant Coating, Ashley N. Keobounnam, M. Hawker**, California State University, Fresno

When a burn injury occurs, the heat damage caused by said burn increases the permeability of the microvasculature. This increased permeability leads to the leakage of plasma into the interstitial spaces of cells, which can lead to hypovolemic shock. One approach to reduce the likelihood of hypovolemic shock is to reduce microvascular permeability. Oxidants are an agonist that increase post-burn permeability through increasing the concentration of reactive oxygen species, ultimately leading to oxidative stress. Microvascular permeability remains in an increased state so long as the rate of reactive oxygen species generation is greater than the body's rate of detoxifying. One strategy to inhibit the effects of oxidative stress is to introduce antioxidants directly to the burn site. Current studies regarding burn wounds focus on the healing process after the initial injury. However, methods to stabilize the patient before significant plasma leakage occurs remain relatively unexplored.

This work focused on developing a burn wound patch with an antioxidant coating towards the goal of reducing microvascular permeability. We opted to use a plasma enhanced chemical vapor deposition (PECVD) strategy to deposit an antioxidant coating on a model polymer substrate (chitosan). Specifically, we utilized cinnamaldehyde - an organic compound with antioxidant activity - as a plasma precursor. Chitosan substrates were modified using optimized plasma parameters, where both pulsing and continuous plasma power conditions were explored. In previous studies, continuous PECVD films exhibited limited monomer functional group retention, whereas pulsed PECVD films exhibited greater monomer functional group retention. Antioxidant activity relies heavily on chemical structure, therefore, we explored how plasma power conditions (continuous vs pulsed) impact antioxidant effectiveness. Surface wettability was analyzed using water contact angle goniometry. X-ray photoelectron spectroscopy was used to characterize surface chemistry. Additionally, radical scavenging activity of PECVD treated materials was evaluated using a 2,2-diphenyl-1-picrylhydrazyl assay. Overall, this work opens new directions for antioxidant therapy in burns.

**BI-TuP-3 Modifying Commercially-Available Wound Dressing Materials with Continuous and Pulsed 1,8-Cineole Plasma, Mia Rose Kayaian, M. Hawker**, California State University, Fresno

Hospital-acquired infections (HAIs) are one of the primary causes of death. According to Medicare data, HAIs are estimated to cost the United States anywhere from 28.1 to 96.8 billion dollars yearly. Most HAIs begin with bacterial attachment to the wound. If left untreated, the infection site

can become a chronic wound. The clinical standard for existing chronic wounds are oral and topical antibiotics, but this can quickly become problematic due to the possible development of antibiotic resistance. As an alternative, designing a wound dressing to actively kill bacteria on contact would be optimal for chronic wound treatment. Plasma-enhanced chemical vapor deposition (PECVD) using 1,8-cineole as the plasma feed gas has been shown to actively kill bacteria on glass slide surfaces. Yet, 1,8-cineole-based PECVD strategies have not been extended to wound dressing materials.

The goal of the present study is to use 1,8-cineole PECVD to modify commercially-available wound dressing materials: hydrofibers and hydro polymers. Our strategy was to deposit a film with antibacterial properties using plasma treatment. By adjusting plasma parameters, it is possible to control the coating chemistry. However, no attempt has been made to compare pulsing vs. continuous-wave deposition. In other PECVD systems, pulsing has enabled the plasma precursor's functional groups to be maintained within the coating. Since the functional groups give 1,8-cineole its antibacterial properties, we anticipated that pulsing would enable the functional groups to be maintained upon PECVD. This study utilized 20 W peak power and a 20 minute application time for both continuous and pulsed deposition. The pulsed deposition used 10%, 25%, and 50% duty cycles. Water contact angle goniometry was used to evaluate changes in surface wettability of the material before and after plasma treatment. Additionally, x-ray photoelectron spectroscopy was used to quantify the elemental composition of plasma-treated and control surfaces. Zone of inhibition testing was performed to evaluate antibacterial properties against both gram-positive and gram-negative bacteria. Overall, 1,8-cineole PECVD strategies were effectively applied to wound dressing materials. This work represents progress towards addressing the need to directly target chronic wound infectious sites.

**BI-TuP-4 Fractional Analysis Process of Surface-Adsorbed Proteins Using Sds-Page, Naofumi Ohtsu**, Kitami Institute of Technology, Japan

When a biomaterial is implanted in a human body, an immediate event occurring on its surface is competitive adsorption of proteins. Such surface adsorbed proteins predominate cell attachment, proliferation, and differentiation that relate with material's biocompatibility. On the other hand, tissue fluids comprise many protein species, of which electrostatic properties are different by their structure. Compositions of the adsorbed proteins thus depend on the material's surface property. Fractional analysis of surface-adsorbed protein would thus provide significant clue for understanding the tissue-material interfacial reaction. However, separation of the surface-adsorbed proteins is difficult task; conversely, the proteins dissolved in a solution is capable to be separated by an electrophoresis, easily. Based on these, in the present study, we attempted to perform the fractional analysis of surface-adsorbed proteins through the extraction into a solution and subsequent separation by electrophoresis.

A prescribe amounts of bovine serum albumin (BSA) and lysozyme (LSZ) as model proteins were dissolved into a phosphate buffered saline (PBS) solution. Initially, a titanium (Ti) plate widely used for medical implants was immersed into the protein-contained PBS solution for 60 min at 310 K, aiming to adsorb BSA and LSZ on its surface. Next, the proteins adsorbed on the surface was extracted into a distilled water or a sodium dodecyl sulfate (SDS) solution of various concentrations. The extraction was conducted by immersing the Ti substrate into such solutions filled in a glass beaker, along with an ultrasonication for 10 min. Thereafter, the extracted proteins were separated by polyacrylamide gel electrophoresis (PAGE). Concentration of each separated protein was determined from the corresponding band intensity in PAGE gel.

When using a distilled water as the extraction solution, the proteins could not be detected in PAGE gel because almost proteins were re-adsorbed onto an inner-wall of glass beaker. Such re-adsorption was prevented when using the SDS solution exceeding 0.5 %, and actually, over 85% of adsorbed protein could be extracted. Additionally, when measuring the band intensity in the gel, we could confirm the linear correlations between the concentrations and the band intensity, in the range from 0.5 to 5 µg·mL. Based on these, we conducted fractional determination of surface-adsorbed BSA and LSZ though the analysis process above. The results demonstrated that the ratio of adsorbed BSA and LSZ was varied with the mixture ratio of these proteins, evidencing the validity of the suggested fractional analytical process.

**BI-TuP-5 Advanced Surface Analysis of Porous Bioactive Polymer Coatings on a TiAl6V4 Substrate Prepared by Supercritical Foaming for Orthopedic Applications, Katja Andrina Kravanja, M. Finšgar, Ž. Knez, M. Marevci Knez, University of Maribor, Slovenia**

Ti-based alloys are increasingly used as medical implants due to the combination of excellent biocompatibility, high strength, and corrosion resistance. However, their biological inertness and persistent postoperative complications such as inflammation and infection necessitate the development of bioactive coatings for orthopedic implants that enable localized, controlled release of active ingredients (AIs) at the implant site for improved osteointegration [1]. Formulation of AIs with supercritical fluids is one of the leading and well-established strategies to produce high-quality products by incorporating environmentally friendly and economically feasible properties. Supercritical (SC) foaming yields porous polymer matrices with a large specific surface area, allowing encapsulation and tailored release of AIs [2, 3].

This work aimed to develop and characterize porous bioactive coatings on TiAl6V4 surface made of biodegradable and biocompatible polymers using SC foaming technique to achieve controlled release of model synthetic and natural AIs with anti-inflammatory and antibiotic properties. The chemical structure, interactions, and morphology of the bare and coated substrates were characterized by advanced surface analysis, particularly tandem time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and 3D profilometry. Chemical information about the surface of multicomponent coatings was evaluated by determining molecular-specific signals for the coating components. The in-depth molecular distribution was determined by gas cluster ion beam (GCIB) 3D imaging by ToF-SIMS. In addition, the elemental composition, elemental environment, and depth profiling using GCIB for effective sputtering were acquired by XPS measurements. The topography of the newly prepared coatings and the agglomeration of the AIs were determined by AFM, while the large-scale study of the coatings and substrate roughness is presented by 3D profilometry. The results demonstrate that the fabricated coatings provide a good foundation for future pharmacokinetic and cellular research.

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**BI-TuP-6 PEG-b-PLA-NHS based Self Assembled Vaccine Platform as an Adjuvant-free Influenza Virus Vaccine, Jaehyun Hwang, Chonnam National University, Republic of Korea; G. Park, Yonsei University, Republic of Korea; J. Lim, Seoul National University, Republic of Korea; E. Ga, S. Moon, Chonnam National University, Republic of Korea; C. Park, Yonsei University, Republic of Korea; H. Kim, Kangwon National University, Republic of Korea; D. Song, Seoul National University, Republic of Korea; S. Haam, Yonsei University, Republic of Korea; W. Na, Chonnam National University, Republic of Korea**

Vaccines have been considered most effective tool to defend against viruses that can cause disease. However, some current vaccines are still suboptimal due to obstacles such as a risk of side effect and low immunogenicity. In the present work, we developed a self-assembled vaccine (SAV) platform based on antigen conjugated with an amphiphilic block copolymer, mPEG-b-PLA-NHS. To improve immunity of subunit vaccine, SAV was designed to display repetitive antigens in nanoscale for eliciting efficient antigen delivery and immune cell activation via multivalent recognition. SAV showed enhanced cellular uptake by dendritic cells (DCs), accelerating an efficient initiation of the adaptive immune system. SAV also showed high level of induction of IgG through *in vivo* analysis. These results implicate that SAV facilitate both efficient B cell activation and efficient T cell mediated immune response. In animal models, we confirmed that SAV comprising of hemagglutinin (HA) efficiently protected mice from mortality following challenge with influenza A virus. These findings suggest that the self-assembled nanosystem composed of antigen-polymer conjugate can be a potent vaccine platform with effectiveness and versatility.

**BI-TuP-7 Polymersome Based Co-Delivery System of Antigen and Immunostimulant for Improvement of Humoral Immune Response, Eulhae Ga, Chonnam National University, Republic of Korea; J. Lim, Seoul National University, Republic of Korea; J. Hwang, S. Moon, Chonnam National University, Republic of Korea; M. Yeom, D. Song, Seoul National University, Republic of Korea; W. Na, Chonnam National University, Republic of Korea**

Cellular uptake of antigen (Ag) by antigen-presenting cells (APCs) is vital for effective functioning of the immune system. Intramuscular or subcutaneous administration of vaccine Ag alone is not sufficient to elicit optimal immune responses. Thus, adjuvants are required to induce strong immunogenicity. Here, we developed nanoparticulate adjuvants that assemble into a bilayer spherical polymersome (PSome) to promote the cellular uptake of Ag into APCs. PSomes were synthesized by biodegradable and biocompatible block copolymer methoxy-poly(ethylene glycol)-b-poly(D,L-lactide) to encapsulate both hydrophilic and lipophilic biomacromolecules, such as ovalbumin (OVA) as a model Ag and monophosphoryl lipid A (MPLA) as an immunostimulant. After co-encapsulation of OVA and MPLA, the PSome synthetic vehicle exhibited the sustained release of OVA in cell environments and allowed efficient delivery of cargos into APCs. The administration of PSomes loaded with OVA and MPLA induced the production of interleukin-6 and tumor necrosis factor- $\alpha$  cytokines by macrophage activation *in vitro* and elicited effective Ag-specific antibody responses *in vivo*. These findings indicate that the nano-sized PSome may serve as a potent adjuvant for vaccine delivery systems to modulate enhanced immune responses.

**BI-TuP-8 Rapid and Effective Intradermal Application of Canine Influenza Vaccine Without Removal of Hair Using Patchless Insertion-Responsive Microneedle (Irmn) and Its *in Vivo* Efficacy Evaluation, Suyun Moon, E. Ga, J. Hwang, Chonnam National University, Republic of Korea; A. Kang, QuadMedicine R&D Centre, QuadMedicin, Republic of Korea; S. Baek, QuadMedicine R&D Centre, QuadMedicine, Inc., Republic of Korea; H. Jun, QuadMedicine R&D Centre, QuadMedicine, Inc., Seongnam, Republic of Korea; S. Choi, QuadMedicine R&D Centre, QuadMedicine, Inc., Republic of Korea; J. Lim, M. Yeom, Seoul National University, Republic of Korea; J. Park, Gachon University, Republic of Korea; H. Kim, Kangwon National University, Republic of Korea; D. Song, Seoul National University, Republic of Korea; W. Na, Chonnam National University, Republic of Korea**

Novel tip-separable microneedle system called Insertion-responsive microneedles (IRMNs) is painless application system, compensating the existing disadvantages of conventional vaccine administration such as intramuscular vaccination. IRMNs are composed of dissolvable hyaluronic acid (HA) tips and biocompatible polycaprolactone (PCL) bases, which is immediately isolated right after needle insertion and retraction. In this study, we conducted several *in vivo* and *ex vivo* tests to prove stability, safety and efficacy of IRMNs. *Ex vivo* porcine skin injection tests confirmed IRMNs penetrates skin and successfully releases coated components with no damage on skin tissues. Immunization in Guinea pigs using IRMNs induced two times higher hemagglutination inhibition (HI) antibodies compared to intramuscular injection groups, and complete elimination of viral shedding was found at 8 days post infection challenged with influenza A/canine/Korea/O1/2007 (H3N2) wild-type virus after second vaccination. Similar result has been shown in the H3N2 vaccine inoculation into dog's ears compared with intramuscular injection group. Tips of IRMN were well separated from the base, successfully delivering vaccine materials into dog's hairy skin without pain. The veterinarian assed behavior of dog during injection and compared entire response of IRMN group with intramuscular administration. Dogs treated with IRMs appeared to be more comfortable and painless compared to syringe injection group. IRMNs are potential candidate of rapid and convenient vaccination, which will be particularly useful and attractive in veterinary research fields using animal vaccination.

**BI-TuP-9 Probing Bacterial Membrane Composition in the Study of Antibacterial Resistance using GCIB-SIMS, John Fletcher, University of Gothenburg, Sweden**

The spread of antibiotic resistance is an increasingly difficult problem to deal with as more bacterial infections survive treatments with commercial antibiotics. One of the main routes for the spreading of resistance among bacterial population is horizontal gene transfer, mainly through conjugation where mobile genetic elements are transferred from a donor cell to a recipient cell through a conjugative pilus.

One way to deal with the increasing levels of antibiotic resistance in bacteria is to develop new antibiotics for which resistance has not yet

emerged, which can be both laborious and not always a lucrative market. An alternative is to inhibit the conjugation itself so that the rate at which new resistance genes spread between populations is reduced and the usefulness of existing and new antibiotics is extended.

A previous study, performed at the University of Gothenburg, used a high-throughput screen to identify chromosomal *Escherichia coli* genes in the donor cells that were important for conjugation of the F-plasmid and could be potential targets to reduce conjugation. Among these hits were several genes that are involved in the cell envelope through stress response pathways, biogenesis, outer membrane protein assembly and homeostasis, which formed an interest into the role and importance of the cell envelope for conjugation.

Here, recent findings on the influence of different mutations and conditions on the highlighted mutants detected by secondary ion mass spectrometry (SIMS) using a gas cluster ion beam (GCIB) are presented.

## **BI-TuP-10 Soft, Precision Engineered Porous, Hydrogel Scaffolds Mechanically Tailored towards Applications in the Central Nervous System, Ningjing Chen, B. Ratner, University of Washington**

Largely incurable diseases and traumatic injuries to the central nervous system (CNS) demand the development of new biomaterials to improve healing and treatment options. Matching material mechanical properties to the CNS tissue and optimizing material porous structures are two central goals for improving better biomaterials for the CNS. However, biomaterials with both precision-controlled porous structure and brain-matched mechanical properties are still lacking. In this study, we developed a copolymeric hydrogel of 2-hydroxyethylmethacrylate and glycerol monomethacrylate (pHEMA-co-GMA) with mechanical properties tunable into the range of CNS tissues, and a uniform 40  $\mu\text{m}$  porous structure. The two characteristics were achieved by a new fabrication process combining phase separation and sphere templating. We used scanning electron microscopy (SEM) to image their morphology and an Instron mechanical testing apparatus to examine their compressive Young's Moduli. The resulting scaffolds are non-cytotoxic and endotoxin-free according to the ISO 10993-5 standard and commercialized endotoxin testing kit. In addition, 3D culture of microglial cells within the scaffolds demonstrates cell attachment and maintenance of a rounded, quiescent morphology, potentially due to spatial confinement. These results support further *in vivo* studies and suggest broad potentials in CNS applications, such as brain-computer interfaces, neural regeneration, and basic neurobiology.

## **BI-TuP-11 Zwitterionic Copolymer for the Bio-Compatible Coating on Medical Devices to Prevent Protein Fouling and Complement System Activation, Kan Wu, B. Ratner, University of Washington**

In the past decades, the demand for biocompatibility is increasing with the rapid development of advanced medical technologies, such as biosensors, implantable chips, and hemodialysis apparatus. Among all the biocompatible materials, zwitterionic carboxybetaine (CB) distinguishes itself for its superior hydration capability and stability as well as its potential for further functionalization. However, a reliable yet easy method to introduce the CB material onto the target surfaces is still challenging.

We developed a series of PCB-DOPA conjugates with different architectures of combining polycarboxybetaine (PCB) and mussel-inspired binding groups (DOPA) groups and investigated the structural effect on their coating performance. We found that a molecule with a linear PCB chain and quadruple DOPA groups at the chain end (PCB-4DOPA) can significantly increase the coating coverage and stability. Next, we applied the PCB-4DOPA conjugate on blood-contacting devices (hemodialysis membrane, catheters, respiratory devices, etc) to test the performance of this method in the real application. We demonstrated that the PCB-DOPA conjugate can form a protective coating on the device surfaces and significantly reduce the fibrinogen attachment and complement system activation. The complement proteins C5b9 generated by PCB interface is only 1.96  $\mu\text{g}/\text{ml}$ , compared to 12.16  $\mu\text{g}/\text{ml}$  generated by poly(poly(ethylene glycol)methacrylate)(PEGMA) at the same incubation condition. In addition, we also propose a new standard method to detect the complement reaction activation level in the blood samples for most prevailing biomaterials. This new detection method optimized the current measuring techniques and achieved a more accurate measurement.

## **BI-TuP-12 Enhanced Antithrombogenicity of 3D Templated Artificial Vascular Grafts Through Heparin Complex Conjugated with PEG Spacer, ChaeHwa Kim, Advanced Textile R&D Department, Korea Institute of Industrial Technology, Republic of Korea; J. Kim, Material & Component Convergence R&D Department, Korea Institute of Industrial Technology, Republic of Korea; J. Lee, T. Kim, Advanced Textile R&D Department, Korea Institute of Industrial Technology, Republic of Korea**

Artificial vascular grafts to replace blood vessels are necessary in cases where irreparable damage to blood vessels occurs due to circumstances such as disasters or accidents. Furthermore, blood compatibility is also vital in the transplantation of artificial blood vessels. In this study, we designed the vascular graft with 3D printing techniques and developed heparin derivatives that have better adherence to the surface and avoid thrombosis. Heparin complex conjugated with PEG spacer was synthesized and coated on the artificial vascular graft fabricated by 3D templated printing technology. We fabricated the 3D-printed polyvinyl alcohol (PVA) templates according to the blood vessel size and shape, and these were dip-coated with salt-suspended thermoplastic polyurethane (TPU). The core template was removed to obtain a customized porous TPU graft. Next, the dopamine-PEG-heparin conjugate was prepared through NHS/EDC coupling reaction. PEG spacers were also introduced to increase the heparin surface arrangement and inhibit blood component adherence. PEGs having various molecular weights were conjugated to heparin to investigate antithrombotic properties according to the length of the PEG linker. Using an NHS/EDC coupling procedure, a heparin-PEG-dopamine complex was generated and subsequently coated onto TPU vascular grafts for robust immobilization. Then, heparin release studies, blood coagulation, and platelet adsorption tests were performed. The use of a PEG linker improved the coating stability, which lowered the release rate of heparin and reduced platelet adhesion. In addition, the longer the molecular weight of the PEG linker, the stronger the antithrombotic effect. The results demonstrated that heparin-PEG-dopamine can substantially enhance the coating strength and anticoagulant properties of porous TPU vascular grafts.

## **BI-TuP-13 Impact of Amino Acid Conformation on the Efficacy of Antimicrobial Cyclic Peptides Against Medically- and Industrially-Relevant Microbes, Q. Lu, D. Regan, D. Barlow, Kenan Fears, US Naval Research Laboratory**

Microbial growth on surfaces, if unmitigated, poses health concerns and can accelerate the biodegradation of engineered materials and coatings. Cyclic peptides have emerged as a promising class of agents to combat biofouling. Cyclic peptides are more resistant to enzymatic degradation than their linear counterparts and can be designed to interact with extracellular targets, intracellular targets, and/or self-assemble into transmembrane pores. Here, we compare the antimicrobial efficacy of two pore-forming cyclic peptides,  $\alpha\text{-K}_3\text{W}_3$  and  $\beta\text{-K}_3\text{W}_3$ , against bacterial and fungal liquid cultures, and fungal biofilms. These two peptides display an identical series of side-chain chemistries, but the additional methylene group in the peptide backbone of  $\beta$ -amino acids results in two structural differences: 1)  $\beta\text{-K}_3\text{W}_3$  has a larger pore diameter, and 2) all backbone carbonyl (C=O) groups point in the same direction, with all amide (N-H) pointing in the opposite direction, leading to an enhancement in the dipole moment that drives self-assembly. In liquid cultures,  $\beta\text{-K}_3\text{W}_3$  was more efficient at reducing the number of colony forming units (CFU) when exposed to a gram-positive bacterium, *S. aureus*, and two fungal strains, *N. albida* and *P. laurentii*. To evaluate efficacy against fungal biofilms, cyclic peptides were incorporated into surface coatings of Irogran<sup>®</sup>, a polyester-based thermoplastic polyurethane. We detected no survival of *N. albida* and *P. laurentii* microcolonies ( $10^5$  per inoculation) on coatings containing either peptide a 7-day exposure. To determine if antimicrobial activity persists upon repeated exposure, we reinoculated coatings with *P. laurentii* live cells every 7 days for 4 weeks and detected no CFU after 14 and 21 days. In direct comparison, the number of CFU from Irogran<sup>®</sup> coatings without cyclic peptides was  $> 5 \log$  CFU.

## Plasma Processing

### Room Naupaka Salon 1-3 - Session PS-TuP

#### Plasma Processing Poster Session

##### PS-TuP-1 Flexible Atmospheric Pressure Plasma Jet Device with Built-in Electrodes for Operation in Wet Environments, *Jae Young Kim, G. Bae, E. Jung, H. Tae*, Kyungpook National University, Republic of Korea

The AP-plasma jet (APPJ) device, which can realize nonthermal AP-plasma with a simple configuration of an electrode and a conduit, ignites the discharge gas flowing through the conduit by a powered electrode, and delivers the plasma plume to the outside of the conduit. In order to effectively utilize the APPJ for material processing, various efforts have been tried to transfer the plasma and its by-products as close to the target as possible. For this purpose, there are several reports of fabricating APPJ devices using flexible conduits such as plastic tubes instead of glass or ceramic conduits [1,2].

In this study, we describe a new flexible atmospheric pressure plasma jet (APPJ) device made of hollow-core optical fibers and introduce two potential applications: endoscopic plasma treatment and de-composition of aqueous phosphorus compounds. A long and highly flexible micro-plasma jet device made of three hollow-core optical fibers has been proposed for use in humid environment. In spite of a small inner diameter and a low gas flow rate of the APPJ device, the generated plasma plume is stable and capable of treating small target materials. In the proposed APPJ device, the wire electrode is completely isolated inside the hollow inside of the optical fiber, so there is no contact with the environment at the end of the device from which the plasma plume is emitted. This feature allows the device to operate both safely and reliably in humid environment or even under water.

The proposed long flexible APPJ device is ideal for endoscopic surgery due to the plasma characteristics and stability in environments with significant amounts of moisture. The exceptional flexibility and length of the device will enable it to reach diverse areas inside the human body with a biopsy channel of endoscopes. This work enables directed therapeutic methods based on a flexible APPJ device and presents AP-plasma endoscopy as a new physical therapeutic method. As another potential application, we also demonstrate that the proposed APPJ device can be used to decompose phosphorus compounds in water into their phosphate form. The preliminary works on the decomposition of phosphorus compounds show that the decomposition method by in-liquid plasma can be directly used as a promising pretreatment process for the ascorbic acid method to determine total phosphorus in fresh water.

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##### PS-TuP-2 Enhanced Hydrogen Production from the Cracking of Waste Hydrocarbons Using Liquid-Phase Plasma, *Kyong-Hwan Chung*, Suncheon National University, Republic of Korea; *S. Ki*, Gyeongsang National University, Republic of Korea; *J. Yun*, Jeonnam Bioindustry Foundation, Republic of Korea; *S. Jung*, Suncheon National University, Republic of Korea

Hydrogen is firmly recognized as a future clean energy that will replace fossil fuels and solve environmental pollution. However, most of the H<sub>2</sub> production still depends on steam reforming using fossil fuels or natural gas. In order to realize a future H<sub>2</sub> energy society, it is necessary to develop a technology that can produce a large amount of H<sub>2</sub> using renewable energy. CO<sub>2</sub>-free H<sub>2</sub> production is essential for this technology. This study was conducted the cracking of waste hydrocarbons. Plasma was directly discharged to liquid reactant. Synthesized perovskites and metal oxide

were introduced as catalysts. The correlation between the reaction results according to the characteristics of the catalyst was investigated.

Catalytic properties of perovskites were proposed in the decomposition of waste hydrocarbons using liquid-phase plasma (LPP) for H<sub>2</sub> production. Perovskite-type catalysts and metal oxide catalysts were applied to the cracking reaction. Hydrogen was generated by decomposing the liquid hydrocarbons by the LPP. The only gaseous product was H<sub>2</sub> and no CO<sub>2</sub> was formed. As a solid product, nano-sized carbon containing no impurities was produced.

Decomposition of waste organic solvents was performed in a liquid-phase plasma reaction system connected to a mass flow meter (MFM) and a gas chromatograph (GC). Benzene, toluene, and n-hexane were used as reactants. The H<sub>2</sub> production rate was measured using MFM. GC was used to analyze the composition of the gaseous product. Plasma was emitted between the two electrodes filled with liquid reactant and catalyst.

The only gaseous product was H<sub>2</sub> and no CO<sub>2</sub> was formed. As a solid product, nano-sized carbon containing no impurities was produced. The H<sub>2</sub> production rate and carbon yield obtained by reacting for 1 h under liquid plasma irradiation was measured. About 35 L/h of H<sub>2</sub> was obtained even under no catalyst condition. The yield of carbon black was also about 10%. It was further increased in the perovskite catalysts. TEM image of carbon produced as the reaction time elapsed was measured. The carbon products were similar in crystal shape and size regardless of the reaction time. The crystal size was small and uniform (10 nm or less). The H<sub>2</sub> production rate was greatly increased on perovskite catalysts. The yield of carbon black was also improved.

##### PS-TuP-3 Tailoring of Mg Thin-Film Corrosion Properties with Dielectric Barrier Discharge Plasma Treatment, *Lisa Hanke, T. Hartig, F. Weisheit, T. Tjardts*, Kiel University, Germany; *M. Valtiner*, Vienna University of Technology, Austria; *F. Faupel, E. Quandt*, Kiel University, Germany

Magnesium based implants are studied as biodegradable alloys with the possibility to release therapeutically relevant ions such as lithium locally in the body. For degradation and, thus, corrosion, the surface structure and composition play a significant role and can be used to adjust the corrosion rate and ion release. Techniques such as plasma electrolytic oxidation using a liquid electrolyte are well studied to change surface properties, also for MgLi alloys. However, symmetric volume dielectric barrier discharge (DBD) plasma treatments without additional precursors are not widely investigated. DBDs are scaled up in industrial applications and allow a fast and cheap surface treatment at atmospheric pressure. It is known to modify surface properties such as the wettability and effect the surface chemistry. In this study, the effect of DBD plasma on Mg based thin films as an easy and fast surface treatment for controlling the corrosion rate and ion release is investigated. Mg and MgLi based thin films with a Li content of 5.4 at% and 26.9 at% are produced by magnetron sputtering and are treated with DBD plasma for different treatment times between 5 and 30 seconds with fixed plasma parameters. The influence on the surface topography is measured by SEM and the composition of the film by EDX and XPS. After the plasma treatment, a thin layer is formed on the surface which exhibits small cracks for the longest treatment time. This layer can be identified by XPS measurements as carbonate and oxide components in higher amounts than for the untreated samples. If those surface films are stable during corrosion, they slow down the degradation and ion release. The corrosion rate is determined by potentiodynamic polarisation measurements in Hanks' balanced salt solution at 37 °C and pH 7.4. By in situ measurements with an electrochemical flow cell connected to inductively coupled plasma – mass spectrometry (ICP-MS) the ion release is determined. It can be seen that the corrosion rate is decreasing with longer treatment time and is only half of the corrosion rate of an untreated sample after a treatment for 15 seconds. For all samples, a high increase of lithium release is determined at the beginning while magnesium release is stable which identifies a surface layer with high Li content. However, identification of ion release over long open circuit potential (OCP) measurements and at potentials above the OCP allow further analysis of the influence of the treatment. The results show a slower ion release and stronger passivation for plasma-treated films which support the idea of the formation of a protective layer.

##### PS-TuP-4 Improvement of Reliability in a-IGTO Thin-Film Transistors by H<sub>2</sub>S Plasma Treatment, *Jin-Hwan Hong, D. Kim, B. Choi*, Sungkyunkwan University (SKKU), Republic of Korea

In this work, amorphous indium-gallium-tin-oxide thin-film transistors (a-IGTO TFTs) with H<sub>2</sub>S plasma treatment was demonstrated for the first time. Through the H<sub>2</sub>S plasma treatment, both the electrical performance and

reliability of the a-IGTO TFTs were improved. The carrier mobility and bias stress under temperature significantly increased with the H<sub>2</sub>S plasma treatment, which is due to the incorporated sulfur not only providing an extra electron to the a-IGTO, but also passivating the interface trap density induced by exceeded oxygen vacancies. In addition, by conducting the a-IGTO TFTs with H<sub>2</sub>S plasma treatment, the hysteresis effect of the TFTs has been improved and tolerance of the TFTs against moisture from the ambient atmosphere has been improved. We believe that the proposed H<sub>2</sub>S plasma treatment is suitable for the efficient fabrication of oxide semiconductor-based TFTs, as well as for accelerating the electrical performance and reliability of their electrical characteristics in a wide range of modern applications such as oxide semiconductor-based flexible and display electronics.

**PS-TuP-5 Effects of Plasma Induced by Extreme Ultraviolet (EUV) Radiation on the Material Surfaces,** *Juyoung Jung, J. Hong*, Sungkyunkwan University (SKKU), Republic of Korea; *H. Park, Y. Jung*, Samsung Electronics Co., Inc., Republic of Korea; *B. Choi*, Sungkyunkwan University (SKKU), Republic of Korea

Currently, the extreme ultraviolet (EUV) plasma, which is one of the laser produced plasma, is an essential fabrication for producing miniaturized integrated circuits in semiconductor manufacturing processes. The tin plasma produced by CO<sub>2</sub> laser emits high energy photons of 92 eV through electron transition to a lower energy state. Both plasma and photon of high energy excite molecules or atoms to produce highly reactive ions or ligands, and create particles to contaminate most parts in beam path. The environment of the equipment that generates EUV light maintains a high vacuum state, including approximately 5 bar of gas. These gases turn plasma with extremely high energy, and permeates the surface of liquid tin and solid materials. As a result, highly reactive plasma permeates and accumulates under the surface of the material. When the plasma release onto the material surfaces, it becomes a contamination sources. In this paper, we have researched the contamination mechanism and solution of the material surface in EUV system. To reduce the contamination generated by plasma, we have experimented with various types of method such as materials, voltage, shape of patterns, and arcing. We believe that various experiments and results will provide a method to control contaminants by plasma in the EUV system.

**PS-TuP-6 Effects of Ambient Air Conditions on Characteristics of Decomposing Aqueous Phosphorus Compounds by a Pin-to-Liquid Dielectric Barrier Discharge,** *Gyu Tae Bae, J. Kim, E. Jung, H. Jang*, Kyungpook National University, Republic of Korea; *D. Kim, H. Lee*, Electronics and Telecommunications Research Institute, Republic of Korea; *H. Tae*, Kyungpook National University, Republic of Korea

Recently, non-thermal plasma (NTP) has proved to be an important tool for efficient water treatment [1]. In particular, NTP generated in the gas-liquid phase can produce in situ highly reactive species such as N<sub>2</sub>, NO•, O<sub>2</sub>, H<sub>2</sub>O<sup>+</sup>, OH•, OH•, H<sub>2</sub>O<sub>2</sub> which contribute to the decomposition of organic materials [2]. Among the various NTP sources, the pin-to-plate discharge is one of the simplest methods to effectively generate NTP containing reactive species radicals at atmospheric pressure. The pin-to-plate electrode configuration allows for easy air discharge without additional gas discharge due to the pointed tip of the pin-shaped electrode, which induces local electric field enhancement. As this NTP device has a simple structure and is easy to control, which is advantageous for device miniaturization.

More recently, a pin-to-liquid dielectric barrier discharge (DBD) structure using a water-containing vessel body as a dielectric barrier for total phosphorus monitoring in water has been reported [3]. In this study, characteristics of water treatment using a pin-to-liquid DBD structure are investigated in three different ambient air conditions: open atmosphere, closed atmosphere, and closed atmosphere with air flow. The results showed that the changes in pH and electrical conductivity with plasma treatment time are highly dependent on the ambient air conditions, when the electrical input is kept the same for all systems. Since the proposed pin-to-liquid DBD structure does not use any additional discharge gas except for the atmosphere, the generated reactive nitrogen species originates from the atmosphere and its amount also varies with atmospheric air conditions. As a result, we observed that the water treatment efficiencies were different under three different atmospheric air conditions by comparing the decomposition properties of phosphorus compounds. In addition, we demonstrate that the decomposition performance of phosphorus compounds comparable to that of an open atmosphere can be obtained by circulating a few air flows in a closed atmosphere.

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**PS-TuP-7 Influences of Asymmetric Bipolar Voltage Pulse on Film Properties of Polypyrrole Prepared by Solution Plasma Process,** *Hyo Jun Jang, E. Jung, J. Kim, G. Bae, H. Tae*, Kyungpook National University, Republic of Korea

A solution plasma process uses intermediate products generated by the interaction between an ionized gas (plasma) and solution substances for material processing [1]. The process that generates plasma in liquid maximizes the plasma-liquid interface and concentrates plasma energy into the reaction because the plasma avoids quenching by air. Most plasma reactors that generate in-liquid plasma are designed with a pin-to-pin type electrode structure facing each other at a narrow distance in a solution to facilitate discharge [2]. This electrode configuration generates an instantaneous strong discharge, causing activation of the liquid molecules to create intermediate products. As these intermediates move away from the plasma source, they passivate in the form of nanoparticles based on themselves in solution. Recently, the solution plasma reactor having a pin-to-surface electrode structure with the argon gas addition has been proposed to control excessive plasma energy and generate stable plasma in solution [3]. The presence of the surface-type electrode enables film deposition as well as nanoparticle synthesis in solution.

In this study, we observed that a polypyrrole (PPy) film can be deposited on the surface electrode in liquid pyrrole by a solution plasma process in which a negatively biased bipolar voltage pulse is applied to the pin electrode. The plasma generated during the negative period of the applied waveform produces pyrrole anions that do not react with the pyrrole solution. Instead of forming PPy nanoparticles in a pyrrole solution, they drift and deposit onto the surface electrode as relative anode by the negatively biased voltage applied to the pin electrode. In PPy film synthesis using the solution plasma process, an asymmetric voltage waveform with a larger negative magnitude is essential, and the generation of pyrrole anions in the solution plasma depends on the negative amplitude of the driving waveform. In the solution plasma process with the pin-to-surface electrode, the effects of the negative amplitude of asymmetric bipolar waveform on PPy film properties are investigated in detail.

[1] Rezaei et al., *Materials*, vol. 12, p 2751, 2019

[2] Jang et al., *Polymers*, vol. 13, p. 2267, 2021

[3] Shin et al., *Polymers*, vol. 12, p. 1939, 2020

**PS-TuP-8 Liquid Crystal Alignment Effect in Inorganic Alignment Layer Applied with Atmospheric Pressure Plasma,** *Jin-Ah Kim, S. Choi*, Department of Smart Manufacturing Engineering, Changwon National University, Republic of Korea; *H. Park*, Department of Electrical, Electronic, Control Engineering, Changwon National University, Republic of Korea

The liquid crystal alignment process has a great impact on the performance of liquid crystal displays (LCDs). As a liquid crystal alignment method, various liquid crystal alignment methods such as an oblique deposition method, an ion-beam deposition method, and a photo-alignment method have been studied, but they have disadvantages in that the equipment required for the process is expensive and an additional cleaning process is required. Recently, studies for applying atmospheric pressure plasma to liquid crystal alignment have been actively conducted.

In this study, by applying atmospheric pressure plasma as an alignment method, the liquid crystal alignment effect on the alignment layer doped with various kinds of inorganic nanoparticles was confirmed. It was confirmed that the alignment was made uniformly without partial defects through observation under a polarized light microscope. The pretilt angle was measured using a crystal rotation method to confirm the LC arrangement. Surface contact angle measurement allows observation of changes in surface modification after atmospheric pressure plasma treatment. Voltage-transmittance characteristics and response time were measured by electro-optical characteristics. Through this study, it was possible to confirm the liquid crystal alignment effect of atmospheric pressure plasma in the inorganic alignment layer, and the possibility of

industrial application was confirmed.

**PS-TuP-9 Effect of Atmospheric Plasma - Rubbing Treatment on the Liquid Crystal Alignment on Inorganic Layer, *Se-Hoon Choi, J. Kim***, Department of Smart Manufacturing Engineering, Changwon National University, Republic of Korea; *H. Park*, Department of Electrical, Electronic, Control Engineering, Changwon National University, Republic of Korea

Liquid crystal alignment is one of the important technologies in fabrication liquid crystal display (LCD), and lots of research is being done. This technology has an important role in controlling the light transmitted from the backlight and has been established as an essential technology in the fabrication process. Inorganic alignment layers that can replace the conventional polyimide (PI) alignment layer have been studied in advance. We confirmed the effect on liquid crystal alignment by performing the plasma-rubbing method as a process variable on the inorganic alignment layer, respectively. We measured LV-SEM to confirm the deposition of the alignment layer on the surface of the fabricated cell, the uniform alignment was confirmed through a polarized light microscope, and the contact angle was measured to confirm the modification change on the surface. In addition, the pre-tilt angle was checked, and the UV/Vis transmittance measurement for the transmittance analysis in the visible ray band and the electro-optical characteristics such as voltage-transmittance and response time were measured.

**PS-TuP-10 Deposition and Characterization of Carbon Nanowalls Synthesized by Microwave Discharge System Using Different Carbon Sources, *K. KWAK, Abdessadk ANAGRI, F. BOHLOOLI, S. MORI***, Dept. of Chemical Science and Engineering, Tokyo Institute of Technology, Japan

In this study, we synthesized carbon nanowalls by microwave plasma-enhanced chemical vapor deposition system using different feed gas mixtures CO/H<sub>2</sub> and CH<sub>4</sub>/H<sub>2</sub> system. Carbon nanowalls (CNWs) are interconnected stacks of graphene sheets that oriented vertically on a substrate; each sheet is composed of a few layers of graphene with length and height ranging from a few nanometers to microns. is micrometre-wide freestanding flakes consisting of stacked graphene layers. The experimental apparatus used in this study is the same as that in the previous study [1]. The microwave plasma-enhanced CVD system is a modified ASTeX DPA25 plasma applicator in which the quartz discharge tube of a 15 mm inner diameter is utilized. The maximum power of microwave source is 250 W. Silicon single crystal wafers were used as substrates with a size of 10×10 mm<sup>2</sup> square. No catalyst materials were used in this study. The parameters of the CNWs deposition process were as follows: CO flow rate, 0-50 sccm; H<sub>2</sub> flow rate, 0-50 sccm; CH<sub>4</sub> flow rate, 0-50 sccm; total pressure, 20-250 Pa; microwave power, 60-120 W. The plasma emission was monitored by a spectrometer. Carbon deposits grown on the substrate were observed by scanning electron microscopy and transmission electron microscopy and analyzed by Raman spectroscopy. It was found that the CNW synthesized using CO has a larger flake size than the CNW from CH<sub>4</sub> as a carbon source. Generally speaking, the flake size was larger when hydrogen was present at higher concentrations. We have analyzed the crystallinity of CNWs by the Raman spectroscopy. The crystallinity of the CNW is evaluated by the intensity ratio of D peak which relates to the disorder and G peak which means the presence of crystalline graphene layers, ID/IG, and half width of G peak, WG. Here, a low ID/IG value and a small half width WG of the G peak indicate good crystallinity. As you can see these results, we can find Id/Ig of CO CNWs is lower and half width of CO CNWs is also lower than CH<sub>4</sub> CNWs. Therefore, it is concluded that the CNWs synthesized using CO have a more crystalline graphene layers. We will discuss the reason why CO CNWs have more crystalline graphene layers than CH<sub>4</sub> CNWs. One of the possible reasons for the difference in the crystallinity comes from the amorphous carbon etching ability of hydrogen and oxygen. When CH<sub>4</sub> is used as carbon source, only H is present in the reactor, while when CO is used as carbon source, O and H are present. And since oxygen has a higher ability to etch amorphous carbon, CNWs synthesized from CO have more crystalline graphene layers than those from CH<sub>4</sub>.

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## Nanomaterials

### Room Naupaka Salon 4 - Session NM-TuE1

#### NanoCatalysis

Moderator: Ellen Fisher, Colorado State University

5:40pm **NM-TuE1-1 Layered Iron Vanadate Electrocatalyst for Large Current Density Water Splitting**, *Fitri Nur Indah Sari, J. Ting*, National Cheng Kung University (NCKU), Taiwan

Electrocatalysis water splitting is an attractive method to generate hydrogen from water. To date, the state-of-the-art catalysts to split water are based on noble metals, such as platinum for hydrogen evolution reaction (HER) and IrO<sub>2</sub> and RuO<sub>2</sub> for oxygen evolution reaction (OER). However, their scarcity and high cost limit the application. Therefore, great efforts have been devoted to exploring highly active and cost-effective catalyst materials. Recently, noble-metal-free Fe-based catalysts have been demonstrated to be highly efficient for OER. It would be a great advance if such Fe-based catalysts could become bifunctional for overall water splitting. This work investigates a unique layered iron vanadate Fe<sub>5</sub>V<sub>15</sub>O<sub>39</sub>(OH)<sub>9</sub>·9H<sub>2</sub>O (FVO) catalyst. The electrocatalytic activity of FVO is controlled by tuning the surface oxidation state and introducing anion and cation vacancies. This work provides a new avenue to design an efficient and stable electrocatalyst Fe-based material with a large current density.

Keywords: layered iron vanadate, surface oxidation state, anion and cation vacancies, water splitting.

6:00pm **NM-TuE1-2 Size Dependence of the N-Doped Graphene Nanocluster on the Oxygen Reduction Reaction Activity**, *H. Matsuyama*, The University of Electro-Communications (UEC Tokyo), Japan; *L. Arellano Sartorius*, The University of Electro-Communications (UEC Tokyo) and Instituto Politécnico Nacional, Mexico; *Jun Nakamura*, The University of Electro-Communications (UEC Tokyo), Japan

N-doped graphene nanocluster (N-GNC) has been proposed as a promising candidate for catalysts of oxygen reduction reaction (ORR) in fuel cells, but its cluster size or concentration dependence has been unknown so far. In this study, the dependence of the ORR activity on the size of N-GNCs was investigated using first-principles calculations. With a radius of about 14 Å, the reaction step which determines the maximum electrode potentials U<sub>Max</sub> is switched from the H<sub>2</sub>O generation step to the OOH adsorption step. Thus, the volcano-shaped trend of U<sub>Max</sub> was predicted as a function of the cluster size [1,2]. Such a size-dependent ORR activity of the N-GNC is derived from the change in the confinement of a donor electron from the doped N atom. The adsorption energy of the reaction intermediates varies continuously because the spread of the supplied electrons from the doped nitrogen atoms to the surrounding atoms varies with the cluster size. This is due to the development of the so-called edge states as the cluster size increases, causing a decrease in the number of electrons contributing to the chemical bond of the reaction intermediate at the reaction site [3].

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[2] H.Matsuyama and J.Nakamura, ACS Omega 7, 3093 (2022).

[3] Y. Uchida, S. Gomi, H. Matsuyama, A. Akaishi, and J. Nakamura, J. Appl. Phys. 120, 214301 (2016).

6:20pm **NM-TuE1-3 a New High Entropy Glycerate for High Performance Oxygen Evolution Reaction**, *Thi Xuyen Nguyen, Y. Su, C. Lin, J. Ruan, J. Ting*, National Cheng Kung University, Taiwan

Herein, we report a new high entropy material, i.e., a noble metal-free high entropy glycerate (HEG), synthesized via a simple solvothermal process. The HEG consists of 5 different metals of Fe, Ni, Co, Cr, and Mn. The unique glycerate structure exhibits an excellent OER activity with a low overpotential of 229 and 278 mV at current densities of 10 and 100 mA cm<sup>-2</sup>, respectively, in 1M KOH electrolyte, outperforming its subsystems of binary-, ternary- and quaternary-metal glycerates. The HEG also shows outstanding stability and durability in the alkaline electrolyte. The result demonstrates the significance of synergistic effect that gives additional freedoms to modify the electronic structure and coordination environment. Moreover, HEG@HEG electrolyzer shows good overall water splitting performance and durability, requiring a cell voltage of 1.63 V to achieve a current density of 10 mA cm<sup>-2</sup>.

6:40pm **NM-TuE1-4 Shape Matters, Nanostructured Materials with Unique Properties in Carbon Capture and Catalysis**, *Ryan Richards*, Colorado School of Mines

The Richards' group is working on new synthetic methods to control the size, shape and composition of nanoscale materials and applying them in systems integral to alternative energy technologies and carbon capture. In particular, 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 and from mixing metal oxides including the formation of high entropy systems. The initial synthesis of MgO and NiO with (111) facets as the primary surface (Angew., Adv. Mater.) has been followed by recent work utilizing a multiscale characterization platform to discover the underlying phenomena associated with the electrolytic properties of NiO(111) for Li ion batteries (Nature Comm., Nano Letters) and electrochromics. In a joint experimental-theoretical work with international collaborators, we unravelled the potential of (111) polar surfaces for carbon capture (JACS). Most recently, in-situ microscopy studies have revealed insights into the NiO active sites for electrolysis (PNAS) and the underlying dynamics of doping with iron (JACS).

7:00pm **NM-TuE1-5 Molecular Single Iron and Cobalt Catalysts Over Carbon Nanotubes for Electrochemical CO<sub>2</sub> Reduction and H<sub>2</sub> Production**, *Paulina R. Martinez-Alanis*, Institut de Recerca en Energia de Catalunya, Spain; *A. Berlanga*, Universidad Nacional Autonoma de Mexico; *G. Montaña, K. Mejía*, Institut de Recerca en Energia de Catalunya, Spain; *F. Güell*, Universitat de Barcelona, Spain; *I. Castillo*, Universidad Nacional Autónoma de México; *A. Cabot*, Institut de Recerca en Energia de Catalunya, Spain; *T. Kallio*, Aalto University, Finland

Molecular single Iron or Cobalt p-terbutyl-calix[8]arene compounds were bonded over carbon nanotubes (CNTs) or multiwall carbon nanotubes (MWCNTs) by  $\pi$ - $\pi$  stacking. The obtained composites were deposited over a gas diffusion layer and proved in a flow cell in a KHCO<sub>3</sub> solution in a saturated atmosphere of CO<sub>2</sub>. High Current densities around 80 mA/ cm<sup>2</sup>, with faradaic efficiencies of 100 % for hydrogen production were achieved at pH near 7 in aqueous solutions in the flow cell. The selective production of acetate by the Fe and Co calixarene composites was obtained. The reaction conditions analysis, such as temperature, carbonate concentration, and salt, with the characterization of the samples' pre and post-catalysis by ultraviolet-visible, infrared, raman, x-ray photoelectron, and photoluminescence spectroscopy, scanning, and transmission electron microscopy were used to go further in the analysis of the mechanism around these catalytic systems. The understanding of these catalytic performances provides additional criteria for a new strategy for designing materials based on carbon composites as an option for the rational use of the transition metals, which is an environmentally friendly alternative to energy applications.

## Plasma Processing

### Room Naupaka Salon 4 - Session PS-TuE2

#### Practical Applications of Plasma

Moderators: *Mia Rose Kayaian*, California State University, Fresno, *Ashley N. Keobounnam*, California State University, Fresno

7:40pm **PS-TuE2-7 VHF Plasma Enhanced Atomic Layer Deposition of SiN<sub>x</sub>**, *Y. Ji, H. Kim*, Sungkyunkwan University (SKKU), Republic of Korea; *A. Ellingboe*, Dublin City University, Ireland; *Geun Young Yeom*, Sungkyunkwan University (SKKU), Republic of Korea

**INVITED**  
Silicon nitride (SiN<sub>x</sub>) thin films serve as important materials for various semiconductor/display devices and extensively used as a gate spacer in logic or memory devices, thin film passivation layer, etc. For these applications of SiN<sub>x</sub>, conformal deposition on high aspect ratio structures and good film quality are required at low processing temperatures. To satisfy the requirements of SiN<sub>x</sub> for a broad range of applications, plasma enhanced atomic layer deposition (PEALD) methods employing capacitively coupled plasma (CCP) for high pressure operation are widely investigated for high conformality, precise thickness control, excellent repeatability based on self-limiting features of the ALD processes, and for fast cyclic processing. In this presentation, the characteristics of PEALD SiN<sub>x</sub> films deposited at a low processing temperature of 100 °C with various precursors and N<sub>2</sub> plasma excited by using a very high frequency (VHF, 162

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MHz) CCP and floating multi-tile electrodes are reported. The properties of PEALD SiN<sub>x</sub> films deposited with a N<sub>2</sub> plasma excited by the floating multi-tile electrodes were compared with those excited by a conventional 13.56MHz capacitively coupled plasma (CCP) source. It is found that the use of VHF and floating type power electrodes instead of conventional 13.56MHz diode-type CCP for N<sub>2</sub> plasma improve the step coverage and quality of deposited SiN<sub>x</sub> due to high dissociation of N<sub>2</sub> and low ion bombardment energy to the substrate.

**8:20pm PS-TuE2-9 Instant Inactivation of Infectious Bioaerosols by Plasma Filter Technologies, Seunghun Lee**, Korea institute of materials science, Republic of Korea; *K. Baek*, Korea institute of materials science, Republic of Korea; *S. Jung, J. Park, E. Byeon, D. Kim*, Korea Institute of Materials Science, Republic of Korea; *S. Ryou*, Masan National Tuberculosis Hospital, Republic of Korea; *S. Lee*, Korea Conformity Laboratories, Republic of Korea  
Management of infectious bioaerosols in indoor air has emerged as an important technology due to the COVID-19 pandemic. Bioaerosol management can be divided into physical capture and physicochemical inactivation steps. KIMS is researching technologies to inactivate physically captured aerosols with plasma application technologies.

The plasma filter generates surface plasma on the porous ceramic to oxidize the bioaerosol, and supplies reactive oxygen species including ozone to the polymer filter located at the rear for secondary oxidation. Ozone emission, an inevitable problem of atmospheric pressure low-temperature plasma technology, has been solved through a catalyst, and ozone concentration of 0.05 ppm or less can be maintained for more than 1000 hours. It was demonstrated that the SARS-CoV-2 aerosol was inactivated by more than 99% immediately after passing the plasma filter.

In this presentation, we will briefly introduce the developed technologies and report the commercialization results.

**8:40pm PS-TuE2-10 Fabrications of High-Adhesion Copper-Coated Fiber for Antibacterial and Antiviral Filter by Ion-Beam Irradiation, Sunghoon Jung**, Korea Institute of Materials Science, Republic of Korea

Filters are essential products used in masks and air purifiers to prevent pathogens such as SARS-CoV-2. Membrane filters, which are assembled of fine fibers, work in a way that filters out harmful factors (droplets, dust, etc.) in the air by physically preventing them from passing through. Recently, due to issues such as the corona pandemic, there has been an increasing demand for removing harmful factors by adding the simple physical blocking of harmful particles. Various methods exist to remove harmful factors such as plasma, ultraviolet rays, and ozone. However, these methods have a disadvantage because electricity is essential, and the factors that kill the virus mentioned above are also harmful to the human body. Therefore, a means for preventing human exposure is essential, which leads to an increase in price.

Our research team attempted to develop a non-powered antibacterial and antiviral filter. For this purpose, ion-beam surface treatment and copper coating were used. Copper is a representative antibacterial and antiviral material known for a long time. However, copper may also be harmful to the human body if inhaled. If copper is formed on the filter fiber without surface treatment on the filter fiber, the copper may escape from the filter, and a person may inhale the copper. Therefore, it is essential to secure strong adhesion between copper and filter fibers. In order to coat copper with high adhesion on the filter, the research team introduced an ion-beam surface treatment technique. When copper was deposited after ion beam surface treatment, it was confirmed that copper was coated with very high adhesion to the filter fibers without damage to fibers. Furthermore, the virus removal evaluation confirmed that more than 99% of the SARS-CoV-2 was removed on copper-coated filter. This process was able to proceed with a roll-to-roll process through a linear ion beam and sputtering process, so mass productivity could also be secured.

## Thin Films

### Room Naupaka Salon 5-7 - Session TF-TuE

#### Next-generation Protective Coatings and Tribological Applications

**Moderator: Hisao Ishii**, Chiba University

**5:40pm TF-TuE-1 Functional Coatings for Aerospace Applications – Perspectives and Sustainable Development, Jolanta-Ewa Klemberg-Sapieha**, Polytechnique Montréal, Canada

INVITED

Materials exposed to harsh environments continue to face ever-increasing technological, environmental, and economic challenges. Consequently, the field of coating and surface engineering (CSE) technologies has been extremely active, addressing numerous challenges related to the increasingly stringent requirements for the performance of coatings and surface engineering solutions. This frequently includes a controlled combination of several functional properties and long-term environmental stability and durability (multifunctional character of the coatings).

These requirements call for novel thin film fabrication processes and new materials with a synergistic combination of tailored characteristics, while solutions must fit into a sustainable (green) development approach including new “clean” (environmentally friendly) fabrication technologies, and life cycle compatible with economic and environmental constraints.

Protection against materials deterioration is particularly important in the context of aircraft components as operation conditions can vary very widely from severe erosive wear to exposure to hot oxidative gases, extreme thermal loads, or even instant icing of critical surfaces. The reduction of emissions through better engine efficiency can be achieved by using lighter structural materials while preserving the integrity of gas path aerodynamic characteristics; this can be accomplished by surface engineering and application of coatings resulting in the reduction of friction, erosion, wear, and corrosion.

In response, our Functional Coating and Surface Engineering Laboratory (FCSEL, [www.polymtl.ca/larfis](http://www.polymtl.ca/larfis)) has proposed, a comprehensive approach to surface engineering problems. This is based on a simultaneous action of the following key elements: (i) in-depth understanding of the technological problem, (ii) availability of the appropriate metrology tools (testing methods) that allow one to seek appropriate solutions in terms of (iii) nanostructured coating materials, and (iv) their integration in specific coating architectures while applying (v) suitable fabrication processes.

In this presentation, the global approach described above will be illustrated by examples related to the development of protective coating systems against solid particle erosion, high-temperature oxidation, and ice accumulation, as well as our work on the next-generation low-emissivity thermal barrier coatings.

**6:20pm TF-TuE-3 How to Manage Friction and Wear of Diamond-Like Carbon Coatings Lubricated with ZDDP Additive by Tuning Their Mechanical Properties, Maria Isabel De Barros Bouchet**, LTDS - Ecole Centrale de Lyon, France

In various industrial applications, friction and wear reduction by diamond-like carbon (DLC) can be severely affected by the presence of zinc-dialkylidithiophosphate (ZDDP) additive in formulated oils. Tribological experiments show that DLCs friction and wear behaviour in the presence of ZDDP-additivated oils can be managed by tailoring their stiffness, surface nano-topography and hydrogen content. An optimal combination of ultralow friction and negligible wear is achieved using hydrogen-free tetrahedral amorphous carbon (ta-C) with moderate hardness. Softer coatings exhibit similarly low wear and thin ZDDP-derived patchy tribofilms but higher friction. Conversely, harder ta-Cs undergo severe wear and subsurface sulphur contamination. It appears that high local contact pressures caused by the contact stiffness and average surface slope of hard ta-Cs favour ZDDP fragmentation, inducing free sulphur release and its penetration in coating subsurface. Plastic deformation and the formation of graphitic regions and onion-like structures are observed in the weakened sulphur-rich zones by HRTEM<sup>1</sup>.

The effect of sulphur element was further investigated by testing other sulphur-containing and sulphur-free additives. Similar tribochemical wear and high friction were observed for hard ta-Cs lubricated with Sulphur-containing molecules. On the contrary, no wear was observed with the sulphur-free additive. This work sheds light on the underlying micro/nano-scale mechanisms that are responsible for macroscopic tribological behaviour of DLC coatings lubricated in the presence of ZDDP and similar sulphur-containing additives.

<sup>1</sup> Valentin R. Salinas Ruiz, Takuya Kuwahara, Jules Galipaud, Karine Masenelli-Varlot, Mohamed Ben Hassine, Christophe Héau, Melissa Stoll, Leonhard Mayrhofer, Gianpietro Moras, Jean Michel Martin, Michael Moseler & Maria-Isabel de Barros Bouchet, NATURE COMMUNICATIONS (2021), <https://doi.org/10.1038/s41467-021-24766-6>.

## 6:40pm TF-TuE-4 Corrosive Properties of Y<sub>2</sub>SiO<sub>5</sub> Environmental Barrier Coatings, *Byung-Koog Jang*, Kyushu University, Japan

Silicon-based ceramics such as SiC/SiC<sub>r</sub> composites and silicon carbide (SiC) are of interest as candidate materials for the hot-section components of new-generation gas turbines in order to meet future higher fuel efficiency and lower emission goals for engines because of their excellent high-temperature mechanical properties (e.g., retention of high-temperature strength and toughness up to 1400°C). However, since it is prone to hot-corrosion in thermally extreme environments (ex. steam), the development of environmental barrier coatings (EBCs) is mandatory. In the present work, Y<sub>2</sub>SiO<sub>5</sub>EBCs have been deposited by plasma spray technique as protection layer of SiC substrate from oxidation and steam corrosion. Y<sub>2</sub>SiO<sub>5</sub> coatings were exposed at 1400°C for 1~50hr by isothermal heat treatment in the presence of an erosive impurity of calcium-magnesium-aluminosilicate (CMAS). At the interface between the Y<sub>2</sub>SiO<sub>5</sub> coatings and CMAS, the coatings were partially dissolved in the CMAS, resulting in the degradation of coatings by the formation of the reacted region. The chemically reacted region from the top surface of the Y<sub>2</sub>SiO<sub>5</sub> coatings showed increasing tendency with an increase in isothermal heat-treatment time. In addition, the hardness and elastic modulus of Y<sub>2</sub>SiO<sub>5</sub> coatings were evaluated by nano indentation.

## 7:00pm TF-TuE-5 The Effect of Morphology in the Diffusion of Ag Inside Hard Coatings, *Diogo Cavaleiro*, University of Coimbra, Portugal; *F. Fernandes*, Instituto Superior Engenharia do Porto, Portugal

One of the most promising solutions for long term lubrication during dry machining operations are self-lubricant coatings. However, the main problem in these kind of coatings is the swift diffusion of the lubricious element and consequent loss of lubricant properties after short periods of time. By combining the mechanically sound TiSiN coating system with its reported anti-diffusion properties of the amorphous SiN a solution to halt the diffusion of the lubricious element can be found. In this work, triple layer coatings constituted by a Ag doped TiN layer sandwiched between two layers of either TiN or TiSiN were deposited by HiPIMS working in deep oscillation magnetron mode (DOMS) with the objective of studying the diffusion of Ag (the lubricious element) in these two different types of matrices (TiN and TiSiN) when exposed to high temperatures. After annealing treatment of the samples at 600°C and 800°C for 2 hours, RBS and TEM analyses allowed to observe that the morphology of the coatings had a big impact in the way Ag diffusion occurred. Open columnar structures facilitate Ag movement through surface diffusion of the columns. While, at first, it seemed that the TiN matrix was a better barrier to the diffusion of the silver, the incorporation of Si<sub>3</sub>N<sub>4</sub> cap layers allowed to disregard the effect of structure and confirm that with the right morphology, the TiSiN matrix can completely halt the diffusion, thus demonstrating its ability to be applied in tools for dry machining operations.

## 7:40pm TF-TuE-7 Comparison of Mechanical and Tribological Properties of Diamond-Like Carbon Coatings Doped with Europium and Gadolinium Produced by HiPIMS, *M. Fontes*, Federal Institute of Education, Science and Technology of Sao Paulo, Brazil; *A. Cavaleiro*, *Fábio Ferreira*, University of Coimbra, Portugal

Hydrogen-free diamond-like carbon (DLC) thin films exhibit properties that make them suitable for a wide range of applications, from biomedical implants to engine components. They have been used as coatings due to their attractive properties including high-temperature stability, high hardness, high wear resistance (wear rate <10<sup>-16</sup> m<sup>3</sup>/Nm), and low friction coefficient (<0.2) even under high load/pressure. One of the major limitations of hard hydrogen-free ta-C coatings applications is related to the low reactivity with oil additives used nowadays. The ionic liquids (ILs) emerged as a novel class of lubricants that can be used in future lubricated systems due to possesses unique physical properties, including high thermal stability, high thermal conductivity, very low volatility, low melting point, and nonflammability. To improve the lubrication performance of DLC with ILs, it was doped the DLC films with rare earth metals such as Gadolinium (Gd) and Europium (Eu). The working hypothesis is that these non-carbide-forming elements can be introduced in the DLC matrix, incorporated as single atoms, and enhance the surface adsorption and reactivity of phosphorus-based IL, improving, consequently, the lubricating

properties of DLC/ILs sliding contacts, with no effect the mechanical and tribological properties of DLC films. Therefore, in this work, the mechanical and tribological properties of the doped-DLC films, with different atomic concentrations of Eu and Gd elements, deposited by High Power Impulse Magnetron Sputtering (HiPIMS), were characterized and compared with the pure DLC films. Results show that for samples doped with a low atomic concentration of Eu or Gd (1% to 3%), despite having a friction coefficient higher than pure DLC films (0.45), shows typical values for pure DLC coatings, like low wear rate and high hardness (23GPa), permitting, in the future, the combination of novel nanostructured alloyed-DLCs and ILs needed to achieve the optimal lubrication performance.

## 8:00pm TF-TuE-8 Reactive Molecular Dynamics Simulation Study on the Chemical Reactions Induced at the Diamond-Like Carbon/Fe Sliding Interface and Their Effects of Friction and Wear, *Mizuho Yokoi*, *M. Kawaura*, Institute for Materials Research, Tohoku University, Japan; *Q. Chen*, New Industry Creation Hatchery Center, Tohoku University, Japan; *Y. Asano*, *Y. Ootani*, Institute for Materials Research, Tohoku University, Japan; *N. Ozawa*, New Industry Creation Hatchery Center, Tohoku University, Japan; *M. Kubo*, Institute for Materials Research, Tohoku University, Japan

Understanding wear phenomena is essential to prevent fatal accidents caused by the destruction of machine systems due to wear. Wear amount is usually governed by mechanical factors, however sometimes chemical factors also strongly affect the wear. For example, a previous experimental study has shown that when water is present at the diamond-like carbon (DLC)/Fe sliding interface wear amount increases due to chemical reactions induced at the sliding interface [1]. Therefore, it is important to clarify the atomic-scale wear mechanism in which mechanical and chemical actions are involved. However, the observation of the atomic-scale wear phenomena at the sliding interface from experiments is difficult. In this study, we successfully revealed the tribochemical reactions and their effects on the atomic-scale wear mechanism at the sliding interface of DLC and Fe pair, which is typically used in automobile engines, in the presence of H<sub>2</sub>O and O<sub>2</sub> by using reactive MD simulation.

The sliding simulation model is shown in a supplementary document (SD) Fig.1. To investigate the effects of H<sub>2</sub>O and O<sub>2</sub>, we prepared the following three models: H<sub>2</sub>O model, O<sub>2</sub> model and H<sub>2</sub>O+O<sub>2</sub> model. H<sub>2</sub>O molecules, O<sub>2</sub> molecules and both H<sub>2</sub>O and O<sub>2</sub> molecules were placed at the DLC/Fe sliding interface of H<sub>2</sub>O model, O<sub>2</sub> model and H<sub>2</sub>O+O<sub>2</sub> model, respectively. In the sliding simulations, the DLC substrate on the Fe substrate was slid along the x-direction at a speed of 100 m/s with the normal load of 1 GPa.

In all sliding simulation models, when the Fe and DLC substrates came into contact with each other, the Fe atoms were scraped off and adhered to the DLC surface with a formation of Fe-C bonds. The amount of atomic-scale wear was smaller in the following order, H<sub>2</sub>O+O<sub>2</sub> model < O<sub>2</sub> model < H<sub>2</sub>O model. In H<sub>2</sub>O model, H<sub>2</sub>O molecules were adsorbed on the surface to prevent adhesion (SD Fig.2(a)). However, they were ejected from the contact surface when the high contact pressure was applied, allowing the direct contact. In contrast, in O<sub>2</sub> model O<sub>2</sub> molecules reacted with the Fe surface, forming chemically inert layer, thereby prevented atomic-scale adhesive wear (SD Fig.2(b)) [2]. Moreover, in H<sub>2</sub>O+O<sub>2</sub> model, in addition to the above roles of H<sub>2</sub>O and O<sub>2</sub>, the reaction of H<sub>2</sub>O with the oxide layer promotes the formation of Fe-O-H groups which passivate nascent Fe surface (SD Fig.2(c)). Thus, the results indicate that H<sub>2</sub>O and O<sub>2</sub> play the different role to reduce atomic-scale wear. Moreover, when H<sub>2</sub>O and O<sub>2</sub> coexist at the sliding interface they play a collaborative role to reduce atomic-scale wear.

[1] A. Alazizi, *et al.*, *Langmuir*, 32, 1996 (2016).

[2] M. Yokoi, M. Kubo, *et al.*, *J. Comput. Chem. Jpn.* in press

## 8:20pm TF-TuE-9 High-Entropy Configuration Strategy for the Synthesis of Oxide, Glycerate, and Sulfide Catalysts for Oxygen Evolution Reaction in Water Splitting, *Jyh-Ming Ting*, National Cheng Kung University (NCKU), Taiwan; *T. Nguyen*, National Cheng Kung University (NCKU), Taiwan, Viet Nam; *Y. Liao*, *C. Lin*, *Y. Su*, National Cheng Kung University (NCKU), Taiwan

INVITED

High entropy material provides an unlimited compositional space that allows an unparalleled possibilities for tailoring the electronic structure favorable for catalysts reaction. We report herein two advanced high entropy electrocatalysts having earth-abundant metals for oxygen evolution reaction (OER) in water splitting. The first one is a high entropy perovskite oxide (HEPO) and the second one is high entropy sulfide (HES). The B-site lattice in the HEPO consists of 5 consecutive first-row transition metals, including Cr, Mn, Fe, Co, and Ni, which have quite similar

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ionic radii. Equimolar and five non-equimolar HEPO electrocatalysts have been studied for their OER electrocatalytic performances. Optimized HEPO having outstanding OER activity is demonstrated. The metals used in the HES are Fe, Ni, Co, Cr, and X where X = Mn, Cu, Zn, or Al. We show that the obtained sulfate-containing  $\text{FeNiCoCrMnS}_2$  exhibits superior OER activity with exceptionally low overpotential of 199, 246, 285, and 308 mV at current densities of 10, 100, 500 and 1000  $\text{mA cm}^{-2}$ , respectively. The electrocatalyst yields exceptional stability after 12000 cycles and 55 h of durability even at a high current density of 500  $\text{mA cm}^{-2}$ . Various *in-situ* and *ex-situ* analyses were used to investigate the self-reconstruction of the sulfides during the oxygen evolution reaction (OER) for the first time. Density function theory calculation is in a good agreement with the experimental result. The result demonstrates a viable strategy that leads to the development of new catalyst materials with excellent OER performance. It also opens a new avenue to explore novel, outstanding high entropy materials for various applications.

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## Energy Harvesting & Storage

### Room Naupaka Salon 5-7 - Session EH-WeM1

#### Surfaces and Interfaces for Solar Cells and Solar Fuels

Moderator: Svitlana Pylypenko, Colorado School of Mines

8:40am **EH-WeM1-3 Surface Recombination and Surface Passivation in Halide Perovskite Semiconductors**, *David Ginger*, University of Washington

**INVITED**

Halide perovskite semiconductors are being aggressively commercialized in solar photovoltaics, and are being explored in the lab as high-performance emitters of both classical and quantum light. While halide perovskites are often hailed as remarkably defect-tolerant semiconductors, they still possess surface defects that limit their performance, both as sources of non-radiative recombination, as well as mobile defects that contribute to mixed ionic/electronic conduction. This talk will describe our work to characterize, and passivate, surface defects in halide perovskite solar cells, beginning with the archetypal halide perovskite, methylammonium lead triiodide (MAPI), and extending to complex mixed-cation and mixed-halide perovskites currently being explored for multijunction tandem cells. We relate surface defects to specific vacancies, correlate their appearance with local strain and chemical defects, and demonstrate robust chemical passivation strategies that allow for increases in device performance and stability.

9:20am **EH-WeM1-5 Passivating Interfaces in Thin Film Photovoltaics**, *Craig Perkins*, *D. McGott*, NREL; *E. Colegrove*, NREL, United States Minor Outlying Islands (the); *A. Hattori*, UC Santa Barbara; *M. Reese*, NREL

**INVITED**

Economic considerations, climate change, and concerns over fossil fuel pollution have all contributed to the rise of solar photovoltaics (PV) as a major power source for humankind. As an example, solar PV is forecast to be ~60% of the 85 GW of new generation capacity to be added to US markets in 2022 and 2023. Although silicon-based PV currently dominates the market, this relatively mature technology is being challenged by several newer technologies based on thin films of compound semiconductors. In this talk, I will touch on some of the scientific advances that have driven down costs of PV power, giving particular emphasis to interfaces in PV cells comprised of polycrystalline thin films. Interfaces are of increasing importance in polycrystalline thin film PV devices because the quality of the bulk semiconductors has been improved to the point where minority carrier lifetimes are in many cases limited by carrier interaction with defective interfaces. This in turn limits the device power conversion efficiency (PCE). The analysis of interfaces in thin film PV devices usually presents complications not typically encountered in the study of "free" surfaces, and we review some of the methods used in our lab to characterize buried interfaces. Among these methods is a thermomechanical technique for cleaving CdTe-based solar cells at the interface between CdTe and the transparent conducting oxide located at the front of superstrate architecture cells. This buried interface is the first active junction that is formed in this technology, is one that changes throughout several high temperature processing steps, and its study remains an active research area even after decades of work. We show how combining thermomechanical cleaving with electron spectroscopy can tease out the details of structure, electronic properties, and passivation mechanisms in CdTe. We highlight a common structural feature found in several very different well-passivated PV materials including CdTe, the halide perovskites, and Cu(In,Ga)Se<sub>2</sub>. I will also describe a recently developed method for room temperature temporary passivation of CdTe thin film surfaces. This passivation strategy, adopted from silicon PV, allows us to measure properties of as-grown absorbers, unlike the previous best known method involving alumina deposition and high temperature processing, both of which affect a film's bulk properties. Finally, I will review a number of ongoing challenges faced by researchers interested in characterizing interfaces of energy materials with electron spectroscopic methods.

## Energy Harvesting & Storage

### Room Naupaka Salon 5-7 - Session EH-WeM2

#### Surfaces and Interfaces for Environmental Processes

Moderator: Craig Perkins, National Renewable Energy Laboratory

10:20am **EH-WeM2-8 Effect of Carbon Support Structures on Electrode Reaction Activity of Catalyst Layer in Polymer Electrolyte Fuel Cell: Large-scale Reactive Molecular Dynamics Simulations**, *Tetsuya Nakamura*, *R. Otsuki*, *Y. Asano*, *Q. Chen*, *Y. Ootani*, *N. Ozawa*, *M. Kubo*, Tohoku University, Japan

For large output of polymer electrolyte fuel cell, the electrode reaction activity in the catalyst layer (CL) consisting of carbon support with meso pores, Pt nanoparticles (Pt NPs), Nafion chains, and water should be improved. Conventionally, to realize high electrode reaction activity, catalyst elements have been designed by first-principle calculation. However, first-principle calculation does not take into the meso-scale CL structures, such as carbon support, a distribution of the Nafion chains, and water content. Thus, we have constructed meso-scale CL structures and successfully clarified the effect of the pore size of the carbon support on the electrode reaction activity by large-scale reactive molecular dynamics simulation [1]. In addition, to design higher-performance CL structures, we consider it important to control the distribution of water on the carbon support and to improve the coverage states of Pt NPs with the Nafion chains. In this study, the hydrophilic group is introduced on the surface of carbon support to form a water film and we investigated coverage states of the Nafion chains over Pt NPs on the carbon support with different water film thicknesses.

The catalyst particle (CP) model was constructed by coating the Nafion chains and water on the carbon support surface. Six pores were created in an amorphous carbon sphere. In addition, the water film whose thickness is 0.7 and 1.0 nm were formed on the carbon support surface.

To clarify the effect of the thickness of water film on the coverage states of the Nafion chains over Pt NPs, we compared two CP models with different water film thicknesses of 0.7 and 1.0 nm. Here, for high electrode reaction activity, the Nafion chains should cover over Pt NPs partially to allow both high oxygen diffusion and high proton conduction. Figs. 2 (a) and (b) shows the coverage states of the Pt NPs interior of the pore after the calculations when the thickness of water film was 0.7 and 1.0 nm, respectively. Consequently, when the film thickness was 0.7 nm, the Nafion chains penetrated the pore and partially covered the Pt NPs. On the other hand, when the film thickness was 1.0 nm, the Nafion chains did not penetrate the pore. These results suggest that when the thickness of the water film is 0.7 nm, both high oxygen transport and high proton conduction to the Pt NPs in the interior of the pore of carbon support are realized.

[1] Tetsuya Nakamura, Riku Otsuki, Shuichi Uehara, Yuta Asano, Qian Chen, Yusuke Ootani, Nobuki Ozawa, Momoji Kubo, *J. Comput. Chem. Jpn.*, 20, 4, 150-154 (2021)

10:40am **EH-WeM2-9 Large Scale Molecular Dynamics Simulation Study on Ionomer Coating of Pt Nanoparticles of Polymer Electrolyte Fuel Cells**, *Riku Otsuki*, *T. Nakamura*, Institute for Materials Research, Tohoku University, Japan; *Q. Chen*, New Industry Creation Hatchery Center, Tohoku University, Japan; *Y. Asano*, *Y. Ootani*, Institute for Materials Research, Tohoku University, Japan; *N. Ozawa*, New Industry Creation Hatchery Center, Tohoku University, Japan; *M. Kubo*, Institute for Materials Research, Tohoku University, Japan

Polymer electrolyte fuel cells (PEFCs) are widely used for automobiles because it does not emit CO<sub>2</sub> during operation. For more popularization of a fuel cell vehicle, its higher output is required. The output of PEFC depends on a catalyst layer (CL) at the electrode composing of carbon supports, Pt nanoparticles (Pt NPs), ionomers and water molecules. Ionomers play an important role in proton conduction and oxygen gas

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diffusion. Especially, if Pt NPs and ionomer are not connected via water, proton transport is impossible. However, if the coverage of ionomer on Pt NPs is too high, oxygen gas diffusion is obstructed. Then, to reveal the CL structure with high electrode reaction activity, the coverage states of ionomer on Pt NPs have been earnestly studied by molecular dynamics (MD) method. For example, W. Wang et al. investigated the ionomer distribution over the Pt NPs and carbon particles in the CL model composed of about one hundred thousand atoms<sup>[1]</sup>. However, such a small model cannot handle the actual agglomerated structure of carbon support, and discussion about an optimal CL structure with high electrode reaction activity is impossible. In this study, we constructed 3 million atoms CL model with the agglomerated structure of the 15 carbon supports (Fig. 1) and analyzed the coverage of Nafion as ionomer over the Pt NPs by MD method to discuss the electrode reaction activity.

Coverage is defined as ratio of number of covered Pt atoms to the number of the Pt atoms on the Pt NPs surface. The distribution of Nafion coverage on each Pt NPs is shown in Fig. 2. The averaged coverage is 69.5%. Coverage of most Pt NPs, which placed on surface of a carbon support or between two carbon supports, ranges from 60 to 90%. On the other hand, it was found that the ionomer coverage of Pt NPs surrounded by three carbon supports is lower than another Pt NPs as shown in Fig. 3. Here, the Pt NPs and Nafion are connected via water clusters, indicating high oxygen gas diffusion and proton conduction. Therefore, we proposed that the Pt NPs surrounded by three carbon supports exhibit high electrode reaction activity. Finally, we conclude Large-scale MD is very effective to reveal how CL structure affect output characteristics of PEFCs

11:00am **EH-WeM2-10 Studying Corrosion Processes of Aluminum Alloys in Diverse Aqueous Environments**, *Micha Ben-Naim, A. Ivanovskaya, S. Cho, C. Orme, M. Bagge-Hansen*, Lawrence Livermore National Laboratory  
Corrosion modes and rates have a strong dependence on environmental conditions. During certain corrosion processes like stress corrosion cracking (SCC) and crevice corrosion, the local chemical environment, including pH and concentration of dissolved ions and gases, can vary dramatically from bulk solution conditions, motivating the study of corrosion properties under a wider range of aqueous environments than would typically be encountered in environmental corrosion. 7000 series aluminum alloys are a class of high-strength alloys used for structural and aerospace applications that are susceptible to corrosion, particularly SCC, but work to date has largely focused on corrosion in aqueous chloride salts.

In this work, we study the corrosion properties of these Al alloys under a wide range of aqueous conditions. We explore new chemical environments that could lead to corrosion in Al alloys while probing the wide pH ranges that can arise in cracks and crevices. We use polished films to both measure bulk corrosion rates and enable the use of surface science techniques. Nondestructive electrochemical

techniques enable high measurement throughput while measuring across pH and salt concentration ranges, so we measure corrosion potentials, corrosion rates, and electrochemical impedance spectra in a nondestructive manner. We also use surface characterization techniques (SEM, EDS, EBSD, XPS) to identify changes in surface chemistry and morphology. By combining electrochemical methods with surface science, we seek to gain a fundamental understanding of the corrosive regimes for these alloys.

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## Nanomaterials

### Room Naupaka Salon 4 - Session NM-WeM1

#### Nanocharacterization

Moderator: **Byron Gates**, Simon Fraser University

8:00am **NM-WeM1-1 Phase Transition Study of 2D NbSe<sub>2</sub> by in-situ TEM/STEM**, *Moon Kim*, The University of Texas at Dallas

Two-dimensional (2D) transition metal dichalcogenides (TMDs) are a family of layered materials with an X-M-X structure, where M and X are transition metal and chalcogen, respectively. TMDs have attracted tremendous interest due to their unique electronic, magnetic, and optical properties with an atomic layer limit depending upon structural elements. The stacking sequence of layers leads to the formation of polytypes such as 1T, 2H, 4H, and 3R, sometimes resulting in significantly different electronic and optical properties.

NbSe<sub>2</sub> is one of the attractive 2D TMDs. It is a superconducting material with a high-superconducting-transition temperature (T<sub>c</sub>) of about 7.0 K and shows metallic characteristics at room temperature. The weak van der Waals force between layers allows superconductivity and charge density wave (CDW) with a transition temperature of about 33K. Interestingly, its phase alters its magnetic and electrical properties. However, its thermal stability, which is important for phase engineering and synthesis, has not been intensively examined.

This study investigated the defect dynamics and thermal evolution of NbSe<sub>2</sub> under vacuum by in-situ heating Scanning Transmission Electron Microscopy (STEM). Low thermal stability of the NbSe<sub>2</sub> was confirmed by direct observation of 2H to 1T phase transition and defects induced by inversion domain boundaries. Interlayer gap expansion, Se atom desorption, and intercalation to the atomic layer gap were also observed. Experimental details will be presented and discussed considering its potential applications.

8:20am **NM-WeM1-2 Development of Atomic Holography Microscope CoDELMA**, *Hiroshi Daimon*, Toyota Physical and Chemical Research Institute, Japan; *H. Momono*, National Institute of Technology, Japan; *H. Matsuda*, Institute for Molecular Science, Japan; *L. Tóth*, University of Debrecen, Hungary; *Y. Masuda*, *K. Moriguchi*, *K. Ogai*, APCO Ltd., Japan; *Y. Hashimoto*, *T. Matsushita*, Nara Institute of Science and Technology, Japan  
**INVITED**

Atomic resolution holography [1] is a powerful technique that can analyze the local stereoscopic atomic arrangement around not only constituent atoms in a crystal but also isolated atoms such as dopants, which has been impossible to be analyzed so far. In photoelectron holography, the photoelectrons emitted from the target atom are used as the reference wave, and the waves scattered by the surrounding atoms are used as the object waves, and the angular distribution (hologram) of their interference patterns can be used to directly derive the three-dimensional atomic arrangement around the emitter atom. Because the atomic-resolution holography required synchrotron radiation facilities so far, its application has been limited. Hence we are developing Atomic Holography Microscope CoDELMA, which can make atomic holography experiment anywhere using a scanning electron microscope (SEM) electron beam.

Atomic-resolution holography microscope is realized by a combination of a SEM and a new two-dimensional electron spectrometer CoDELMA [2]. CoDELMA is the only two-dimensional electron spectrometer that can analyze the angular distribution of high-energy electrons with a high-energy-resolution width of  $\Delta E/E = 1/2000$  over a wide two-dimensional angular range of  $\pm 50^\circ$  at once. This new microscope enables us to easily measure the atomic resolution holography at each nano region observed with SEM.

References:

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9:00am **NM-WeM1-4 Development of a Nanocomposite Based Films with Antifungal Properties and Containing Encapsulated Nanoemulsion Based on Essential Oils: Effect of Combined Treatment with  $\gamma$ -Irradiation,** *Monique Lacroix*, INRS, Canada

Nanocomposite film based on chitosan and nanocrystal cellulose (CNCs) was developed as matrices for incorporation of essential oils as antimicrobial compounds. The addition of CNCs in chitosan based-film has permitted to reinforced the physico-chemical properties of the films. An optimal concentration of 5% (w/w) NNCs improved by 26% the tensile strength (TS) and decreased by 27% the water vapor permeability of the films. A three factor central composite design (CNCs concentration ; microfluidization pressure ; number of cycle of microfluidization) with five levels was designed to optimize the microfluidization process. Microfluidization has permitted to reduce the CNC-chitosan aggregates and improved the mechanical properties of the nanocomposite films by 43%. Two antifungal formulations based on tea tree or on mint in combination with thyme essential oils (Eos) under nano emulsion were developed. When encapsulation under nanoscale, the size of the drop of the antimicrobial formulation was reduced from 219 to 71 nm. The encapsulation efficiency improved from 37 to 83% and the antifungal efficiency was improved from 32 for 3 days to 81% for over one month showing, that the doses required to ensure the biological activity was reduced significantly. The film also showed an effectiveness and slow release of EOs during storage. Combination of active films with  $\gamma$ -irradiation (750 Gy) was synergistic and caused 4 log UFC/gr reduction of fungi for more than 8 weeks of storage. These results showed that the bioactive films and  $\gamma$ -irradiation in combination has commercial potentiality to extend shelf life of rice products.

9:20am **NM-WeM1-5 Tuning Spin Interactions of Magnetic Molecules on Au(111) by Atomic Adsorbates,** *Min Hui Chang*, Korea University, Republic of Korea; *Y. Chang*, Korea Advanced Institute of Science and Technology, Republic of Korea; *N. Kim, Y. Kim*, Korea advanced Institute of Science and Technology, Republic of Korea; *S. Kahng*, Korea University, Republic of Korea

Sensing and tuning spin interactions of magnetic molecules have been actively studied due to possible applications in molecular spintronic and quantum computer. On metallic surfaces, exchange interactions between molecular spins and spins of conduction electrons of substrates have been detected as Kondo resonances at Fermi level. It has been demonstrated that Kondo resonances can be tuned by small molecule bindings, but not by atomic adsorbates. Here, we demonstrate that the Kondo resonances of Co-porphyrin on Au(111) can be tuned by various magnetic atomic adsorbates and be detected using scanning tunneling microscopy and spectroscopy (STM and STS). We observed several adsorbate-induced complexes in STM images, and proposed their atomic structures based on density functional theory calculation results. Our STS results were explained with the redistribution of unpaired spins of Co-porphyrin by atomic adsorbates. Our study shows the spin states and interactions of metallo-porphyrin can be tuned by magnetic atomic adsorbates.

9:40am **NM-WeM1-6 Critical Utilization of Scan Probe Microscopy (Spm) Methods for 2d Materials Research,** *Jason Tresback, J. Deng*, Harvard University

Atomic Force Microscopy (AFM) is a powerful, and critical technology to characterize a diversity of nanomaterials across many interdisciplinary research fields. The use of AFM is rapidly evolving into a myriad of different modes for highly localized (<30nm) property measurement techniques in addition to roughness, and topography with sub-nm spatial resolution. In order to support the momentum of quantum materials research, advanced modes of Scan Probe Microscopy (SPM) techniques are being used to measure electrical, magnetic, and optical properties of new materials as well as Scan Probe Lithography (SP-L) methods for device fabrication. A highly active area of quantum materials research is the characterization and device fabrication of 2d materials (Graphene and TMDs). The goal of this talk is to provide an overview of how SPM is applied for the advancement of 2d materials research, utilizing Kelvin Force (KPFM), Electrostatic Force (EFM), Piezo Force (PFM), and Scattering Near Field Microscopy (s-SNOM) and other advanced modes. The main focus will be on the exquisite, direct imaging of Moire lattice patterns in twisted bi-layer (t-BL) materials by SPM technologies. Each of the imaging modes used to demonstrate direct visualization and angle measurements of t-BL will be discussed. Furthermore, the impact of a closed cell environmental chamber with Ar/N<sub>2</sub> gas flow for each of these modes will be demonstrated. Some examples of direct writing and patterning of 2d structures using a lithography mode for device fabrication will also be presented.

**Nanomaterials**

**Room Naupaka Salon 4 - Session NM-WeM2**

**Nanocomposites**

**Moderator: Ellen Fisher, Colorado State University**

10:20am **NM-WeM2-8 Tuning the Surfaces of Nanomaterials: From a Diverse Chemical Functionality to Applications in Assembly and Imaging,** *Byron Gates, R. Ali, M. Radford, H. Kang, G. Cheema*, Simon Fraser University, Canada

**INVITED**

Controlling the surface chemistry of nanomaterials is equally important to having a fine control over the composition of their core. Nanomaterials, sought for the properties offered by the core material, can be plagued by an inability to control interparticle interactions (e.g., colloidal properties) and/or challenges in precisely controlling the functional groups on their surfaces. Successfully controlling these properties is important for applications of nanomaterials spanning from their use as enhanced contrast agents for use in imaging, to platforms for on-demand drug delivery or triggered hyperthermia, to stabilized catalysts with improved durability and functionality. There are several strategies that can be pursued to tune the chemistry and functionality of nanomaterials. We have specifically been working to broaden the chemistries available for derivatizing the surfaces of metal oxides, whether as a coating (e.g., silica) or as a functional material (e.g., niobates). In this study, we will review the progress made to achieve this surface functionalization of nanomaterials using alcohol condensation reactions. Customized surface chemistries were sought to improve colloidal properties, to diversify the specific chemistries available while simplifying the steps necessary for tuning the surfaces of nanomaterials, and to enable a quantifiable method for adjusting the density of molecular species attached to their surfaces. This presentation will review recent progress towards these goals with examples of custom coatings prepared on a variety of nanomaterials of different core composition.

11:00am **NM-WeM2-10 Preparation of Fluorinated Oligomeric Silica/Magnetite Composites: Application to Selective Removal of Fluorinated Aromatic Compounds from Aqueous Solution under Magnetic Field,** *Hideo Sawada, S. Okada, K. Yamashita*, Hirotsaki University, Japan

It is well known that ABA triblock-type two fluoroalkyl end-capped oligomers [R<sub>F</sub>-(M)<sub>n</sub>-R<sub>F</sub>; R<sub>F</sub> = fluoroalkyl groups; M = radical polymerizable hydrocarbon monomers] can be synthesized by using fluoroalkanoyl peroxide as a key intermediate to form the nanometer size-controlled self-assembled molecular aggregates through the aggregation of terminal fluoroalkyl segments in aqueous and organic media [1, 2]. The fluorinated oligomeric aggregates can interact with a variety of inorganic guest molecules such as silica nanoparticles to afford the colloidal stable fluorinated oligomeric aggregates/guest molecule nanocomposites [2, 3]. Thus, it is of particular interest to develop the colloidal stable magnetite nanoparticles by using two fluoroalkyl end-capped oligomers. Here we report that fluoroalkyl end-capped vinyltrimethoxysilane oligomeric silica/magnetite composites [R<sub>F</sub>-(VM-SiO<sub>3/2</sub>)<sub>n</sub>-R<sub>F</sub>/**Mag**] can be prepared by the sol-gel reaction of the corresponding fluorinated oligomer [R<sub>F</sub>-(CH<sub>2</sub>CHSi(OMe)<sub>3</sub>)<sub>n</sub>-R<sub>F</sub>; R<sub>F</sub> =CF(CF<sub>3</sub>)OC<sub>3</sub>F<sub>7</sub> : R<sub>F</sub>-(VM)<sub>n</sub>-R<sub>F</sub>] in the presence of magnetite (Fe<sub>3</sub>O<sub>4</sub>: **Mag**) nanoparticles. The R<sub>F</sub>-(VM-SiO<sub>3/2</sub>)<sub>n</sub>-R<sub>F</sub>/**Mag** composite powders thus obtained were applied to the surface modification of glass to exhibit a superoleophilic/superhydrophobic characteristic on the modified surface. These fluorinated composite powders are also well spread over water interface, not precipitated into water. Especially, it was found that these composite powders can adsorb effectively oil droplets spread on the water interface under a magnetic field (permanent magnet). In addition to the removal of oil over water interface, interestingly, these composite particle powders were applied to the facile removal of aromatic compounds such as bisphenol A and bisphenol AF from aqueous methanol solution under magnetic fields. More interestingly, it was demonstrated that we can observe the more efficient removal ability for the fluorinated aromatic compounds, compared to that of the corresponding non-fluorinated ones.

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11:20am **NM-WeM2-11 Dielectric Characteristics Comparison between Graphene- and Mxene-Incorporated Composites**, *S. Jun*, Korea Institute of Industrial Technology, Republic of Korea; *K. Ahn, SeGi Yu*, Hankuk University of Foreign Studies, Republic of Korea

Polymer-based dielectric composites were synthesized using fillers of two dimensional (2D) nanomaterial, such as graphene and MXene, and barium titanium (BaTiO<sub>3</sub>, BTO) in a ferroelectric cyanoethylated pullulan (CEP) polymer matrix, in order to use the interface polarization of interfaces between fillers and a polymer matrix. For graphene, two materials of graphene oxide (GO) and reduced graphene oxide (rGO) and two mixing methods—simple mixing of graphene with BTO and elaborate mixing, i.e., encapsulation of BTO in graphene and subsequent mixing. rGO was synthesized by reducing GO chemically with hydrazine. Among four dielectric composite samples with graphene, the sample with rGO-encapsulated BTO (rGO@BTO) fillers showed better dielectric performance, such as high dielectric constants and low dielectric losses. Mixing conducting nanomaterials in a polymer matrix generally yields to a high dielectric constant due to metal-insulator transition (MIT), when the concentration of nanomaterials approaches to the critical concentration of percolation. However, around this critical concentration, it is difficult to suppress the soaring of the dielectric loss due to percolative connection among nanomaterials. Encapsulation can inhibit an increase in the dielectric loss by removing the main culprit of free graphene platelets during the chemical process of encapsulation. MXene was used as a filler in the simple mix method resulting in positive results comparable to the graphene cases—higher dielectric constant than rGO encapsulation (220 vs. 200) and slightly higher dielectric loss (0.08 vs. 0.04 in  $\tan \delta$  at 1 kHz). It is possibly due to its higher conductivity than graphene. AC driven inorganic electroluminescence devices, with a dielectric layer having the above five fillers (four graphene and one MXene), also yield to the similar trend to the dielectric composite. Details will be explained in the presentation.

11:40am **NM-WeM2-12 The Thermal Stability of Separated Configurations in Surface-Segregated Nanoparticles: Atomistic Modeling of Pd-Ir Nanophase Diagrams**, *Micha Polak, L. Rubinovich*, Ben-Gurion University of the Negev, Israel

Compared to alloy bulk phase diagrams, the experimental determination of phase diagrams for alloy nanoparticles (NPs), which are useful in various nanotechnological applications, involves significant technical difficulties, making theoretical modeling a feasible alternative. Yet, being quite challenging, modeling of separation nanophase diagrams is scarce in the literature. The task of predicting comprehensive nanophase-diagrams for Pd-Ir fcc-based three cuboctahedra is facilitated in this study by combining the computationally efficient statistical-mechanical Free-energy Concentration Expansion Method (FCEM) [1], which includes short-range order (SRO), with coordination-dependent bond-energy variations [2] as part of the input, and with rotationally symmetric site grouping for extra efficiency. This nanosystem has been chosen mainly because of the very small atomic mismatch that simplifies the modeling, e.g., in the assessment of vibrational entropy contributions based in this work on fitting to the Pd-Ir experimental bulk critical-temperature.

This entropic effect, together with SRO, leads to significant destabilization of Pd surface segregated Quasi-Janus (QJ) asymmetric configurations of the NP core, which transform to symmetric partially mixed nanophases. First-order and second-order intra-core transitions are predicted for dilute and intermediate-range compositions, respectively. The computed separation diagrams and intra-core solubility diagrams reflect enhanced elemental mixing in smaller QJ nanophases. In addition to these diagrams, the revealed surface and near-surface compositional variations are likely to be pertinent to the utilization of Pd-Ir NPs in heterogeneous catalysis, e.g., of CO oxidation in excess H<sub>2</sub>.

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## Energy Harvesting & Storage

### Room Naupaka Salon 1-3 - Session EH-WeP

#### Energy Harvesting and Storage Poster Session

##### EH-WeP-1 Spintronic Diode as a Signal Detector and RF Energy Harvester, *Andrei Slavin*, Oakland University

The spin-torque magnetic diode (STMD) effect [1] is a quadratic rectification effect of the input microwave current  $I_{RF}(t)$  in a magneto-resistive nano-junction, which is commonly observed in a traditional regime of operation of an STMD, when the magnetization of the “free” layer lies *in-plane*, and when the frequency  $f_s$  of the current  $I_{RF}(t)$  is close to the ferromagnetic resonance (FMR) frequency  $f_0$  of the junction. It was demonstrated theoretically in [2] that in an STMD, biased by an *out-of-plane* static magnetic field, a novel dynamical regime of STMD operation characterized by large-angle out-of-plane magnetization precession can be realized.

It was demonstrated experimentally in [3] that the out-of-plane magnetization precession regime in an STMD predicted in [2] can be realized without *any bias magnetic field*, if an STMD “free” layer has a *perpendicular magnetic anisotropy*. It was further shown in [3] that the developed bias-free STMD provides sufficient dc voltage to power a practical nanodevice – a black phosphorus photosensor.

Here we present an analytical and numerical theory explaining the performance of such a bias-free STMD with perpendicular magnetic anisotropy [4]. We show that such a device can operate as a broadband energy harvester capable of converting incident RF power into a DC power with a conversion efficiency of ~5%.

#### References

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- [4] P. Yu. Artemchuk, O. V. Prokopenko, E. N. Bankowski et al., *AIP Advances.*, Vol. 11, p. 025234 (2021).

##### EH-WeP-2 Strain Imaging of a $\text{LiTi}_2\text{O}_4$ Anode in a Li-Ion Battery, *Keiji Takata*, Kansai University, Japan

Li-ion batteries have advantages including high energy density, high output voltage, and the absence of the memory effect, and so they are recognized as promising candidates for energy storage. These advantages are mainly provided by the lowest electrode potential of  $\text{Li}^+/\text{Li}$  and low density of Li, which are -3.04 V and 0.534 g/cm<sup>3</sup>, respectively. Li-ion batteries have advanced a great deal through the use of intercalation and have been applied in portable electronic devices and electric vehicles.

Li-ion batteries operate through the migration of Li ions between the electrodes. Therefore, non-destructive observation of the migration with high spatial resolution is important.

When charging and discharging, Li-ions are extracted or inserted into electrode materials, which generally causes changes in volume. An atomic force microscope (AFM) can detect and image these volume changes through current collectors with high spatial resolution, which enables us to investigate Li-ion migration without destruction.

Here, we present our results of  $\text{LiTi}_2\text{O}_4$ .  $\text{LiTi}_2\text{O}_4$  is an anode material with high safety having a theoretical capacity of 160 mA h g<sup>-1</sup> (from  $\text{LiTi}_2\text{O}_4$  to  $\text{Li}_2\text{Ti}_2\text{O}_4$ ). The phase change from spinel to rock-salt lead to very small volume changes. Therefore, it might be difficult to observe the Li migration by this method. Cathode of observed samples was layered  $\text{LiCoO}_2$ , and electrolyte and separator are commonly used materials. AFM detects surface displacements synchronizing the charging/discharging cycle, and provides strain images along with topography.

The strain images consist of dark regions that any strain was not detected and bright regions that relatively constant strains were detected. We considered these images together with the frequency dependence of the images and impedance spectroscopy, and concluded that the dark regions were  $\text{LiTi}_2\text{O}_4$  particles and the bright regions resulted from electrolyte flux induced by the gradient of Li-ion concentration in the interspace of the particles. The gradient of Li-ion concentration and electrolyte flux in the interspace were generated by the charging/discharging.

Electric fields, the electrolyte flux, and diffusion move Li ions from one electrode to another electrode. This electrolyte flux is one of the most important issues for increasing the energy density of lithium ion batteries.

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##### EH-WeP-3 A Novel Doping Strategy of PTAA for High-Performance Inverted Perovskite Solar Cell, *Jihyeon Heo, H. Park, H. Park*, Hanyang University, Korea

Organic-inorganic hybrid halide perovskite solar cells (PSCs) have achieved great developments with their high-power conversion efficiency (PCE) surpassing 25.8%. Among various research to maximize the performance of PSCs, a modification of charge transport materials plays an important role to attain such a high-performance of PSC. Particularly, doping engineering can enhance the charge extraction/transport capability of the charge transport layer. Although organic hole transport materials (HTM) including small molecules such as 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD) and conducting polymers such as poly(3-hexylthiophene-2,5-diyl) (P3HT) and Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) are advantageous with high-quality thin films by a simple solution process, an additional doping process is necessary due to their inherent low hole mobility. Therefore, a search for suitable p-type dopants and their fabrication methods for organic HTM should be further studied. In this work, we propose a simple interfacial doping (ID) strategy of PTAA/F4-TCNQ double layer structure with the application of a new solvent 2-butanone. Through this approach, the optoelectrical performance with high power conversion efficiency of 20.67% (p-i-n structure) is achieved and the reproducibility of PTAA-based PSCs is improved with significantly reduced process time compared to the existing solution blend doping (SBD) method. To compare the SBD and ID strategies, both doping methods are analyzed from an electrochemical and morphological viewpoint. As a result, it is confirmed that the ID method improves the thin film properties of PTAA, and the maximized dispersion of F4-TCNQ by 2-butanone achieves effective doping of PTAA, enabling the realization of high-performance PSCs.

##### EH-WeP-4 The Role of Artificial Intelligence in Minimizing Analysis Errors, Illustrated with EXAFS, Nanoindentation, and Core Level Photoemission, *Jeff Terry*, Illinois Institute of Technology

We have developed artificial intelligence based methodology that can be utilized to reliably analyze experimental results from Extended X-ray Absorption Fine Structure (EXAFS) measurements. This development will help to address the reproducibility problems that slow research progress and inhibit effective tech transfer and manufacturing innovation in these scientific disciplines. A machine learning approach was applied to the analysis of extended X-ray absorption fine structure (EXAFS) spectroscopy measurements collected using a synchrotron radiation facility. Specifically, a genetic algorithm was developed for fitting of the measured spectra to extract the relevant structural parameters. The current approach relies on a human analyst to suggest a potential set of chemical compounds in the form of feff.inp input files that may be present. The algorithm then attempts to determine the best structural paths from these compounds that are present in the experimental measurement. The automated analysis looks for the primary EXAFS path contributors from the potential compounds. It calculates a goodness of fit value that can be used to identify the chemical moieties present. The analysis package is called EXAFS Neo and is open source written in Python. It requires the use of Larch and Feff for calculating the initial EXAFS paths. We have recently extended the code to make use of Feff8.5lite so it can calculate the paths needed for populating the analysis from within the EXAFS Neo package. We have expanded the use of the base genetic algorithm software to fitting of Nanoindentation, X-ray astronomy data, and to the analysis of core level photoemission. The publication describing the analysis package and where to obtain the software can be downloaded at: <https://doi.org/10.1016/j.apsusc.2021.149059> or by contacting the speaker.

# Wednesday Afternoon, December 14, 2022

**EH-WeP-5 In Situ Cryo-Xps Analysis of Intercalation Mechanism in Aqueous Zn-MnO<sub>2</sub> Batteries**, *Bhuvana M. Sivakumar, H. Chang, K. Hankins, M. Fayette, V. Shutthanandan, V. Murugesan, D. Choi, X. Li, D. Reed*, Pacific Northwest National Lab

Aqueous Zinc ion batteries (ZIB) based on Zn<sup>2+</sup> intercalation chemistry is gaining attention as large scale energy storage system due to zinc's high capacity (820 mA h g<sup>-1</sup>), high abundance and stability along with lower material costs. However, a comprehensive understanding of the principles governing Zn-MnO<sub>2</sub> electrochemistry has not yet been achieved. In particular, the identity of intercalating cationic species (i.e. Zn<sup>2+</sup> and/or H<sup>+</sup>) and subsequent redox evolution in MnO<sub>2</sub> cathode material is still not clear. Towards understanding the electrochemical changes in the MnO<sub>2</sub> cathode (such as oxidation changes at metal centers) during the battery cycling process, we employed *in situ* cryogenic x-ray photoelectron spectroscopy (cryo-XPS) technique. Our unique *in situ* coin cell setup coupled with cryo-XPS characterization uniquely reveals the chemical identity and distribution of active participants in MnO<sub>2</sub> cathode under various charge and discharge conditions without the need for disruptive sample preparations such as solvent washing or Ar sputtering. By preserving the interface, we observed the broadening of Zn 2p core spectra indicating the evolution of Zn-O and Zn-SO<sub>4</sub> bonding environment during long term cycling process (up to 200 cycles). Similarly, the Mn 2p core spectra reveal the emergence of Mn<sup>3+</sup> from parent Mn<sup>4+</sup> indicating the Zn intercalation induced redox reactions within cathode material. These new molecular-level insights about the intercalation mechanism and subsequent redox state changes will be discussed based on electronic states evolutions within MnO<sub>2</sub> cathodes.

**EH-WeP-6 High-Generating Electrical Power of Chemo-Mechanical Energy Harvesters from Carbon Nanotube Yarn Twist**, *Seongjae Oh*, Department of Energy Science Sungkyunkwan University, Republic of Korea; *S. Kim*, Department of Advanced Textile R&D Korea Institute of Industrial Technology, Republic of Korea

The ocean covers 70% of the Earth, and monitoring the ocean conditions (wave height, wave frequency, temperature, pH, etc.) that play an important role in modern life is emerging as an important technology. In the ocean, it is difficult to use secondary batteries or supercapacitors because the ocean has infinitely wide space and fluidity, so research on energy harvesting for self-powered is required. In this regard, research on chemo-mechanical harvesters that converts mechanical energy in the ocean into electrical energy has been recently conducted, and expectations for the possibility of using an actual self-powered system are growing.

Among chemical mechanical harvesters, a carbon nanotube (CNT) based chemo-mechanical harvester was reported in 2017[1]. The chemo-mechanical harvester showed remarkable harvesting performance of frequency normalized peak power or highest peak power between a few Hz and 600 Hz compared to other types. This harvester used a coiled CNT yarn made by highly twisting a CNT yarn. As stretching the coiled CNT yarn, the density of the coiled CNT yarn increases. When the density of the coiled CNT yarn increases, it is to escape the ions of the electrochemical double layer formed on the surface of the CNT inside the coiled CNT yarn, just like water comes out when a wet towel is pulled out. In this way, the mechanical contraction is converted into electrical energy. In this work, to improve the performance of this harvester, we propose a novel internal structure that can facilitate ion access inside the coiled CNT yarn and maximize the density change when the coiled CNT yarn is stretched[2]. The coiled CNT yarn with a novel internal structure has four times the peak power and more than twice the efficiency compared to the performance reported in 2017[1]. This structure opened up the possibility to further improve the performance of the harvester and it was analyzed by molecular dynamics modeling. Our results are expected to contribute to the implementation of self-powered IoT systems in the ocean.

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**EH-WeP-7 TOF-SIMS Analysis for Power Semiconductors**, *Jaeyeong Lee, Y. Jeong, H. Moon, J. Jin*, Korea Basic Science Institute, Korea (Democratic People's Republic of)

Power semiconductors convert, control, and distribute power in electronic devices, which increases battery life and reduces power usage, which is very important for improving the efficiency of energy harvesting devices.

Power semiconductors are being applied in various energy harvesting fields such as batteries for electric vehicles and solar power generation, and the demand is increasing due to the rapid growth of mobile devices such as smartphones. Among them, power semiconductors using Silicon Carbide (SiC) are attracting attention due to their small size and stability against high temperature and high voltage, but they are experiencing difficulties in developing more diverse devices due to the advanced technology required for production. In this study, we have conducted analysis for Power semiconductor using Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS). Using TOF-SIMS, it is possible to check the behavior of component ions by depth of the metal-oxide-semiconductor field-effect transistor (MOSFET) device through depth profile analysis as well as the distribution of ion components on the surface of the device. By comparing the TOF-SIMS data of a device that failed due to exposure to harsh environments such as high temperature and high humidity with that of a normal device, it was possible to check where the change occurred in the case of a failure and the change in components. In Figure 1, the failed device was analyzed using TOF-SIMS. Ti<sup>+</sup> and Al<sup>+</sup> were mainly detected at the interface of the junction, and Si<sup>+</sup> ions, an insulating film component, were observed at the interface of the gate pad. In addition, a lot of Si<sup>-</sup> and P<sup>-</sup> ions were detected at the defective site. The distribution of Si<sup>+</sup> in the underlying layer of Al<sup>+</sup> ions indicates that the wire bonding lift occurred at the junction of the Al metal and the underlying Si layer.

## Nanomaterials

### Room Naupaka Salon 1-3 - Session NM-WeP

#### Nanomaterials Poster Session

**NM-WeP-1 Array of Freestanding Graphene Variable Capacitors on 100 mm Silicon Wafers for Vibration-Based Energy Harvesting Applications**, *Paul Thibado, F. Harerimana, J. Mangum*, University of Arkansas

Highly flexible, electrically conductive freestanding graphene membranes hold great promise for vibration-based applications. This study focuses on their integration into mainstream semiconductor manufacturing methods. We designed a two-mask lithography process that creates an array of freestanding graphene-based variable capacitors on 100 mm silicon wafers. The first mask forms long trenches terminated by square wells featuring cone-shaped tips at their centers. The second mask fabricates metal traces from each tip to its contact pad along the trench and a second contact pad opposite the square well. A graphene membrane is then suspended over the square well to form a variable capacitor. The same capacitor structures were also built on 5 mm by 5 mm bare dies containing an integrated circuit underneath. We used atomic force microscopy, optical microscopy, and capacitance measurements in time to characterize the samples.

**NM-WeP-2 On the Theory of the Energetic Spectrum of Lateral Superlattices (LSL) on Vicinal Planes: The Role of Crystal Potential**, *Victor Petrov*, Institute of Radio Engineering and Electronics Russian Academy of Sciences, Russian Federation

As is known, the existence of superlattice effects in quantum wells (QWs) on vicinal planes predicted [1] and discovered independently in 1977 [2] initiated with the appearance in these systems of a new crystallographic translation period in the plane of quantum wells  $A \gg a$  ( $a$  - lattice constant). The emergence in these LSL of the periodic system of atomic steps allows to explain the appearance of minigaps (MG) in the energetic spectrum of particles in QWs by the scattering of electrons on such steps. At the same time it is evident that the contribution to the MG formation should also be made by all crystallographic planes in the area of localization of the particle wave function.

This paper theoretically shows that the consideration of only crystal potential and of the potential locating the particle in LSL on vicinal planes results in the appearance of MG even without taking into account of the step structure of the QW boundaries. A method has been developed that makes it possible to calculate the energetic spectrum of these systems for the arbitrary localizing potential by leaving the effective mass approximation in single-valley semiconductors of the GaAs type.

For the cases of the rectangular QW and inversion layer analytical expressions have been obtained for MG magnitudes which depend on the parameters of the crystal and localizing potentials as well as on angles that define the orientation of the QW planes in the crystal. It has been shown that for LSL of the GaAs type the magnitudes of MGs approximate several meV.

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**NM-WeP-3 Fabrication and Physicochemical Analyses of Core-Shell Fe<sub>3</sub>O<sub>4</sub>-TiO<sub>2</sub> Particles Applicable to Plasmid DNA Purification, Gye Seok An, J. Kim, Kyonggi University, Republic of Korea; J. Shin, Hanyang University, Republic of Korea**

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) and titanium dioxide (TiO<sub>2</sub>) composites with core-shell structures have been applied in various applications owing to the advantages afforded by their combined characteristics. In this study, TiO<sub>2</sub> was adsorbed onto Fe<sub>3</sub>O<sub>4</sub> by an aqueous process under reflux conditions using titanium(IV) isopropoxide as the TiO<sub>2</sub> precursor. In order to increase the adsorption efficiency of TiO<sub>2</sub> particles, the surface of Fe<sub>3</sub>O<sub>4</sub> was treated using a reagent having a hydroxyl group, a carboxyl group, and a citric acid bond. The functional group formed on the Fe<sub>3</sub>O<sub>4</sub> surface was expected to act as a site where TiO<sub>2</sub> particles were adsorbed through electrostatic interaction. After the Fe<sub>3</sub>O<sub>4</sub>-TiO<sub>2</sub> fabrication step, the analyses identified functional groups most suitable for TiO<sub>2</sub> adsorption. In addition, various physicochemical analyses analyzed the characteristics of Fe<sub>3</sub>O<sub>4</sub>-TiO<sub>2</sub> particles prepared using the particles with the optimal functional group. The surface functional groups and TiO<sub>2</sub> particles on Fe<sub>3</sub>O<sub>4</sub> were observed by Fourier transform infrared spectroscopy and adsorbed TiO<sub>2</sub> particles were observed by electron microscopy and elemental composition analysis. Additionally, agarose gel electrophoresis tests confirmed the suitability of the Fe<sub>3</sub>O<sub>4</sub>-TiO<sub>2</sub> particles for plasmid DNA purification.

**NM-WeP-4 Synergistic Effects of Carbon Nanotube and Modified Reduced Graphene Oxide Covalently Bonded Hybrid and 3D-Foam on Electromagnetic Interference Shielding Properties of Polymer Composites, Keun-Byoung Yoon, S. Lee, J. Kang, D. Lee, Kyungpook National University, Republic of Korea**

Exploring light-weight electromagnetic interference (EMI) shielding material with high EMI shielding effectiveness (SE) is of great significance to alleviate the growing EMI pollution problem, prevent electronic instruments from the EMI, and protect human health. Hence, several methods are being explored to efficiently restrain EM pollution. Among these studies, carbon nanotubes (CNT) and graphene nanoplates are of particular favor on account of their unique structures and remarkable conductivities.

In the frame of this work, hybrid reduced graphene oxide (rGO) and multi-walled carbon nanotube (MWCNT) nanofiller were designed and covalently bonded through an amide bond. A hybrid nanofiller was prepared through the reaction of modified GO with ethylenediamine and oxidized MWCNT and reduced to hydrogen iodide. Another design is 3D-foam of modified GO and oxidized MWCNT, which is mixed, and 3D-foam is manufactured using various surfactants and used as a nanofiller of the epoxy and polydimethylsiloxane (PDMS) matrix.

The chemical and electrical properties of the hybrid and 3D-foam nanofillers are characterized to establish the correlation between the material characteristics and the EMI shielding performance of the nanocomposites. The mechanical and electrical properties and EMI shielding effectiveness of nanocomposites as functions of hybrid and 3D-foam nanofillers types and contents were investigated in detail.

The addition of rGO significantly increases the electrical conductivity, because CNTs can fill the gaps between rGO sheets [<https://www.sciencedirect.com/topics/engineering/graphene-sheet>], and bridge the neighbor graphene sheets to form a preferable conductive network. In a low areal density 3D-foamed MWCNT/rGO aerogel, vein-structured MWCNT expands the conductive network of mesophyll-structured rGO, which promotes reflection and absorption of electromagnetic waves inside the materials, resulting in excellent EMI shielding effectiveness of 65dB in C-band and absorption-dominant shielding mechanism.

This study not only put forward a facile and effective approach to fabricating epoxy nanocomposites with excellent electrical conductivity and EMI shielding effectiveness but also provided a framework to study the interfacial interaction in rGO/MWCNT hybrid and 3D-foam nanofillers.

**NM-WeP-5 Synthesis of Vertically Aligned Carbon Nanotubes Using Carbon Monoxide as a Carbon Source, Kosuke Homma, S. Mori, M. Endo, Tokyo Institute of Technology, Japan; H. Nakamura, Tokyo Institute of Technology / Yaskawa Electric Corporation, Japan; S. Tanaka, Yaskawa Electric Corporation, Japan**

Recently, vertically aligned carbon nanotubes (VACNT) grown vertically from substrates have been attracting attention in fields such as Through Silicon Via (TSV). Although hydrocarbons such as ethylene and acetylene have been mainly used as carbon sources for the synthesis of VACNT, there have been few reports of VACNT growth using carbon monoxide as a carbon source. This study is aimed at searching for and modeling the optimum conditions for aligned growth of CNTs from carbon monoxide. As the catalyst preparation method, we use the dip-coating method, which has been reported for the aligned growth of CNTs from carbon monoxide. The sputtering method, which has been used in many reports on the aligned growth of CNTs from hydrocarbons, was also investigated.

In the dip coating method, cobalt and molybdenum were used as catalysts. Cobalt acetate was used as the source of cobalt and molybdenum acetate as the source of molybdenum, and ethanol was used as the solvent. The optimum conditions for dip coating were investigated using the lifting speed of the dip-coating and the concentration of the solution as parameters. Experiments were conducted in the range of 0.03~0.9 cm/s as the lifting speed of the dip-coating. The concentrations of cobalt and molybdenum in the solution were 0.01~1.2 wt%. Quartz substrates were dipped in a mixed solution of cobalt and molybdenum and pulled up to coat the surface with cobalt and molybdenum. Subsequently, calcination was performed at 400°C for 5 minutes in an atmosphere. The substrate after calcination was inserted into a quartz tube reactor, and after being evacuated with a vacuum pump, a mixture of Ar and H<sub>2</sub> flowed into the reactor for reduction treatment at 700°C for 10 minutes under atmospheric pressure. After that, the feed gas was switched to CO and synthesis was performed at 700°C for 60 minutes under atmospheric pressure. The surface and cross-section of the substrate after synthesis was observed by SEM. The crystallinity of the CNTs was evaluated using Raman spectroscopy. The results showed that CNTs grew randomly on the surface of the substrate in most conditions; the Raman spectroscopy analysis indicated that single-walled CNTs were synthesized since the strong RBM peak was observed. VACNT was observed when the lifting speed was 0.9 cm/s and the concentrations of cobalt and molybdenum were 0.2 wt%. Based on the results, the conditions necessary for aligned growth and the model were discussed. We also tried to specify the conditions for aligned growth of CNTs using the sputtering method and its optimum condition and growth model are discussed.

**NM-WeP-6 Electrical Characteristics of Multi-Layer Germanium Telluride Switching Device, Chae Ho Lim, J. Park, S. Park, H. Kim, Sungkyunkwan University (SKKU), Republic of Korea**

## Abstract

Various ovonic threshold switching (OTS) materials with unique insulator-metal transition (IMT) characteristics are being actively studied for applications in phase-change memories [1]. Germanium telluride is one of the most actively studied materials and some variants, including germanium-antimony-telluride, are already in commercial use [2]. To improve the switching characteristics of germanium telluride, many approaches, such as stoichiometric control, doping, and process optimization, have been proposed [3,4].

In this presentation, we propose a multi-layer GeTe<sub>6</sub>/GeTe structure to increase the on/off current ratio of OTS devices with a single GeTe<sub>6</sub> layer. The GeTe<sub>6</sub> layers with distinctive IMT characteristics were deposited by adjusting the power ratio during co-sputtering of GeTe and Te targets, and the GeTe layers were deposited in situ by sputtering the GeTe target. For fabrication of the switching device with a metal-insulator-metal structure, tungsten was used for both top and bottom electrodes having a crossbar shape. The on/off ratio of the multi-layer structure was increased compared to that of the single-layer structure (GeTe<sub>6</sub>). Additionally, the threshold voltage was increased, and cycle stability was improved. The detailed origins for the improved characteristics will be discussed based on the experiments with various GeTe<sub>6</sub>/GeTe stack numbers.

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## **NM-WeP-7 Vertically Enhanced Ferroelectric $\alpha\text{-In}_2\text{Se}_3/\text{GaN}$ Heterostructure for Steep Switching High Electron Mobility Transistors,** *M. Yeom, J. Yang, Geonwook Yoo*, Soongsil University, Republic of Korea

A highly crystalline two-dimensional (2D) ferroelectric material,  $\alpha\text{-In}_2\text{Se}_3$  has been extensively studied for neuromorphic, ferroelectric tunnel junction devices, and phototransistors [1-3] because of its unique material characteristic, a ferroelectric semiconductor. Here, we demonstrate, for the first time, a ferroelectric  $\alpha\text{-In}_2\text{Se}_3/\text{GaN}$  HEMT van der Waals heterostructure, in which the switchable ferroelectric polarization of  $\alpha\text{-In}_2\text{Se}_3$  can induce steep subthreshold switching (SS) and large memory window. In-plane polarization within the  $\alpha\text{-In}_2\text{Se}_3$  layer was successfully suppressed via self-aligned-gate etching process as analyzed by micro-Raman spectroscopy. On the other hand, out-of-plane polarization is strongly coupled to two-dimensional electron gas. Therefore, a record low SS of  $\sim 12$  mV/dec with high on/off ratio of  $\sim 10^{10}$  was obtained. The transfer curve exhibits a counter-clockwise hysteretic behavior with a memory window of  $\sim 0.9$  V, induced by the ferroelectric switching above the coercive field of  $\alpha\text{-In}_2\text{Se}_3$ . The results show that ferroelectric polarization and semiconductor characteristic of  $\alpha\text{-In}_2\text{Se}_3$  is a promising for ferroelectric/III-V heterostructures, enabling emerging III-V based reconfigurable and neuromorphic applications.

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## **NM-WeP-8 Electrochemical Powered Nano-Actuator from Carbon Nanoscroll,** *Chae-Lin Park*, HYU-KITECH Joint Department, Republic of Korea; *K. Kim, S. Kim*, KITECH, Republic of Korea

Recently, nanobots are receiving great attention due to their high potential for use in various fields such as intelligent robots, biomedical devices, and drug delivery. Nanobots are realized through the use of nanomaterials and assembly of nanomaterials, and research on driving nanobots using electromagnetic fields, electrochemistry, and specificity of enzymes is in progress. Among them, studies on actuators of carbon nanotubes and graphene based structures driven by electrochemical power have been reported. Electrochemical-based actuators have the advantage of being operated with a low voltage and can be used in places made of electrolyte, such as the human body. However, a useful electrochemical power-based nanoactuator is driven by ion entry and exit, so it is difficult to drive it with a single nanomaterial rather than structures. The development of electrochemical-powered single nanomaterial-based nanoactuators remains a challenge. In this work, we implemented an electrochemical-powered actuator by using graphene as a carbon nanoscroll (CNS) structure with a diameter of 50 nm. Unlike carbon nanotubes and graphene, CNS has a scroll structure and is a material that can be driven independently based on electrochemical power through the input and output of ions between layers. We measured the actuation performance of CNS. When the voltage was applied to CNS on electrolytes, CNS charged and it let the apparent diameter of the scroll increase significantly. Changes of the CNS diameter were measured in real-time using atomic force microscope equipment. It was confirmed that the type of electrolyte and the magnitude of the applied voltage play an important role in controlling the performance of the CNS. Additionally, we have structured the CNS and confirmed that it operates electrochemically. It is expected to see the possibility of using it as a nanobot.

## **NM-WeP-9 Nanopattern Transferred Oxide and UV Curable Polymer Hybrid Films for Liquid Crystal Systems,** *Da-Bin Yang, D. Seo*, Yonsei University, Korea

In the present study, nanopatterns were transferred using the UV-NIL method; in this method, the patterns are cured with UV radiation to produce the LC alignment layers. For high-quality LC alignment layers, transparent conducting oxides (TCOs) with excellent transmittances are mixed with a UV-cured polymer to prepare a hybrid solution.[1] In this

study, we assessed whether high-quality nanopattern transitions can be obtained while reducing the steps of the NIL process by mixing these inorganic materials and polymers. The hybrid solution was coated on a glass substrate and cured by UV irradiation to prepare the nanopattern, and the nanopattern and LC alignment characteristics were analyzed by varying the UV curing time. The film surface was analyzed through X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) analyses. The LC alignment characteristics were confirmed via polarized optical microscopy (POM) and pretilt angle measurements.

### ACKNOWLEDGE

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## **NM-WeP-10 Advanced Nanostructured Architectures via Nanoimprint Lithography on Hybrid Sol-Gel of SnGaO Thin Films,** *Jin Young Oh, D. Seo*, Yonsei University, Korea

Line pattern replication process through nanoimprint lithography (NIL) method has been used in numerous of research fields. NIL technology is not yet utilized for displays industry, and we propose an alignment layer of the sol-gel process using NIL. One-dimensionally nanopatterned by polydimethylsiloxane sheets cause surface changes in hybrid SnGaO thin films mixed in a 3:7 ratio, which aligns the liquid crystals (LCs) uniformly in the line pattern direction. These surface changes are confirmed through atomic force microscopy data analysis, and changes in surface shapes for different the curing temperatures in the furnace are analyzed. X-ray photoelectron spectroscopy (XPS) shows that the chemical composition of the thin films changes according to curing temperatures, and the intensities of SnO and GaO increase exponentially at 200°C compared to those at 50 °C. Through this, the van der Waals force increases between surface molecules, in the anisotropic direction to help align the LCs. Furthermore, we performed polarized optical microscopy and pre-tilt angle analysis confirm that the LCs are energized uniformly. Finally, the performance of an actual display device transmittance and electro-optical properties; the transmittance of SnGaO is 4.51p% higher than that of the currently commercialized PI-rubbing thin films, and the voltage-transmittance curve is a perfect graph. Thus, nanopatterned SnGaO thin films using NIL are expected to become the basis for next-generation displays.

Keywords: Nanoimprint lithography, Sol-gel method, Tin-gallium oxide, Atomic force microscopy, X-ray photoelectron spectroscopy

### ACKNOWLEDGE

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## **NM-WeP-11 First Demonstration of the Fully Euv Patterned Dram Capacitor,** *Seung Jin Kim, J. Hong, B. Choi*, Sungkyunkwan University (SKKU), Republic of Korea

DRAM is continuously scaled down to improve productivity and low power operation. A DRAM cell consists of one transistor and one capacitor, and the pattern of the capacitor consists of storage poly (s-poly) and supporters. The s-poly is main body of capacitor, which is ultra-high aspect ratio structure with metal (Storage TiN)/dielectric/metal (Plate TiN) composition. The supporter prevents leaning or bending of the capacitor. To fabricate both s-poly and supporter, previous immersion-argon-fluorine (I-ArF) technology had been used up to 3rd generation 10 nm devices. In this process, a line-and-space simple double patterning technique (sDPT) was used to create a honeycomb array of highly integrated s-poly contacts. However, the sDPT method has significant problems such as multiple process steps and unit block s-poly not opening due to complex mask stacks and line-space asymmetry. The EUV technology simplifies mask

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stack and expose all s-poly cell by 1-set, which allow uniformity of contact. We believe that this work opening a feasibility of an inevitable EUV era to guarantee the extremely scaled sub-10nm patterning with high performance, high yield, and cost-effective process.

## Thin Films

### Room Naupaka Salon 1-3 - Session TF-WeP

#### Thin Films Poster Session

##### TF-WeP-1 Fabricating Optical Coatings on Complex Surface Using Atomic Layer Deposition, *Liangge Xu*, Harbin Institute of Technology, China

The unique layer-by-layer growth mechanism of atomic layer deposition (ALD) enables exceptional uniformity, conformality, and accurate film thickness control for many thin films. To date, ALD has been limited to relatively small-sized substrates. In optical systems, these properties are of utmost importance as sustaining optical performance requires not only a high degree of uniformity (large size substrates) but also excellent conformality when it comes to complex micro-or macrostructures (Complex shape substrates). For the traditional physical vapor deposition, to reach a high level of uniformity and conformality on domes, need to design specialized motion structures. This comes with an extensive load of mechanical work and process optimization, ultimately leading to tight control of the process parameters, even if the results may not be ideal. In this work, A new ALD tool has been designed, constructed, and tested to apply uniform protective coatings in a deposition dome with over 0.2 m diameters. We have named it as conformal ALD system (CAS), which employs a unique chamber design, and our design approach is adapted to any size of hemispherical dome and dome with Von Karman curves. To demonstrate our idea, we have used a hemispherical dome holder (radius = 100 mm), deposited on the inner side by depositing Al<sub>2</sub>O<sub>3</sub> films, and on the outer side by depositing Ta<sub>2</sub>O<sub>5</sub> films. Measuring their thickness distribution at the typical position of the dome, we have been able to achieve a revolutionary change in the range of non-uniformity, that is, to achieve non-uniformities close to 1 % over the entire structure.

##### TF-WeP-2 Gas Encapsulating Layer for Stretchable Electronics by Selective Infiltration of Al<sub>2</sub>O<sub>3</sub> in Polymer Films, *Sangho Cho*, Korea Institute of Science and Technology, Republic of Korea

Atomic layer infiltration (ALI) has been performed for the preparation of the Al<sub>2</sub>O<sub>3</sub>-polymer hybrid layer as thin gas barrier films. Filling of the free volumes of polymers at the subsurface region with Al<sub>2</sub>O<sub>3</sub> resulted in an excellent water vapor transmission rate (WVTR) low enough to be used as gas encapsulating films for display applications. Among various polymeric substrates, PET, PI, and Nylon 6 formed hybrid thin layers with the infiltration depth in the nanometer ranges while Al<sub>2</sub>O<sub>3</sub> could not infiltrate into PFA and PS films. The selectivity of Al<sub>2</sub>O<sub>3</sub> infiltration into polymer films was employed to prepare stretchable gas encapsulating films by encapsulating individual segments of 144 Ca dots by Al<sub>2</sub>O<sub>3</sub>-PET hybrid films on a PFA polymer substrate. Regardless of bending and stretching, it exhibited extremely low gas barrier properties with WVTR of <10<sup>-7</sup> gm<sup>2</sup>day<sup>-1</sup>. This strategy would be a promising way of hermetic sealing in the stretchable electronic system.

##### TF-WeP-3 Background Removal Limitations on Absolute Accuracy in XPS of Homogeneous Materials, *C. Richard Brundle*, C. R. Brundle and Associates; *B. Crist*, The XPS Library; *P. Bagus*, University of North Texas

The precision achievable in XPS is very good. Accurate quantitation from relative peak intensities is more difficult (1). Normalizations for photoionization cross-sections,  $\sigma$ , and variation of analysis depths,  $\lambda$ , are required, but the procedures are well understood. Separation of the intrinsic photoelectron spectrum from its associated scattered electron background is on less secure ground, as there are several approaches, and implementation requires using the software of the instrument vendor or commercial analysis package vendor. The situation is most difficult when an XPS core level "peak" consists of strong overlapping structure spread over a wide BE range, such as with Fe 2p and O1s in Fe<sub>2</sub>O<sub>3</sub> (2). We have examined, for a single crystal sample, the implementation of different background removal procedures: Tougaard (U2 version), T, Shirley, S, Linear, and total signal. The choice of the high BE endpoint, implying there is no further intrinsic signal beyond that BE, is most important. It is possible to adjust endpoints to return the "expected" answer, 40% atomic Fe, but this is somewhat arbitrary, and assumes 100% accuracy of the relative  $\sigma$ 's,

and relative  $\lambda$ 's, in addition to assuming a) that the Transmission Function of the instrument is correct and b) for our particular case here (and much of the prior literature!), that a small signal from OH is properly accounted for in the analysis. The best consistency is obtained by a compromise between a wide enough range (start to end points) of background removal to include all observable substructure associated with Fe 2p and with O1s, while keeping the BE range very similar for Fe2p and O1s. If such a situation is achievable, there is only a small difference between using T, or S, backgrounds. Even a linear background, or no removal at all, will return values within 10% of the T or S derived Fe %age values. The reason for the close agreement of T and S compositions, despite the huge difference in the amounts of backgrounds removed, is that *the background is proportional to the signal generating it*, so provided the same removal procedure is adopted for both Fe2p and O1s, the functional form of the removal is of secondary importance. It is important to note that the analyst should **never** pick ranges where substructure is included for one of the elements, but not the other.

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##### TF-WeP-4 Electrical Properties of Metal-dual Insulator Type Buried Channel Array Transistor, *INKYUM lee*, Sungkyunkwan University, Korea

In this study, we suggest channel array transistor (BCAT) structure with dual insulator(HfO<sub>2</sub> and SiO<sub>2</sub>) to solve short channel effect(SCE) in the cells of dynamic random-access memory (DRAM) using 2D TCAD simulations BCAT is widely used to make high performance sub 30nm DRAM cell transistors. However, as the device size becomes smaller, device characteristics deteriorate due to SCE. We changed the single insulator currently used for BCAT to dual insulator to improve SCE characteristics. The electrical properties were analyzed according to the thickness changes of HfO<sub>2</sub> and SiO<sub>2</sub> while the total thickness of the insulator is equal. As a result, the higher the HfO<sub>2</sub> layer ratio, the better the value of Threshold voltage, Drain induced barrier lower (DIBL), body effect and swing, 25.2%, 39.8%, 20.9% and 7.0% respectively. HfO<sub>2</sub> with Highly dielectric permittivity would have increased electronic polarization in the insulator and reduced changes by external stress other than gate voltage. Finally, we also discuss disadvantages such as the insulator breakdown to suggest optimal device design scheme in terms of insulator.

##### TF-WeP-5 Effects of Ga Doping on the Optical Properties of Tetrahedral Amorphous Carbon Coatings Synthesized by FCVA & Sputter Hybrid PVD Process, *HoeKun Kim*, Korea Aerospace University, Republic of Korea; *J. Kim*, University of Incheon, Republic of Korea; *S. Lee*, Korea Aerospace University, Republic of Korea

For the decade, it has been shown that diamond-like carbon (DLC) coatings are very promising anti-reflection (AR) and protective coatings for optical device application. The advantages of DLC include high chemical stability, radiation stability and high hardness with the possibility of changing their optical properties by varying the deposition conditions. Especially, tetrahedral amorphous carbon (ta-C) coatings with extremely high hardness, smooth surface, excellent wear resistance, and better thermal stability than DLC have been paid much attention to an alternative protective coating materials. Additionally, optical properties of the ta-C coating could be improved by various metals doping. In this study, various contents of Ga were doped in the ta-C coating to improve the optical properties of the ta-C coatings. Filtered cathodic vacuum arc (FCVA) and sputter hybrid system was co-deposited to synthesize the metal doped ta-C coating. As the Ga doping content increased, surface morphology of ta-C coating changed to more rough and certain nipple arrayed, and surface roughness value increased to 118nm. In the ta-C coating with 8.9at% Ga, the Ga carbide phase was formed in carbon matrix, and this formation contributed lattice disorder and defects on surface. Raman spectroscopy analysis showed that all the coatings had high sp<sup>3</sup>/sp<sup>2</sup> fraction over 56%, and the hardness showed high values of 48 GPa, and these values showed relatively high compared to other AR coating. 8.9at.% Ga doped ta-C coating showed high transmittance in the field of ultraviolet light about 92.4% compared to pure ta-C coating of 88%. This indicates that surface morphology change to nipple array influenced to minimized reflection over wide angles of incidence, and improve transmittance by reducing reflections.

## Acknowledgement

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**TF-WeP-6 Improved Leakage Currents of ALD ZrO<sub>2</sub> by Controlling Surface Reaction with Plasma Source, Il-Kwon Oh**, Ajou University, Republic of Korea; *H. Kim*, Korea Electronics Technology Institute (KETI), Republic of Korea

The use of metal-organic precursors and low temperature growth conditions in the process of depositing oxides with ALD often results in incomplete decomposition of the precursors and residual concentrations of impurities. Since these impurities adversely affect electronic performance such as carrier trapping and fixed charge formation, reducing these impurities is an important issue. These impurity content could be removed by reaction between the precursors and reactants used during the process.

Metal oxide ALD processes are classified according to several oxidant, such as thermal ALD, PE-ALD, and O<sub>3</sub> ALD, each using reactants such as H<sub>2</sub>O (or other oxidants), O<sub>2</sub> plasma, and O<sub>3</sub>. We systematically and comparatively investigated thermal ALD and PE-ALD ZrO<sub>2</sub> using a widely used precursor of CpZr(NMe<sub>2</sub>)<sub>3</sub>. We observed that Zr-Cp and Zr-N(CH<sub>3</sub>)<sub>2</sub> have different degrees of ligand exchange, which leads to different surface-reaction with reactants. The weak oxidizing power of H<sub>2</sub>O showed difficulties on breaking the Zr-Cp bond, while the O<sub>2</sub> plasma reacts due to the high reactivity of oxygen radicals. The use of plasma reactant results in dramatic lowering the impurity level in the deposited ZrO<sub>2</sub> film, leading to superior film properties such as roughness (RMS 0.293 nm) and film density (5.8 g/cm<sup>3</sup>). In contrast, the case of H<sub>2</sub>O was observed not easy to break the Zr-Cp bond, leading to relatively low film quality. The difference in the density and impurity content of the film also affects the performance of the electrical device, such as dielectric constant, interface trap density, trapped oxide charges, and leakage currents (9.11 E-05 A). We believe this study will be useful to develop ALD ZrO<sub>2</sub> process with Cp-containing Zr precursor.

**TF-WeP-7 High Performance Amorphous Oxide Semiconductor Thin-film Transistors with HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Gate Insulator Deposited by Low Temperature ALD, Se-Hyeong Lee**, S. Bak, C. Park, D. Baek, M. Yi, Pusan National University, Republic of Korea

Amorphous oxide semiconductor (AOS) thin-film transistors (TFTs) have been extensively studied because of their applicability to next-generation display. Because SiO<sub>2</sub> exhibits excellent insulating properties and uniformity, the doped Si and thermally grown SiO<sub>2</sub> are generally used as a gate electrode and a gate insulator in the conventional AOS TFTs, respectively. However, the thermally grown SiO<sub>2</sub> cannot be used as the gate insulator in AOS TFTs of the next-generation display since they are required to be transparent in the visible light region and compatible to the flexible substrate.

Therefore, in this study, we fabricated indium-zinc oxide (IZO) TFTs with HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> gate insulator deposited by low temperature atomic layer deposition (ALD). Because Al<sub>2</sub>O<sub>3</sub>, a representative high-k dielectric material, has a wide bandgap (~7.5 eV), low leakage current can be obtained when used for TFTs as a gate insulator. However, since Al diffusion into the channel layer occurs easily due to the small ionic radius of Al cations, an HfO<sub>2</sub> high-k dielectric layer was deposited as a buffer layer to reduce the defects at the channel-insulator interface. Also, the high-k dielectric insulator has the advantage of reducing power consumption by lowering the driving voltage of the fabricated TFTs.

Fig. 1 represents the cross-sectional schematic diagram of IZO TFTs with HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> gate insulator. The Al<sub>2</sub>O<sub>3</sub> gate insulator and HfO<sub>2</sub> insulator buffer were deposited on a heavily doped p-type Si substrate by low temperature ALD at 120 °C using tri-methyl-aluminum (TMA), tetrakis [ethyl-methyl-amino] hafnium (TEMAHf) and H<sub>2</sub>O as an Al precursor, a Hf precursor and an oxidant, respectively. The IZO channel layers and S/D electrodes of the fabricated TFTs were deposited by radio-frequency (RF) magnetron sputtering and thermal evaporator, respectively. The RF magnetron sputtering was conducted with IZO (In: Zn = 90 wt.%: 10wt.%) target in R.T. and 2.0 x 10<sup>-3</sup> Torr. After depositing the channel layers, annealing was performed using a hot plate at 250 °C for 1h. The fabricated TFTs were analyzed with a semiconductor parameter analyzer (Elec Co. EL423).

Fig. 2 shows (a) output curves and (b) transfer curves of IZO TFTs with HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> gate insulator. The electrical properties of the fabricated TFTs exhibited 6.02 cm<sup>2</sup> / Vs of carrier mobility ( $\mu_{sat}$ ), 1.18 x 10<sup>6</sup> of on-off current ( $I_{ON/OFF}$ ), 0.55 V of threshold voltage ( $V_{th}$ ), and 0.31V/dec of subthreshold

swing (SS). Afterward, to improve the electrical properties, we are due to optimize the IZO TFTs with HfO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> gate insulator by varying the thickness of insulator, the thickness ratio of Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>, and growth temperature, respectively.

**TF-WeP-8 Advanced Surface Analysis of Very Thin Surface Coatings, MATJAŽ FINŠGAR**, University of Maribor, Slovenia

Very thin surface coatings in the range of a few nanometers are very challenging to analyze. Identification and knowledge of the distribution of molecular species within these surface coatings are very important for the final performance of most materials. Such surface information can be obtained using advanced surface analysis techniques such as tandem (MS/MS) time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and 3D profilometry. In addition, the gas cluster ion beam (GCIB) sputter source provides new opportunities for the analysis of such thin organic coatings.

In this work, the analysis of very thin organic surface coatings is presented. These organic coatings formed (self-assembled) in a corrosive chloride solution on a brass surface. The molecular conformation was completed using tandem ToF-SIMS capability by describing the molecular fragmentation mechanisms of the various precursor ions. Moreover, organometallic complexes were identified on the surface, which formed between the metal ions released due to corrosion and the organic molecules. Such analyses are still very rare and new to the SIMS database in general. After obtaining the ToF-SIMS signals describing the molecule, 3D distribution analysis was performed using GCIB sputtering associated with 3D ToF-SIMS imaging. The chloride was found to be located below the coating, indicating that the formation of metal chlorides is faster than the adsorption of the organic molecules. The latter was also confirmed by the GCIB-XPS analyses using Ar cluster sputter beams at different acceleration energies and cluster sizes. Finally, surface topography and agglomeration of the molecules in the surface coating were demonstrated by AFM (smaller surfaces) and 3D profilometry (larger surfaces).

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**TF-WeP-9 Temperature Dependence of Dielectric Function for WSe<sub>2</sub>**, X. Nguyen, *Tae Jung Kim*, Kyung Hee University, Republic of Korea; *V. Le, H. Nguyen*, Vietnam Academy of Science and Technology, Viet Nam; *Y. Kim*, Kyung Hee University, Republic of Korea

The transition metal dichalcogenides (TMDC) form a group of layered, highly anisotropic compounds which exhibit interesting and unusual physical properties. Among these TMDC materials, WSe<sub>2</sub> has been a subject of great interest. Besides common characteristics of TMDC family i.e., van der Waals layered structure, indirect-to-direct bandgap transition in the monolayer regime, and spin-valley coupling, WSe<sub>2</sub> also constitutes a high quantum yield in 2D system and can be synthesized on a large area by chemical vapor deposition, opening various potential applications. To meticulously design and understand 2D optoelectrical device's function correctly, the optical constants of monolayer WSe<sub>2</sub> are needed. Although there are a few studies on the dielectric functions, systematic study on temperature dependence of critical points (CPs) of monolayer WSe<sub>2</sub> has not been reported, yet. In this work, we report the dielectric function of monolayer WSe<sub>2</sub> from 0.74 to 6.42 eV at temperatures from 40 to 350 K using dual rotating compensators ellipsometry. The sample is a large area WSe<sub>2</sub> thin film grown on sapphire substrate by low pressure chemical vapor deposition. The sample's quality was confirmed by AFM, Raman, photoluminescence spectra, and spectroscopic ellipsometry. The CP energies were determined by standard lineshape analysis of numerically calculated second derivatives of  $\epsilon$  with respect to energy. Several CPs are distinguished at low temperature where the CPs are blue shifted and sharpened as a result of the reduced lattice constant and electron-phonon interaction. Especially, by carefully examining the region from 1 to 2 eV, the existence of three peaks can be diagnosed, which can be identified by the combination of a neutral exciton A, a negatively charged exciton A<sup>-</sup>, and a superposition of biexciton emission (AA) with defect-bound exciton

emission (L1). The *B*-exciton structure also shows a significantly asymmetric lineshape, indicating contributions of at least two CP structures. These results will be useful for physical understanding and application for the device based on WSe<sub>2</sub>.

**TF-WeP-10 Surface-treated ZnO/Ag/ZnO Mesh Electrodes for High-efficiency Blue TADF OLEDs**, *Ho Jin Lee, N. Kim*, Korea University, Republic of Korea; *W. Ren*, Korea University, China; *S. Hong, H. Kim, T. Kim*, Korea University, Republic of Korea

The demand of highly efficient and deformable flexible organic light-emitting diodes (FOLEDs) has recently increased drastically with the rapid advance of wearable devices. To develop a high-performance FOLEDs, the development of flexible transparent conductive electrodes (FTCEs) and emitting materials is essential. Mesh-structured electrodes are one of the promising FTCEs as substitute of indium tin oxide [1,2], owing to their excellent optoelectrical properties with highly deformable mechanical properties. Despite such remarkable properties, a few characteristics other than transmittance or deformability must be considered to practically use mesh electrodes for demonstration of high-performance FOLEDs [3]. One of the intrinsic problems is the bumpy surface of mesh pattern, which induces leakage current or charge accumulation. Yet, PEDOT:PSS or SU-8 are used for planarize the rough surface however, these layers are lack of conductivity, which increases the turn-on voltage of FOLEDs [4]. In addition to the rough surface issue, the work function mismatch between the FTCE and organic transport or injection layers deteriorate the charge injection efficiency.

In addition to the development of FTCEs, it is hard to get high-performance of FOLED without the development of emission layer. To date, thermally activated delayed fluorescence (TADF) emitters have shown improved device performance however, few research have been focused on verifying the stability of the materials.

Herein, high-performance and flexible blue TADF OLEDs are proposed using nickel (Ni)-doped zinc oxide (ZnO)/silver (Ag)/ZnO mesh (Ni:ZAZ) electrode and a boron-based TADF emitter. The Ni doping is conducted through co-sputtering process of ZnO and Ni dopants. As shown in Fig. 1, the Ni:ZAZ mesh electrode shows remarkably high optical transparency (>90%), and low sheet resistance (<10 Ω sq<sup>-1</sup>), together with superior flexibility. Additionally, the increase of work function (4.8 eV → 5.1 eV) is observed via surface doping. Notably, the similar (or enhanced) optical and electrical property is observed after Ni doping, which indicates the effective penetration of Ni dopant to the surface of ZnO. The Ni:ZAZ mesh electrode is then applied as an anode of flexible OLEDs with no additional layers for planarization.

We also synthesized a boron-based deep blue TADF dopant material in powder for thermal evaporation system, and co-evaporated with the host material. As a result, the proposed FOLEDs exhibited superior device efficiency, which is attributed to the enhanced opto-electrical properties of Ni:ZAZ mesh electrode and highly efficient boron-based TADF emitter material.

**TF-WeP-11 Low Power Consumption in Superlattice-Like NiOx/GeSb Multilayer Film for Phase Change Memory Application**, *Tae Ho Kim, T. Kim, K. Yoo, H. Lee, S. Park, D. Kim, J. Choi, T. Kim*, Korea University, Republic of Korea

As computing technologies such as big data, artificial intelligence and machine learning develops, the development of memory device that stores and processes vast amounts of data is also required. From various performance of memory device, phase change memory (PCM) is the powerful candidate for next-generation memory. Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST-225) based PCM has outstanding performance such as non-volatility, long write endurance and high inherent scalability with existing complementary metal-oxide-semiconductor process. Despite its advantages, the GST-225 based PCM is hindered by reliability such as low switching speed, low crystalline temperature, and resistance drift.

In this study, we propose GeSb-based phase change memory device that can obtain a fast switching speed, owing to the fragile Sb-Sb bond while excluding Te atoms that degrade repeatability of memory operations due to high vapor pressure and low melt point. In addition, we insert the NiOx layers on the GeSb layer to generate the thermal boundary resistance (TBR) at the interface of the GeSb layer and the NiOx layer. The superlattice-like NiOx/GeSb multilayer film has the higher crystallization temperature than the single layer of GeSb and suppresses heat dissipation by TBR to efficiently utilize the heat required for phase change in GeSb layer. The adding of NiOx can improve the stability of GeSb material and lower power consumption phase change memory devices. The results of the I-V sweep

from PCM devices with different structures. The threshold voltage of the NiOx/GeSb superlattice PCM device is 1.6 V, which shows significantly lower power than the GeSb-based PCM device (~ 3.4 V). Consequently, NiOx/GeSb multilayer might show low power consumption behavior on pulse operations and thermal stability by inserting NiOx layers.

**TF-WeP-12 Hydrothermally Deposited Biochar Coating on the Surface of a Plain Steel**, *Yong Gan, C. Negrete*, California State Polytechnic University Pomona; *W. Hung, K. Anderson*, California State Polytechnic University, Pomona; *J. Gan*, University of California, Los Angeles; *C. Grice*, University of Toledo

**Hydrothermally Deposited Biochar Coating on the Surface of a Plain Steel**

Yong X. Gan<sup>1,\*</sup>, C.J. Negrete<sup>1,2</sup>, Wesley Hung<sup>1</sup>, Kevin R. Anderson<sup>1</sup>, Jeremy B. Gan<sup>3</sup>, Corey R. Grice<sup>4</sup>

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## Abstract

In this work, a sugar-derived, hydrothermally carbonized biochar coating on an ANSI-1018 low carbon plain steel was prepared. First, hydrothermal carbonization of 10% sugar (sucrose) solution at 200°C and 1.35 MPa for 4 h was performed to generate a carbon rich biochar coating on the steel. Then microstructure and composition of the biochar coating were studied using scanning electron microscopy (SEM). The corrosion resistance of the steel with coating and without coating was evaluated by comparing the Tafel slopes of each sample measured in seawater. In addition, the corrosion current and the potential of corrosion were calculated to show the effect of the carbonized biochar coating on the corrosion behavior of multiple steel specimens. It was found that hydrothermal carbonization of sugar generated a dense carbon-rich biochar layer on the surface of the steel. This biochar layer is corrosion resistant as shown by the increase in the corrosion potential and the decrease in the corrosion current for the low carbon steel. This hydrothermally produced carbon layer is like a passivation coating on the steel to protect the steel from corrosion. The change in the seawater corrosion behavior of pure iron due to the existence of such a carbonized layer was also studied. The carbonized coating did not reduce the corrosion current obviously, but caused the positive shift in the corrosion potential. The integrity of the coating is thickness dependent. For thick coating, localized cracking was found and the exposure of the steel surface was observed under electron microscope. The cracking of the biochar coating resulted in the iron oxide formation on the surface of the steel in the ambient environment.

Key words: Hydrothermally carbonized biochar coating; low carbon steel; seawater corrosion resistance; corrosion potential; corrosion current; Tafel slope.

**TF-WeP-13 Comparison of Continuous and Pulsed Low Power DC Sputtered Ti Thin Films**, *Anna Maria Reider*, University of Innsbruck, Austria

In this work, titanium thin films with thicknesses up to 105 nm were deposited on borosilicate glass implementing low power continuous (25 W) and pulsed (85 W) DC magnetron sputtering. The characteristics of the resulting films were studied via atomic force microscopy (AFM), X-Ray Photoelectron Spectroscopy (XPS), VIS spectroscopy and four-point-probe measurements. For both the continuous and pulsed sputtering, the films exhibit a comparably low surface roughness with no visible column-and-void structure. Additionally, the films show overall high reflectivity and constant transmission and reflectance for wavelengths in the visible range of the spectrum. The electric resistivity could be measured even for film thicknesses down to the single nanometer range and approaches the bulk value for higher film thicknesses. The low power regime of magnetron sputter deposition does not only offer the possibility of studying the development of physical characteristics during the growth of ultra-thin films but also provides the advantage of extremely low heat development and no mechanical force on the substrate during the coating process. This

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concept may hence be utilized in temperature-sensitive coating processes, such as the fabrication of conductive coatings on flexible antennas.

**TF-WeP-14 Sputter-Deposited High Entropy Alloy Thin Film Electrocatalyst for Enhanced Oxygen Evolution Reaction Performance,** *Siang-Yun Li*, National Cheng Kung University (NCKU), Taiwan; *T. Nguyen*, National Cheng Kung University (NCKU), Taiwan, Viet Nam; *Y. Su, C. Lin, Y. Huang, Y. Shen, C. Liu, J. Ruan, K. Chang, J. Ting*, National Cheng Kung University (NCKU), Taiwan

Thin film catalyst, giving a different morphology, provides a significant advantage over catalyst particles for gas evolution reaction. Taking the advantages of sputter deposition, we hereby report high entropy alloy (HEA) thin film electrocatalyst for oxygen evolution reaction (OER). We investigate the catalyst characteristics not only in its as-deposited state but also during and after the OER. For comparison, unary, binary, ternary, and quaternary thin film catalysts were prepared and characterized. The surface electronic structure modification due the addition of a metal is studied experimentally and theoretically using density function theory calculation. We demonstrate that sputtered FeNiMoCrAl HEA thin film exhibits OER performance superior to all the reported HEA catalysts with robust electrocatalytic activity having a low overpotential of 220 mV at 10 mA cm<sup>-2</sup>, and excellent electrochemical stability at different constant current densities of 10 and 100 mA cm<sup>-2</sup> for 50 h. Furthermore, we have investigated the microstructure transformation during the OER, which is important for the understanding of the OER mechanism provided by HEA electrocatalyst. Such finding would contribute to future catalyst design.

**TF-WeP-15 Fabrication of Antimicrobial and High Transparency TiO<sub>2</sub> Thin Films by Superimposed High Power Impulse and Medium Frequency Magnetron Sputtering,** *Bih-Show Lou*, Chang Gung University, Taiwan; *W. Chen, J. Lee*, Ming Chi University of Technology, Taiwan, Republic of China; *W. Diyatmika*, Leibniz Institute of Surface Engineering, Germany; *J. Lu*, Ming Chi University of Technology, Taiwan, Republic of China; *C. Chang, P. Chen*, Institute of Nuclear Energy Research, Taiwan

Titanium dioxide thin film has been widely studied and applied because of its excellent photocatalytic, antimicrobial, and optical performance. The application of TiO<sub>2</sub> films as the antibacterial and transparent coatings deposited on touch screens and touch panels by sputtering methods for preventing the infection of microorganisms is required. The high power impulse magnetron sputtering (HiPIMS) technique is characterized by its ability to fabricate oxide thin films with dense microstructure and better film quality. In this work, critical processing parameters including, target poisoning ratio/oxygen gas flow rate, peak power density, substrate bias, substrate heating temperature, and gas pressure for achieving high antimicrobial ability, transparent and anatase rich TiO<sub>2</sub> films with more {001} facets by the superimposed HiPIMS and medium frequency (MF) magnetron sputtering techniques were discussed. This study explores the superimposed HiPIMS-MF deposition approach to produce the TiO<sub>2</sub> thin films, which exhibit good adhesion (> 30N critical load), high transmittance (>80%), and 100% antimicrobial ability in large-scale production.

**TF-WeP-16 Annealing Effects of Multi-Layered Titanium Dioxide (TiO<sub>2</sub>) Thin Film by Sol-Gel Method,** *Moniruzzaman Syed, J. Gibson, D. White*, LeMoyne-Owen College

Titanium dioxide (TiO<sub>2</sub>) multilayer thin films (2-layers) have been deposited on glass substrate by using Sol-Gel technique. TiO<sub>2</sub> has anatase crystal structure and the grain size is increased when the annealing temperature have been increased, according to XRD results. Four point probe measures the electrical properties showed that the average resistivity is decreased with increasing the annealing temperature. Optical properties of the films were measured by UV-Vis spectroscopy which showed the high transmittance in the visible region. The optical band gap energies were found to be decreased with increasing annealing temperature. These properties showed that the multilayer films of TiO<sub>2</sub> can be enhanced the properties of optoelectronic devices.

**TF-WeP-17 Impact of Micron Structures, Substrates and Protective Covering on the Thermochromic Property of Vanadium Dioxide Grown by Magnetron Sputtering,** *Jazmyne Smith, A. Adedeji*, Elizabeth City State University

Vanadium dioxide is known for its optical and electrical switching characteristics at a transition temperature of about 68°C. Thin films of pure vanadium was deposited by DC magnetron sputtering on crystalline and amorphous quartz substrates and subsequently oxidized in N<sub>2</sub>/O<sub>2</sub> ambient at 500°C for 4 hours at a pressure of 800 milli-torr. Microscopic structures

(circles and stars) were defined by photolithography techniques before sputtering vanadium on some of the substrates. Transmittance of 160 nm thin films on quartz substrates jumped reversibly from about 35% to less than 5% at a wavelength of 1600 nm. The star and circular structured samples have higher transmittance but less change in transmittance at transition temperatures which are higher than for plain thin films. X-ray diffractometry, Scanning Electron Microscopy with Energy Dispersive and Atomic Force Microscopy are some of the techniques employed for surface characterization of the samples. Optical characteristics were determined with filmetrics equipment that measured both the transmittance and reflectance simultaneously in the range 200 – 1700 nm. Electrical transport characteristics of the plain films were determined with Ecopia Hall Effect measuring system.

**TF-WeP-18 Topology Phase Diagram of Metal Oxides Nanoflake in Skyrmion-based Spintronic Devices,** *D. Huang, Y. Lai*, Dept. Materials Sci & Eng., National Cheng Kung University,, Taiwan; *C. Kaun*, Research Center for Applied Sciences, Academia Sinica, Taiwan; *Yen-Hsun Su*, Dept. Materials Sci & Eng., National Cheng Kung University,, Taiwan

Half century ago, a kind of quasi-particle is observed from the surface of magnetic material. Such topologically protected quasi-particle, skyrmion, is known to produce via spintronic in various magnetic materials. Skyrmion with wide applicability has unique properties in many fields, including particle physics and optoelectronics devices and so on. These special properties allow skyrmion to exist in the interface of devices with ultralow accumulation rate and high transportation rate. However, types of skyrmion and magnetic domain wall such as Néel-type skyrmion, Blöch-type skyrmion and multiple wormhole domain wall which modulated by parameters of Dzyaloshinskii-Moriya interaction (DMI), saturation magnetization, and stiffness coefficient are elusive and unexplored. The most important thing is building the phase diagram of skyrmion from featured parameters for modulating the appearance of skyrmion by presenting magnetization vortex. Here, we calculate the parameters of skyrmion to estimate and plot out the phase diagram of skyrmion in fine scale for precisely predict the type of skyrmion and the vortex of magnetization by Object Oriented Micro Magnetic Framework (OOMMF). We classify the different kinds of magnetic domain wall by the skyrmion number N, which is calculated by Python. Skyrmion creates a stable and high capacity in the applications of storage devices. The skyrmion crystals with nanoscale are much smaller than the traditional magnetic crystals created by lithography techniques. After getting the skyrmion phase diagram, the shapes, and states of the skyrmion can be changed by adjusting the parameters easily. Different shapes of the skyrmion also be used in very mini-size logic devices since the size of skyrmion allows to carry higher information density in skyrmion-based spintronic devices.



## Biomaterial Surfaces & Interfaces

### Room Naupaka Salon 4 - Session BI-WeE1

#### Bioimaging and Bionanotechnology

Moderator: David G. Castner, University of Washington

#### 5:40pm BI-WeE1-1 Machine Learning for Prediction of TOF-SIMS Spectra of Peptides, *Satoka Aoyagi*, Seikei University, Japan **INVITED**

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is one of the most powerful surface analysis methods because ToF-SIMS provides molecular 3D imaging with high spatial resolution and detailed chemical structures. ToF-SIMS has extremely rich chemical information and so that it is often difficult to extract all of the important information from ToF-SIMS data by manual analysis. Multivariate analysis techniques such as principal component analysis have successfully been applied to TOF-SIMS data interpretation [1] and are generally useful for understanding TOF-SIMS results. Moreover machine learning and deep learning methods have been applied to ToF-SIMS data interpretation [2]. In order to interpret ToF-SIMS spectra, the processes of the data analysis should be opened, but most of the deep learning methods do not provide readable information on the analysis processes. Through a VAMAS (Versailles Project on Advanced Materials and Standards) interlaboratory study, the identification of peptide sample TOF-SIMS data by machine learning (Fig. 1) was investigated. In this study, unknown peptide spectra were predicted using Random Forest [3]. Moreover, this method can be applied to the prediction of other organic materials by improving the data format.

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#### 6:20pm BI-WeE1-3 Strategy for Constructing Accurate 3D NanoSIMS Depth Profiling Images of Cells Despite Lateral Variations in Surface Erosion, *M. Brunet, B. Gorman, Mary L. Kraft*, University of Illinois Urbana-Champaign

We have developed a strategy for constructing accurate 3D NanoSIMS depth profiling images of cells when the rate of surface erosion varies laterally. To accomplish this, we reconstruct the morphology of the cell each time a depth profiling image was acquired from the secondary electron images acquired in parallel with the negatively charged secondary ions during NanoSIMS depth profiling. Then the morphologies created for every imager plane in the depth profile are adjusted so the height of the cell at every x, y location decreases each time a new image was acquired. Finally, these reconstructions of the cell's morphology are used to shift the voxels in the 3D NanoSIMS images to the correct height. This strategy was validated by comparing morphology reconstructions for secondary electron depth profiling images acquired from a cell with focused ion beam - secondary electron microscopy and AFM data acquired from the cell before depth profiling. The general shape and relative height of the reconstructed cell morphology was in good agreement with the AFM data. Application of this strategy to 3D NanoSIMS depth profiling data of a metabolically labeled mammalian cell produced visually accurate 3D images of the intracellular  $^{18}\text{O}$ -cholesterol and  $^{15}\text{N}$ -sphingolipids distributions. Moreover, transport vesicles and organelle membranes containing  $^{18}\text{O}$ -cholesterol and  $^{15}\text{N}$ -sphingolipids could be more clearly visualized. Accurate 3D NanoSIMS images showing the distributions of molecules of interest within cells may now be constructed when the sputter rate varies laterally and without requiring the collection of topography data prior to depth profiling.

#### 6:40pm BI-WeE1-4 Multimodal Studies of Cellular Membrane Chemistry using GCIB-SIMS, *John Fletcher*, University of Gothenburg, Sweden

Changes in the lipid membrane of cells has implications for cell survival, function and in the case of diseases treatment efficacy. For example lipid changes in secretory cells can alter exocytosis with implications for neuronal communication while cell membrane composition can effect permeability to pharmaceuticals, along with mechanical properties that may influence cell mobility, and in the case of cancer cells, metastatic potential.

Secondary ion mass spectrometry (SIMS) provides unique opportunities for analysing cells with both high spatial resolution, surface sensitivity and chemical specificity. The ability to characterise the cellular membrane lipid composition has been greatly enhanced by the introduction of gas cluster ion beams (e.g.  $(\text{CO}_2)_{6k}^+$ ) that provide increased secondary ion signals for intact biomolecules.

The presentation will illustrate the capabilities of GCIB-SIMS analysis of cell samples in studies of cancer and Parkinson's disease and highlight the complementarity of multimodal analysis using fluorescence microscopy and electrochemical analysis approaches.

#### 7:00pm BI-WeE1-5 Self-assembling Antimicrobial Peptide Coatings for Prevention of Infections, *Zhou Ye*, The University of Hong Kong

Antimicrobial peptides (AMPs) are promising candidates as antimicrobial coatings due to its broad-spectrum activity, low bacterial resistance, and good biocompatibility. Previous works have explored the coatings of AMPs by covalent immobilizations or the introduction of an intermediate layer/nanoparticles. However, the fabrication processes were costly, complicated, and non-versatile, which limited the clinical applications. We have developed new strategies to form strong physical coatings by self-assembled AMPs and determined the significant roles of self-assembly and secondary structures in forming the AMP coatings. The dominant interactions between self-assembled AMPs and the substrate surfaces were studied to be hydrogen bonding, instead of electrostatic forces. We also correlated the self-assembly dynamics of AMPs to the antimicrobial activity by comparing L and D enantiomers of one model AMP, GL13K in aqueous solutions or interacting with phospholipid double layers and other bacterial envelope components. With the understanding of the coating mechanisms, we applied the self-assembled GL13K peptide coatings on various substrates, such as etched titanium implants, dentin, enamel, or mineralized collagen/hydroxyapatite. The AMP coatings presented excellent antimicrobial activities in mouse models or on *ex vivo* tooth with potentials in clinical settings.

#### 7:40pm BI-WeE1-7 Development of a Process for Flame Retardant Coating of Textiles with Bio-Based Anchor Peptides, *Rahel Krause, I. Bettermann, R. Paul, T. Gries*, Institut of Textiltechnik of RWTH Aachen University, Germany; *M. Nöth, L. Feng, U. Schwaneberg*, Institute of Biotechnology of RWTH Aachen University, Germany; *C. Hummelsheim, L. Kampas*, Klevers GmbH & Co. KG, Germany

The fire protection of materials has an important role in our everyday life and covers a highly diverse spectrum of substances, materials and fields of application. Important fields of application for fire protection, especially in public areas, are construction and transport, electronic devices, furnishings and textiles (e.g. applications for occupational safety, carpets, curtains, upholstery, insulation and technical applications in outdoor areas). The efficient and durable finishing of the materials with flame retardant additives is crucial to ensure effective fire protection. Many of the flame retardant additives currently used are based on halogens, bromides, chlorides, phosphates or antimony. However, these flame retardants are harmful to the environment and/or health. Therefore, the use of these flame retardants is already being restricted by EU directives (e.g. REACH regulation) and it is foreseeable that they will be further restricted in the future. To keep up with this development, innovative and sustainable solutions must be developed in the short term. The amount of flame retardant additives that are harmful to the environment and health must be reduced. In the medium term these harmful additives must be completely replaced by sustainable flame retardant additives that are not harmful to the environment and health. This paper describes research results to reduce the amount of additives in the short term.

In order to reduce the amount of additives used, an innovative refinement process is being developed. In a first step, the flame retardant additives are combined with bio-based adhesion promoters (anchor peptides). Anchor peptides bind with high selectivity, binding strength and occupancy density to a broad portfolio of materials (e.g. synthetic polymers, metals, ceramics, natural materials) and enable the finishing of the materials with a broad spectrum of functional units (e.g. flame retardant additives). Material functionalisation by anchor peptides is energy-efficient and resource-saving at room temperature in aqueous solution and is scalable in its production.

Based on these developments, in this paper, a finishing process is presented with which flame retardant textiles can be equipped with bio-based anchor peptides. A requirements outline for the new finishing process is described. Established processes (e.g. foulard, coating machine, roller application) are compared with each other and evaluated with regard to the requirements and their suitability. The most suitable process is then designed and a laboratory scale as well as an industry scale concept are presented.

8:00pm **BI-WeE1-8 Impact of UV-C Exposure on Single-use Mask Integrity for Reuse to Address PPE Shortages Within At-Risk Communities**, S. Ananthkrishnan, E. Rhoades-Clark, V. Mitchell, Heather Canavan, University of New Mexico

The COVID-19 pandemic significantly disrupted supply chains in the global economy. The American Indian populations of the Southwest United States have been particularly hard hit, due to multi-generational housing, lack of access to running water, and insufficient protective personal equipment (PPE). The limited availability and price of commercial N-95 masks led the public to reuse their masks, rather than treating them as single-use equipment. In turn, this led users to experiment on their own on how best to sterilize their masks for repeated usage, including both low-tech (UV sterilization with sunlight, washing with detergent or soap) and high-tech approaches (fogging with disinfectant, UV lamp apparatuses, etc.). Recommendations by the CDC and mask manufacturers often contradicted each other on best practices; the CDC recommended reusing single-use masks through UV sterilization, while mask manufacturers indicated otherwise due to concern of material degradation. We hypothesized that exposure to UV-C (254 nm) would damage non-woven single-use mask fibers such as those found in N-95, KN-95, and surgical masks due to spalling, which would lead to increased mask pore size, and therefore decreased filtration efficiency. However, woven fabric masks should not suffer spalling from UV exposure due to a difference in the fabrication of the fibers. To test our hypothesis, we subjected N-95, KN-95, surgical, and fabric masks to UV-C exposure for appropriate time scales (0-24 hours) to simulate repeated exposure for sterilization followed by a close inspection of layers using Scanning electron Microscopy (SEM). We examined the pore sizes and density, fiber integrity, and surface morphology of the layers that comprised each mask and compared the resulting damage. We found that limited exposure to UV-C (15 minutes/4 exposure cycles) would result in significant damage to all the masks except for fabric masks. As the acute experiences of the pandemic have receded, the cost and availability of PPE have normalized, and well-funded populations have ceased to focus on the issue of sterilization and reuse. However, members of at-risk communities are still grappling with ways to best adapt to supply chain shortages and masking needs. Therefore, these results will be of interest to those seeking to understand how UV-C affects the reusability of various mask types.

## Thin Films

### Room Naupaka Salon 5-7 - Session TF-WeE

#### Emerging Topics: Growth and Properties of Electronic Materials, 2D Layers, and Metallic-glass Thin Films

Moderator: Ludvik Martinu, Polytechnique Montréal, Canada

5:40pm **TF-WeE-1 Recent Development of Biocompatible Thin Film Metallic Glasses and High Entropy Alloy Coatings**, B. Lou, Chang Gung University, Taiwan; *Jyh-Wei Lee*, S. Ho, Ming Chi University of Technology, Taiwan, Republic of China; Y. Yang, National Taipei University of Technology, Taiwan; J. Chu, National Taiwan University of Science and Technology, Taiwan

INVITED

Biomedical Ti, Ti-6Al-4V alloys, and 316L stainless steels are widely used in biomedical devices for various parts of the human body. It has been reported that the corrosion and erosion-corrosion failures of such biomedical implants are very critical. Therefore, the surface modification of these implants is important for improving their corrosion resistance and extending their surface lifetime. Recently, thin film metallic glass (TFMG) and high entropy alloy films (HEAF) have been intensively studied due to their good physical and mechanical properties, such as high strength and excellent corrosion resistance. The applications of biocompatible TFMGs and HEAFs as surface modification coatings on the biomedical Ti, Ti-6Al-4V alloys, and 316L stainless steel have become an important research topic.

In this work, several Zr-, Ti-, Fe- and W-based TFMGs, TiZrNbTaFe, and TiZrNbTaMo HEAFs were fabricated using the magnetron sputtering method through the collaborative work of several research groups in Taiwan. The in-vitro and in-vivo studies of these biocompatible TFMGs and HEAFs were explored. The application of TFMGs on the surface of surgical instruments, such as dermatome and endodontic files were discussed. For the in-vivo animal study, the TiZrNbTaFe HEAFs coated cp-Ti implants were inserted into the femur of Sprague-Dawley rats. The surrounding bone volumes of implants were examined by a micro-computed tomography after 4- and 12-weeks implantation. The tensile pull-out test was performed together with the histological analysis to investigate the bone tissue regeneration and bone tissue adhesion ability. Better osseointegration

ability and biocompatibility were found for of the HEAF coated cp-Ti implants. Some possible applications of biocompatible TFMGs and HEAFs on biomedical instruments were also proposed in this work.

6:20pm **TF-WeE-3 Influence of Relatively High Density Background Carriers on Photo-Dember Effects at the Surfaces of *n*-type and *p*-type InSb Single Crystals Observed with the Use of Terahertz Time-Domain Spectroscopy: A Study on Ultrafast Photogenerated Carrier Diffusion**, Hideo Takeuchi, Osaka Metropolitan University (formerly Osaka City University), Japan; T. Sumioka, Osaka City University, Japan

Carrier-diffusion phenomena are essential issues on electronic and optoelectronic semiconductor devices. Ultrafast optical spectroscopy, which progresses with the development of femtosecond pulse-laser technology, is effective to investigate transient carrier diffusion. Terahertz electromagnetic waves, which are emitted from surfaces of narrow gap semiconductors with the use of illumination of femtosecond laser pulses, provide information on the photogenerated carrier diffusion process, the so-called photo-Dember effects. The photo-Dember effects result from the difference in a diffusion coefficient connecting with mobility between electrons and holes [1]. The diffusion-coefficient difference builds up transient polarization producing the terahertz wave. In a typical narrow gap semiconductor, InSb, the emission process of the terahertz wave is dominated by the photo-Dember effects. We, here, point the fact that the earlier terahertz time-domain spectroscopic works in InSb was focused on lightly doped samples [2]. It is reasonable to assume that the diffusion process is strongly influenced as the background carrier density is increased. This is because the mobility depends on the carrier density [3]. Accordingly, for verifying the above assumption, it is meaningful to clarify the characteristics of the terahertz wave emitted from the InSb crystals with the relatively high background carrier density. In the present work, we investigated the terahertz-wave emission from *n*-type and *p*-type InSb single crystals with relatively high major carrier density of  $2 \times 10^{17} \text{ cm}^{-3}$ . We observed the terahertz wave originating from the photo-Dember effects in the *p*-type InSb crystal. In contrast, we found that the terahertz wave originating from the photo-Dember effects disappears in the *n*-type InSb crystal. According to Ref. 2, the photo-Dember voltage  $V_D$  is proportional to  $\ln[1 + \{(b+1)\Delta n / (bn_0 + p_0)\}]$ , where  $n_0$  and  $p_0$  is background electron and hole densities, respectively, and  $b$  is the ratio of the electron mobility to hole mobility:  $\mu_e/\mu_h \approx 100$ . In addition, the quantity  $\Delta n$  is the photogenerated electron density. It is apparent that, in highly doped InSb crystal,  $bn_0$  is much larger than  $p_0$ , which reduces the photo-Dember voltage  $V_D$ . We, therefore, attribute the origin of the observed difference between the *n*-type and *p*-type InSb crystals to the fact that the photo-Dember voltage is suppressed in the case where the background electron density is relatively high.

- [1] H. Dember, Z. Physik vol. 32, 554 (1931), 856 (1931), vol. 33, 207 (1932).
- [2] P. Gu *et al.*, J. Appl. Phys. vol. 91, 5533 (2002).
- [3] S. Watanabe, J. Phys. Soc. Jpn. vol. 50, 1049 (1981).

6:40pm **TF-WeE-4 Theoretical Analysis on Alternative Pathway for Low Temperature Atomic Layer Deposition of Nitrides**, J. Lee, S. Lee, Bonggeun Shong, Hongik University, Republic of Korea

Atomic layer deposition (ALD) enables various advantages in deposition of thin films such as excellent step coverage and conformality. ALD is composed of alternative cycles of metal precursors and counter-reactants, whose self-limiting chemical reactions on the substrate surfaces determine the process conditions for the deposition. For example, in ALD of titanium nitride (TiN), TiCl<sub>4</sub> with NH<sub>3</sub> is most commonly used; however, temperatures as high as 500 °C is often required in such process to decrease the contamination of the TiN films by Cl. High thermal budget is often an issue also for other nitride ALD processes in general. Recently, a new recipe for TiN ALD is reported to simultaneously decrease both the deposition temperature and the Cl contamination, by introducing a H<sub>2</sub>S pulse between TiCl<sub>4</sub> and NH<sub>3</sub> reactants [1]. In this study, we conducted a theoretical analysis on comparing conventional versus alternative pathways for nitride ALD, using density functional theory (DFT) calculations. It was found that introduction of H<sub>2</sub>S may decrease the activation energy of the ligand exchange reaction by N for some elements, but not for all nitride species. Our study may be utilized toward development of the new efficient method for ALD of nitride thin films with lower thermal budget.

- [1] ACS Appl. Electron. Mater. 2021, 3, 999.

# Wednesday Evening, December 14, 2022

7:00pm **TF-WeE-5 Morphology and Statistics of Wet-Etched Gallium Oxides (Doped and Undoped) Deposited by RF Magnetron Sputtering**, *Jazmyne Smith, A. Adedeji*, Elizabeth City State University

Gallium oxide is an ultra-wide energy gap, transparent semiconductor with many potential applications including high power electronics and optoelectronics device fabrications. Doped and undoped gallium oxide thin films were deposited on 2-inch silicon substrates by RF-magnetron sputtering with 200 W rf-power, at substrates temperature of 570°C, chamber pressure of 10 milli-torr, and in Ar/O<sub>2</sub> gas mixtures. Wet etching was achieved with phosphoric acid at elevated temperature. Etch rates of the films were determined with micron sizes circular structures defined by photolithography and diced. Etch rates greater than 180 nm/min were measured with contact profiler. Surface morphology, roughness and atomic composition of etched layers were monitored with Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Atomic Force Microscopy (AFM). Statistical analysis of the etch rate, issues associated with wet-etching gallium oxide and its sensitivity to dopants and deposition conditions is discussed.

7:40pm **TF-WeE-7 Spectroscopic Evidence of Highly Correlated Electrons in VSe<sub>2</sub>**, *T. Yilmaz, E. Vescovo*, National Synchrotron Light Source II, Brookhaven National Lab; *J. Sadowski*, Center for Functional Nanomaterials, Brookhaven National Lab; *Boris Sinkovic*, University of Connecticut

We present detailed high-resolution angle-resolved photoemission experiments on thin VSe<sub>2</sub> films grown on single-layer graphene (Gr) and highly ordered pyrolytic graphite (HOPG) substrates under various conditions. The surface electronic structure of optimally grown film on HOPG hosts three distinct features: presence- of the energy gap at the Fermi level, a high-temperature spectral kink in the dispersion of the band close to the Fermi level and appearance of the quasiparticle peak in EDC spectra in vicinity of the Fermi level. These observations combined indicate strong electronic correlation that are usually attributed to the presence of the superconducting state. Temperature evolution of the quasiparticle peak and the Fermi gap also follow the trend observed in high-Tc superconductors. Namely, progressive quenching of the quasiparticle peak, which persists up to ~100 K, and presence of the Fermi gap at higher temperatures, vanishing at ~150 K. These observations will aid the future efforts to induce the high-temperature superconductivity in transition metal dichalcogenides as well as understanding the physics of high-Tc superconductors in general.

8:00pm **TF-WeE-8 Exploring the Magnetoelectric Coupling at the Composite Interfaces of BaTiO<sub>3</sub>/CoFe<sub>2</sub>O<sub>4</sub>/BaTiO<sub>3</sub> Heterostructures**, *Venkata Puli*, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *R. Katiyar*, University of Puerto Rico; *A. Reed, M. McConney*, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *S. Heidger*, Air Force Research Laboratory, USA, United Arab Emirates

Magnetoelectric multiferroic biphasic system with robust ferroelectric and ferromagnetic response at room temperature would be ideally suitable for microelectronic and memory devices and spintronic applications. Multiferroic magnetoelectric BaTiO<sub>3</sub>-CoFe<sub>2</sub>O<sub>4</sub>-BaTiO<sub>3</sub> (BTO/CFO/BTO) heterostructures thin films were synthesized by pulsed laser deposition (PLD) on Pt(111)/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrate. High quality PLD thin films were grown by thermal annealing at 750 °C at oxygen partial pressure of 100 mTorr for 1 hour. Crystal quality and phase formation was monitored using X-ray diffraction (XRD), Raman measurements. XRD and Raman spectra examinations confirm the growth of polycrystalline heterostructures and coexistence of both perovskite BTO and spinel CFO phases in heterostructures at room temperature. X-ray diffraction (XRD) patterns and Raman spectroscopy confirms Scanning electron microscopy (SEM) was used to characterize the grain growth and thickness of the heterostructures. The surface quality/rms roughness values of the films were determined by atomic force microscopy (AFM). In order to obtain robust ME coupling at room temperature, we studied the BaTiO<sub>3</sub>-CoFe<sub>2</sub>O<sub>4</sub>-BaTiO<sub>3</sub> (BTO/CFO/BTO) tri-layer structure as a representative FE/FM/FE system. We report the ferroelectric, magnetic and ME properties of BTO/CFO/BTO trilayer nanoscale heterostructures having dimensions 140/80/140 nm, at room temperature. The presence of perovskite BTO and inverse spinel CFO peaks in the PFM and MFM measurements confirmed the ferroelectric and magnetic nature of these films at nanoscale. These nanostructures exhibit low loss tangent, large saturation polarization (P<sub>s</sub> ~ 99.86 μC/cm<sup>2</sup>), magnetization (M<sub>s</sub> ~ 51.48 emu/cm<sup>3</sup>) and a strong magnetoelectric coupling coefficient of ~274 mV/cmOe at a bias field of +90

Oe, at a frequency of 1 kHz at room temperature revealing them as potential candidates for nanoscale multifunctional applications.

8:20pm **TF-WeE-9 Structural stability of 2D II-V compounds**, *Lucia Guadalupe Arellano Sartorius*, The University of Electro-Communications (UEC Tokyo) and Instituto Politécnico Nacional, Mexico; *T. Suga, T. Hazama, T. Takashima*, The University of Electro-Communications (UEC Tokyo), Japan; *M. Cruz Irsson*, Instituto Politécnico Nacional, Mexico; *J. Nakamura*, The University of Electro-Communications (UEC Tokyo), Japan

In recent years, a variety of two-dimensional materials has been investigated and used for the development of new devices. Recently, it has been theoretically revealed that III-V compound semiconductor ultrathin films can exist stably. This structure has been shown to be different from that of a three-dimensional bulk. The ionic and covalent bond formation is thought to contribute to stability. Most of the two-dimensional materials discovered have been obtained as components of three-dimensional crystals that form layered structures, such as graphene. For example, compounds III-VI ultrathin films, which have been synthesized experimentally, are semiconductors with a layered structure in the three-dimensional bulk. Recently, it was reported that three-dimensional ZnSb with a layered structure can be made by electrochemical treatment of ZnSb, an II-V compound semiconductor. It was also theoretically suggested that ZnSb ultrathin films, can exist stably. However, the structural stabilization mechanism of compounds II-V ultrathin films has not been clarified. In this paper, we propose novel 2D materials, II-V compounds with the double bilayer (DB) structure (BeP, BeAs, BeSb, ZnP, ZnAs, ZnSb, CdP, CdAs, and CdSb) through the systematic analysis of electronic properties and phonon stabilities. Two types of DB stacking fashions were identified, which originate from the size effect due to the difference in the size of group II and group V atoms. The structural stabilities of these materials were systematically explained using indices employed in discussions of the stability of surface structures of compound semiconductors so far, the electron counting (EC) model, and the bond orbital (BO) model. It was found that the surface dangling bonds disappeared and stabilized with a semiconducting electronic state. In the III-VI, strong covalent bonds and lone pairs are formed and in group II-V, covalent bonds do not form as strongly as in group III-VI, and the structure changes depending on the difference in atomic radius between group II and group V atoms. However, in addition to the formation of covalent bonds, the ionic interaction between the bilayers is also thought to contribute to the stabilization of the system. In particular, it was shown that the relationship between atomic arrangement and electronic structure could consistently explain thermodynamical stability and stacking fashions.

## Biomaterial Surfaces & Interfaces

### Room Naupaka Salon 4 - Session BI-ThM1

#### Bacteria Biomaterial Interactions

**Moderator:** Sally M. McArthur, Swinburne University of Technology, Australia

#### 8:00am BI-ThM1-1 Why Mechanism Matters for Antimicrobial Biomaterials, *Bryan Coad*, The University of Adelaide, Australia **INVITED**

Many new antimicrobial biomaterials and coatings are being developed to address the need for implantable medical devices that prevent infections. Researchers, medical device manufacturers, and regulatory bodies are all interested in seeing "promising research results" translated to clinical use, but how are these claims evaluated? What experimental evidence is needed to improve translation of *in vitro* antimicrobial materials to the clinic?

It is illustrative to explore one of the most interesting classes of antimicrobial biomaterials: those which purport to have a contact-inhibition mechanism of action. These materials present covalently attached antimicrobial molecules from surfaces which inhibit or kill adhering microbes on contact. On the one hand, this surface design could open up new paradigms for antimicrobial therapy by virtue of making implants with potentially long-lasting antimicrobial activity. On the other hand, questions about whether these materials release antimicrobials and whether their surface activity would be nullified by protein fouling deserve serious investigation.

This presentation will delve into these issues by explaining why mechanism matters for antimicrobial biomaterials. It can also be viewed generally by biomaterials researchers from other fields who design bioactive surfaces using covalent surface immobilization and face questions about how to interpret the results of cellular assays. The presentation aims to raise awareness of the potential role of confirmation bias in antimicrobial susceptibility experiments which could lead researchers to unwittingly misinterpret antimicrobial mechanisms of action. It discusses ways to avoid this pitfall by proposing a methodological approach that emphasizes the importance of surface analysis. It is hoped that greater awareness of these issues will help "promising" *in vitro* antimicrobial surface technologies to have greater uptake in animal studies and clinical trials.

#### 8:40am BI-ThM1-3 High Throughput Screening for Antibiotics Using Droplet Microarrays, *W. Lei, A. Popova*, Karlsruhe Institute of Technology (KIT), Germany; *Michael Grunze*, Max Planck Institute for Medical Research, Germany; *P. Levkin*, Karlsruhe Institute of Technology (KIT), Germany

Multidrug-resistant (MDR) bacteria are a severe threat to public health and it is urgent to identify novel antibacterial compounds or pathogen-specific mixtures of antibiotics. In a first paper we reported the application of Droplet Microarrays developed by *Aquarray* as a cost effective high-throughput screening method for the evaluation of drug resistance of *Pseudomonas aeruginosa*, an opportunistic human pathogen /1/. The DMA consists of an array of hydrophilic spots divided by superhydrophobic borders to generate arrays of hundreds of nanoliter-sized droplets containing bacteria and different drugs for screening applications. A novel simple colorimetric readout method compatible with the nanoliter size of the droplets was established. Furthermore, the drug-resistance of *Pseudomonas aeruginosa* 49, a multi-resistant strain from an environmental isolate was investigated by screening of a small library containing 18 antibiotics. We were able to show that our methodology reproduces the data obtained with a 96 well microplate.

In the study reported here the search for antibiotic compounds was extended to screen over 2000 compounds for their antimicrobial properties against carbapenem-resistant *Klebsiella pneumoniae* and methicillin resistant *Staphylococcus aureus* (MRSA). A fast single-step detection method measured the inhibitory effect of the compounds on bacterial growth on the whole array. Six hit compounds, including coumarins and structurally simplified estrogen analogs are identified in the primary screening and validated with minimum inhibition concentration assay for their antibacterial effect. This study demonstrates that the DMA-based high-throughput screening system identifies potential antibiotics from novel synthetic compound libraries, and thus offering opportunities for development of new treatments against multidrug-resistant bacteria. Due to its simplicity, the method is suitable for rapid screens in personalized medicine. If time allows, further examples of rapid screens using DMA's which have been designed for personalized medicine will be presented.

/1/ *W. Lei, K. Demir, J. Overhage, M. Grunze, T. Schwartz, P. A. Levkin, Droplet-Microarray: Miniaturized Platform for High-Throughput Screening of Antimicrobial Compounds, Adv. Biosys., 2000073 (1-9), 2020*

#### 9:00am BI-ThM1-4 NAP-XPS Studies of a *Pseudomonas fluorescens* Bacterial Cell-Envelope and Other Biomaterial Surfaces, *Paul Dietrich*, SPECS Surface Nano Analysis GmbH, Germany; *N. Wasio, J. Hilton*, SPECS-TII, Inc.; *A. Thissen*, SPECS Surface Nano Analysis GmbH, Germany

Bacterial interactions with the environment are based on processes involving their cell-envelope. Thus, techniques that can analyze their surface chemistry are attractive tools for providing an improved understanding of bacterial interactions. One of these tools is x-ray photoelectron spectroscopy (XPS) with an estimated information depth of <10 nm for Al K $\alpha$ -excitation. XPS-analyses of bacteria have been performed for several decades on freeze-dried specimens to be compatible with the classical ultra-high vacuum conditions needed. A limitation of these studies has been that the freeze-drying method may collapse the cell structure. However, recent developments in XPS enable the analysis of biological samples at near ambient pressure (NAP-XPS) or as frozen hydrated specimens (cryo-XPS) in vacuum. In this talk, we present the analysis of bacterial samples from a reference strain of the Gram-negative bacterium *Pseudomonas fluorescens* using both techniques. XPS results and reference data from the bacterial strain are provided, and we propose to use planktonic cells of this strain (DSM 50090) as a reference material for surface chemical analysis of such bacterial systems. Further selected examples of NAP-XPS on other biomaterial surfaces will be presented.

#### 9:20am BI-ThM1-5 Tungsten Disulfide Bio-Nanofabrication Using Dissimilatory Metal-Reducing Bacteria *Shewanella oneidensis* MR-1, *Lauren Brady, J. Rees, S. Sawyer*, Rensselaer Polytechnic Institute

A type of bacteria known as dissimilatory metal-reducing bacteria (DMRB) can "breathe metals" to reduce heavy metal ions as part of their metabolic process. *Shewanella oneidensis* MR-1 is a type of DMRB that was first discovered in Lake Oneida, New York for its ability to reduce manganese, but has since been shown to reduce a variety of different electron acceptors including Fe(III), As(V), Cr(VI), and thiosulfate. In previous literature, *S. oneidensis* MR-1 has been grown anaerobically in media enhanced with sulfur and metal ions in order to produce several types of nanoparticles, including molybdenum disulfide, zinc sulfide, and cadmium sulfide.

This work presents the bacterial nanofabrication of tungsten disulfide particles using *S. oneidensis* MR-1. Bacterial nanofabrication synthesis, where the bacteria is the main catalyst for the production of nanomaterials, has numerous advantages compared to traditional chemical synthesis methods in that it can be conducted at room temperature and requires less chemical reagents in the reaction. One of the primary reasons to produce nanomaterials using bacteria is for a low resource input alternative to material fabrication for use in electronic devices.

Tungsten disulfide (WS<sub>2</sub>) is a two-dimensional transition metal dichalcogenide which has a bandgap transition from an indirect bandgap in the bulk material to a direct bandgap in its monolayer form. Tungsten disulfide has a range of potential applications including photodetection, biosensing, and chemical catalysis. These applications are further enhanced when control can be exerted over crystal growth and thickness.

An anaerobic batch culture of *S. oneidensis* MR-1 was incubated at room temperature in the presence of tungsten trioxide, resulting in the production of tungsten disulfide crystalline nanostructures of varied shapes and size. Several characterization techniques were employed to identify the material, including scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, absorbance spectroscopy and X-ray diffraction. In addition to confirming that tungsten disulfide can be produced by *Shewanella* bacteria, the data collected using these methods provide insight on the size, morphology, and photoresponse of nanoparticles generated this way.

#### 9:40am BI-ThM1-6 Nanoengineered Implant Surfaces with Enhanced Osteogenic and Antimicrobial Properties, *R. Shahbazian*, University of Illinois Chicago; *Tolou Shokuhfar*, University of Illinois at Chicago

The lack of osseointegration and implant-related infections are two major complications leading to failure of dental and orthopedic implants. Therefore, the development of effective implant surfaces able to display enhanced osteogenic activity and antimicrobial properties is required. This work aims to study the ability of bio-functionalized TiO<sub>2</sub> Nanotube engineered surfaces to induce osseointegration, and concomitantly, to

# Thursday Morning, December 15, 2022

avoid infection. TiO<sub>2</sub> NTs were bio-functionalized with calcium (Ca), phosphorous (P) and zinc (Zn), by reversepolarization anodization. Morphological and topographical features of NTs were observed through scanning electron microscopy (SEM), while surface chemistry was investigated by X-ray photoelectron spectroscopy (XPS). Biocompatibility studies were conducted with MG-63 and human mesenchymal stem cells (hMSCs) through MTT assay. Furthermore, cell morphology and cytoskeleton organization were observed by SEM and laser scanning confocal microscopy (LSCM). The osteoblastic differentiation capacity of hMSCs was studied by real-time PCR, as well as their angiogenesis ability by measuring the total release of vascular endothelial growth factor (VEGF). Finally, viability of *Staphylococcus aureus* (*S. aureus*) was assessed by live/dead bacterial viability assay. Results show that bio-functionalized TiO<sub>2</sub> nanotubular surfaces are biocompatible and modulated cell morphology. In particular, NTs enriched with Ca, P, and Zn, induced to significantly up-regulated levels of bone morphogenetic protein 2 (BMP-2) and osteopontin (OPN) genes of hMSCs, when compared to conventional NTs. TiO<sub>2</sub> nanotubular surfaces induced hMSCs to release a higher amount of VEGF, and significantly reduced the bacterial viability, both when compared to adequate Ti controls. Osseointegration and antibacterial properties have been shown in vitro and in vivo to improve when implants have modified surfaces that have biomimetic nanostructures designed to mimic and interact with biological structures on the nano-scale. Pre-clinical evaluations show that TiO<sub>2</sub> nanotubes (TNT), produced by anodization, on Ti6Al4V surfaces positively enhance the rate at which osseointegration occurs and TNT nano-texturization enhances the antibacterial properties of the implant surface. In conclusion, the superimposition of TiO<sub>2</sub> nanotubular- textured surfaces and their enrichment with Ca, P, and Zn, is a highly promising approach for the development of novel bio-selective and multifunctional implant surfaces able to improve osseointegration and avoid infection.

## Nanomaterials

### Room Naupaka Salon 4 - Session NM-ThM2

#### Nanofabrication and Nanodevices

**Moderator: Moon Kim**, The University of Texas at Dallas

**10:20am NM-ThM2-8 Harnessing Quantum Effects to Control Nanoscale Properties and Carrier Dynamics in Heterojunction Nanowires**, *Bryan Wong*, University of California, Riverside

The unique electronic properties of quantum-confined semiconducting nanowires hold great promise for their incorporation in next-generation transistors, circuits, and electronic devices. This reduction in dimensionality results in a dramatic change in their carrier dynamics and electronic structure, leading to novel properties such as ballistic transport and conductance quantization. One area of particular interest is the formation and understanding of electron gases in heterostructured nanowires which provides new avenues for exploring enhanced carrier dynamics in these materials.

To tailor these nanostructures with the desired physical properties, we must first understand their electronic properties as a function of size and material composition. To this end, we have developed a series of self-consistent predictive computational methods to calculate the properties of heterojunction electron gases in quantum-confined core-shell nanowires. Under certain conditions (depending on doping density and spatial geometry), we find that quasi-one-dimensional electron gases can localize at the corners of the nanowire, leading to carrier dynamics that are dramatically different than analogous bulk heterojunctions. In addition, we highlight several areas where many-body quantum effects play a significant role in these low-dimensional structures. In particular, we surprisingly find that simple theoretical approaches can (1) considerably overestimate the number of occupied electron levels, (2) overdelocalize electrons, and (3) significantly underestimate the relative energy separation between electronic subbands. Our results allow a guided understanding of electron carrier dynamics in heterostructure nanowires and further indicate that electron gases in free-standing nanoscale systems are qualitatively different from their bulk counterparts.

**10:40am NM-ThM2-9 A New Tool for Quantum and Nanoscale Materials Engineering**, *Kate McHardy, A. Bellew, G. Aresta, P. Blenkinsopp*, Ionoptika, UK

Quantum computing is the next great frontier of science. It has the potential to revolutionise many aspects of modern technology, including digital communications, "quantum-safe" cryptography, as well as 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 <sup>28</sup>Si matrix.

All working devices thus far have been fabricated using hydrogen lithography with an STM followed by atomic layer deposition. It 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 nanometre precision.

We report on a new commercial instrument for the fabrication of quantum materials and devices via ion implantation. A well-established technique in the semiconductor industry, ion implantation is both flexible and highly scalable. 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 ion dose delivered to the sample can be adjusted across a wide range, providing several materials engineering capabilities in a single tool. The deterministic implantation system allows single ion implantation with confidence levels as high as 98%. Operating in a high beam current mode provides direct-write capabilities such as isotopic enrichment and targeted ion-implantation of nanomaterials such as nanowires and graphene.

The liquid metal ion source and mass filtered column can implant many different elements with isotopic resolution. Available sources include silicon, erbium, gold, and bismuth, while many others of technological interest are in development.

**11:00am NM-ThM2-10 On-Surface Synthesis of Higher Acenes and Their Derivatives**, *R. Zuzak*, Jagiellonian University, Poland; *R. Dorel*, Institut Català d'Investigació Química, Spain; *I. Izydorczyk*, Jagiellonian University, Poland; *O. Stoica, R. Bliczek*, Institut Català d'Investigació Química, Spain; *M. Krawiec, Maria Curie-Skłodowska University*, Poland; *A. Echavarrén*, Institut Català d'Investigació Química, Spain; *Szymon Godlewski*, Jagiellonian University, Poland

In recent years we observe renewed interest in the development of electronics based on electron transport through single molecules. Among different families of organic species, acenes and nanographenes hold the special position. In particular a lot of effort is undertaken to achieve efficient synthetic strategies to generate such well-defined sections of graphene or graphene-like modules with diverse topological modifications. However, the reactivity/instability of numerous molecules as well as the insolubility of large polycyclic aromatic hydrocarbons limits the applications of conventional chemistry methods. An attractive alternative to the solution chemistry is based on its combination with the on-surface synthesis approach.

Acenes are attracting considerable interest due to the intriguing electronic properties originating from only one Clar  $\pi$ -sextet regardless of the molecule length. However, the unique  $\pi$ -electron system causes the molecules to be more reactive and less stable with increased number of annulated rings. Consequently this makes their synthesis, detailed characterization and functionalization a very challenging task. In recent years some successful strategies toward fabrication of higher acenes and their derivatives have been reported, e.g. some long acenes were stabilized and detected within noble gas matrices or in polymers. However, only recently the on-surface chemistry approach allowed for synthesis and characterization of higher acenes.

Herein we present the on-surface generation of higher acenes [1-2] and their derivatives [3], as well as the detailed study of their electronic structure on the Au(111) surface. Our method is based on the two-step dehydrogenation and thermally induced cyclization of a stable and easily handled molecular precursors.

High-resolution non-contact atomic force microscopy (NC-AFM) imaging was applied for the detailed visualization of the internal structure of the intermediates, as well as the target molecules with diverse topologies.

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Details on the electronic structure were revealed using high resolution dI/dV mapping.

The research was supported by the National Science Center, Poland (2017/26/E/ST3/00855; 2019/35/B/ST5/02666).

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- [2] R. Zuzak, et al., Angew. Chem. Int. Ed. 2018, 57, 10500–10505.
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11:20am **NM-ThM2-11 Nanotechnology in Plant Protection Applications, Ahmet Ozan Gezerman**, Toros Agri- Industry, Turkey

To date, plant protection research has mainly focused on the suppression of pests, diseases and weeds. Research has been primarily single-disciplinary and cause-effect-oriented, and innovation has often been equated with the development of new product lines or single-component technologies such as agrochemicals. Today, the aim of contemporary "plant protection" approaches is not to completely eliminate the harmful factors in plant production, but to keep and manage them at a certain population level by using the natural mechanisms found in nature. The most important factor in realizing this aim is to know the harmful factors and the factors limiting their populations and to have basic knowledge about the biology of the pests. In this direction, the "Whole War method", which we can name as keeping the populations of harmful agents below the Economic Damage Threshold, is emphasized today, by supporting each other with the methods of combat. Taking this concept one step further, considering the ecosystem as a whole and taking into account the basic demands of agricultural products and their relationship with the environment, using all appropriate plant growing methods and techniques in harmony, "taking into account the population dynamics of harmful species and their relationship with the environment, Integrated Product Management (ICM), which can be defined as a product and pest management system that keeps their populations below the level of economic damage, by using all appropriate control methods and techniques in harmony, has come to the fore. In this context, future plant protection strategies; it is possible to collect them under four headings as preventive practices, monitoring, effective struggle and smart agriculture. These developments, which have emerged in this way, will contribute to the development and realization of much more effective and environmentally friendly plant protection practices in the future, starting from today, and these topics are discussed in this paper.

## Thin Films

Room Naupaka Salon 5-7 - Session TF-ThM

### Nanostructured Surfaces and Thin Films: Synthesis and Characterization

Moderator: Jyh-Wei Lee, Ming Chi University of Technology

8:00am **TF-ThM-1 Electronic Interaction in Graphene/WS<sub>2</sub> Assisted by the Interlayer Rotation Angle, Cecelia Noguez**, UNAM Mexico **INVITED**

Two-dimensional (2D) van der Waals (vdW) heterostructures are a new realm of materials with potential applications and fascinating physical properties. Besides graphene (G), transition metal dichalcogenides (TMDCs) have been considered promising building blocks in 2D vdW heterostructures with improved and new properties. The vertical stacking of at least two atomic monolayers bonded by vdW forces with different electronic behavior, i.e., G/TMDC, leads to new hybrid nanostructures. In principle, hybrids could retain the main advantages of pristine monolayers at the same time that they might achieve superior and unusual properties which cannot be obtained otherwise. In recent years, the combination of G and TMDCs, such as tungsten disulfide (WS<sub>2</sub>) and molybdenum disulfide (MoS<sub>2</sub>) has attracted increasing interest as promising building blocks for future electronics, photonics, and optoelectronic devices. First, we present a general unfolding method for the electronic bands of systems with double-periodicity. Within density functional theory with atomic orbitals as basis-set, our method takes into account two symmetry operations of the primitive cell: a standard expansion and a single rotation, letting to elucidate the physical effects associated with the mutual interactions between systems with more than one periodicity. As a result, our unfolding method allows studying the electronic properties of vertically stacked homo- or heterostructures.

We apply our method to study G/WS<sub>2</sub> heterostructures with different interlayer angles. This allows observing typical mini gaps reported in Thursday Morning, December 15, 2022

heterostructures, as well as other electronic deviations from pristine structures, impossible to distinguish without an unfolding method. Electronic minigaps, band hybridization, and splitting occur in graphene supported on tungsten disulfide (G/WS<sub>2</sub>). These are studied by employing periodic first-principles calculations and an unfolding method to interpret the supercell's crowded-band structure. Electronic alterations because of the interlayer interactions identified as Bragg diffractions, electronic repulsions or avoided crossings, and replicas due to the Moiré potential, all of them depending on the interlayer angle. The results indicate that out-of-plane orbitals interactions from different layers, depending on energy and k-region, induce the avoided crossings, band hybridization, and splitting. At the same time, Moiré replicas emerge because of the superperiodic potential associated with patterns. Finally, the minigaps energy position is intrinsically related to the interlayer angle and the commensurate conditions.

8:40am **TF-ThM-3 Atomic-Scale Probing of Chemically Modified Borophene via Tip-Enhanced Raman Spectroscopy, Nan Jiang**, University of Illinois - Chicago

Two-dimensional boron monolayers (i.e., borophene) hold promise for a variety of energy, catalytic, and nanoelectronic device technologies due to the unique nature of boron-boron bonds. To realize its full potential, it is desirable to chemically modify borophene either by Van der Waals interactions or covalent modification. In this context, the atomic-scale chemical study of functionalized borophene is of critical importance to the understanding of local interfacial characteristics and site-specific chemical properties.

Tip-enhanced Raman spectroscopy (TERS), which couples scanning tunneling microscopy (STM) and surface-enhanced Raman spectroscopy, provides such a powerful capability to concurrently harvest topographic and chemical information with single-bond sensitivity at the angstrom-scale. Herein, we use ultrahigh vacuum (UHV) TERS to measure the angstrom-scale interfacial interactions of a vertical Van der Waals heterostructure of borophene with tetraphenylidibenzoperiflanthene (DBP) molecules. TERS reveals subtle ripples and compressive strains of the borophene lattice underneath the molecular layer. The induced interfacial strain is demonstrated to extend in borophene by ~1 nm beyond the molecular region by virtue of 5 Å chemical spatial resolution. Next, we use our method to probe the local chemical properties of oxidized borophene. The results show that single oxygen adatoms on borophene can be identified and mapped with ~4.8 Å spatial resolution and single bond (B–O) sensitivity. Furthermore, we reveal the propensity of borophene towards molecular oxygen activation at room temperature and phase-dependent chemical properties.

In addition to offering atomic-level insights into the above-mentioned systems, our studies demonstrate UHV-TERS as a powerful tool to probe the local chemistry of surface adsorbates and interfacial structures in the atomic regime with widespread utilities in heterogeneous catalysis, on-surface molecular engineering, and low-dimensional materials.

9:00am **TF-ThM-4 Thin Film Combinatorial Sputtering of Al-Ce Alloys for Mechanical Alloy Design, Reece Emery, M. Thompson, O. Rios**, University of Tennessee Knoxville; *D. Weiss*, Eck Industries; *P. Rack*, University of Tennessee Knoxville

Al<sub>x</sub>Ce<sub>100-x</sub> thin films with a composition range of ~75.0<x<99.5 at. % (36.5<x<97.5 wt. %) were synthesized via combinatorial co-sputtering from an Al and an Al<sub>50</sub>Ce<sub>50</sub> target. The crystal structure, phase fraction, film morphology, and temperature-dependent coefficients of thermal expansion (CTE) are all correlated to the Al<sub>x</sub>Ce<sub>100-x</sub> composition. Temperature dependent x-ray diffraction (XRD) reveals that the two phases expand independently of one another, and the thin film Al temperature-dependent CTE is similar to bulk Al. The thin film Al<sub>11</sub>Ce<sub>3</sub> intermetallic phase has a nearly constant CTE of ~1.5x10<sup>-5</sup>/°C within the temperature range studied (25–550°C). To confirm the thin film Al<sub>11</sub>Ce<sub>3</sub> results, bulk stoichiometric Al<sub>11</sub>Ce<sub>3</sub> and +/- 1 wt.% Ce samples were prepared and the CTE of each was measured under the same conditions. A Rietveld analysis of the bulk data enabled an estimation of the CTE in each of the 3 orthorhombic lattice parameters, which displayed anisotropic behavior. The thin film and bulk CTE measurements were in very good agreement. Additionally, nanoindentation was performed to track the mechanical properties of the combinatorial library. By demonstrating the efficacy of the approach, more complex multi-component rapid materials discovery of

low CTE Al-alloys can be pursued via the combinatorial thin film synthesis, TDXRD measurements, and nanoindentation.

9:20am **TF-ThM-5 Quantum Decoherence of Superconducting Quantum Circuit Interfaces: Niobium on Silicon**, *Frank Ogletree, V. Altoé*, Lawrence Berkeley Laboratory; *A. Schwartzberg, C. Song*, Lawrence Berkeley Lab; *D. Santiago, I. Siddiqi*, Lawrence Berkeley Lab, University of California, Berkeley

The performance of superconducting quantum sensors and qubits is limited by losses associated with few-nanometer amorphous oxide films at the superconductor and substrate interfaces [1,2]. We have localized 92% of the total loss of niobium-on-silicon quantum resonators to the Si substrate-air (SA) and Nb metal-air (MA) interfaces through selective chemical etching, correlated with millikelvin microwave loss measurements and materials analysis of the interfaces [3]. Interfacial materials analysis combining analytical scanning transmission electron microscopy (STEM) and x-ray photoemission spectroscopy (XPS) was used to correlate physical and chemical changes in the surface oxides with reductions in loss [4,5]. We found clear differences in the characteristic losses associated with the Si and Nb oxides. SiO<sub>x</sub> hosted 70% of two-level system (TLS) losses, with only 24% associated with NbO<sub>x</sub>. Although TLS losses dominated decoherence, 39% of loss did not show the expected TLS power dependence [1]. NbO<sub>x</sub> hosted 68% of non-TLS losses, with only 17% associated with SiO<sub>x</sub>. TEM diffraction measurements showed an epitaxial relation between the Nb superconducting film and the Si substrate, with no evidence for the commonly-reported metal-substrate amorphous oxide layer. Post-fabrication surface oxide etching improved our median quantum-resonator quality factors from 0.93 to 5.26 million. Our resonator study gives insights into decoherence in other types of superconducting quantum sensors[5].

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9:40am **TF-ThM-6 Structural Analysis of Few-Atomic Layered Hexagonal Boron Nitride Nanosheets Synthesized with Magnetron Sputtering and Heat Annealing Process**, *Yuki Hirata, K. Yoshii, M. Yoshizato, H. Akasaka, N. Ohtake*, Tokyo Institute of Technology, Japan

Hexagonal boron nitride (*h*-BN) is composed of boron and nitrogen atoms, tightly bound in a hexagonal honeycomb lattice. Since it has the similar structure with the graphene, *h*-BN is called as "white graphene". *h*-BN is known to have excellent properties such as high heat resistance, oxide resistance, wide bandgap and luminescence in far ultraviolet region and so on. Therefore, *h*-BN are expected to be applicable as an insulating layer of electronics device, far ultraviolet light emitting device. In this study, we attempted to develop the newly synthesizing process of *h*-BN with high crystallinity on Cu substrate by using magnetron sputtering while heating at 1000 degree. According to the SEM observation, white-colored domains with facets of 60 degrees were observed. That may be corresponding to hexagonal honeycomb lattice structure. Actually, Auger electron spectroscopy showed the presence of boron and nitrogen on these domains. Furthermore, XPS analysis was conducted to measure the elemental composition ratio and bonding states. It was revealed the presence of equal amounts of nitrogen and boron, as well as a single peak derived from the B-N bond. In Raman spectroscopy, a peak around 1364 cm<sup>-1</sup> was observed, which was corresponding to in-plane six-membered ring vibration of *h*-BN. From these results, it can be said that we succeeded in synthesizing *h*-BN with several atomic layers.

10:20am **TF-ThM-8 High-Throughput Magnetron Sputtering for Microstructure and Alloy Design**, *Andrea Hodge*, University of Southern California

INVITED

With the rapid ascend of machine learning as part of materials development, it is important to find synergy between experimental and computational efforts for faster materials discovery. In this talk, an overview and specific methodologies will be discussed using high-throughput experimental techniques specifically thin metallic films. These techniques allow the creation of experimental data sets which can be used

to construct materials libraries.

In his context, sputtered compositional and microstructure complex metallic alloys will be presented as model systems for high-throughput synthesis and characterization. We will examine the data complexity of going from four to hundreds of compositions in a single sputtering run and how machine learning can be implemented to guide both the synthesis and characterization space.

11:00am **TF-ThM-10 Magnetron-sputtered MgLi Coatings and Freestanding Thin Films for Neurological Implants – Preparation and Degradation Process**, *Lisa Hanke*, Kiel University, Germany; *K. Bhat*, Helmholtz Zentrum hereon, Germany; *L. Kalchgruber, M. Valtiner*, Vienna University of Technology, Austria; *R. Willumeit-Römer*, Helmholtz Zentrum hereon, Germany; *E. Quandt*, Kiel University, Germany

Magnesium based freestanding thin films and structures are easily fabricated by magnetron sputtering combined with UV-lithography and sacrificial layer technique [1]. Such films are of interest for temporary medical applications as biodegradable implants but can also act as a reservoir for therapeutically active alloying elements. During the degradation of the thin film devices, the ions can be released and allow for local treatment with the aim to reduce the necessary dosage and possible side effects.

Lithium (Li) is known as a treatment for mood disorders [2] and, thus, MgLi coatings and freestanding films are investigated as possible future brain implants. The biocompatibility of the produced thin films was proven in first in vitro experiments to underline the possibility for usage as a medical implant.

The MgLi thin films are prepared using magnetron sputtering, leading to films with a lithium concentration ranging from 5.4 at% to 26.9 at%. The range of composition allows the study of the influence of Li content as well as of different phases and microstructures on the properties of the films. The structure and phases are analyzed by XRD, SEM and TEM. While low Li concentrated films show a single hexagonal phase with preferred orientation and columnar growth, for higher Li concentrations an additional Li-rich cubic phase and also Li<sub>2</sub>CO<sub>3</sub> occur. Tensile testing data shows the highest tensile strength and elongation for Mg-5.4(at%)Li. Similar elongation results were obtained for Mg-9.8(at%)Li and Mg-26.9(at%)Li. Additionally, influences of the film thickness and sputtering parameters on the orientation and film properties are studied.

The corrosion rate of the films is determined via potentiodynamic polarization in Hank's balanced salt solution at a pH of 7.4 and 37°C to investigate the ion release and, thus, therapeutic effect. Due to the different phases and microstructures, the lowest corrosion rate is measured for Mg-5.4(at%)Li. Similar corrosion rates occur for Mg-9.8(at%)Li and Mg-26.9(at%)Li, while the corrosion rate for Mg-16.9(at%)Li is three times higher.

Additional in situ measurements via inductively coupled plasma – mass spectrometry coupled with an electrochemical cell and XPS measurements give further insight into the corrosion process itself and formed surface layers. A Li rich layer can be identified on the surface of all MgLi alloys. Additionally, a difference of mainly Li driven corrosion in comparison to Mg based corrosion for lower Li concentrated films is determined.

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11:20am **TF-ThM-11 The Importance of Interface Chemistry and Island Morphology in Granular Metal Thin Films**, *Simeon Gilbert, M. Meyerson, S. Rosenberg, P. Kotula, N. Madden, P. Sharma, J. Flicker, M. McGarry, T. Kmiecik, M. Siegal, L. Biedermann*, Sandia National Laboratories

Granular metals (GMs) consist of nanoscale metal islands dispersed in an insulating matrix. At low volumetric metal fraction ( $\phi$ ), GMs are insulating; at high  $\phi$ , metallic. In the insulating regime, conduction occurs by electron tunneling and capacitive transport between metal islands. The percolation threshold ( $\phi_c$ ) is the metal volume fraction indicating the transition between insulating and metallic regimes. A sharp conductivity ( $\sigma$ ) knee at  $\phi_c$ , with  $\sigma$  increasing 4-6 orders-of-magnitude with  $\Delta\phi=0.1$  indicates a low-defect insulating matrix surrounding metal islands at  $\phi < \phi_c$  and a conductive metallic film with limited insulator inclusions at  $\phi > \phi_c$ . Such 4-6 orders-of-magnitude changes in  $\sigma$  at  $\phi_c$  are seen for Au- and Ag-based GMs with  $\sigma$  as low as 10<sup>-6</sup> S/cm at  $\phi=0.2$ . However, most other GMs exhibit 1-3 orders-of-magnitude  $\sigma$  changes at  $\phi_c$  and comparatively high  $\sigma$  (10<sup>-2</sup>-10<sup>-4</sup> S/cm) at  $\phi=0.2$ . Despite decades of research on GMs, the variations in  $\sigma$

different GM systems have not been closely examined.

We synthesized several 100-200 nm thin films via RF co-sputtering of Mo or Co with yttria stabilized zirconia (YSZ) or  $\text{SiN}_x$ .<sup>1</sup> The resulting thin films form GMs with 1-3 nm metal islands based on scanning transmission electron microscopy (STEM). Unlike the Au and Ag GMs, the as-grown Mo- and Co-based GMs show  $\sim 1$  order-of-magnitude  $\sigma$  changes at  $\varphi_c$  with  $\sigma$  values of  $10^{-1}$ - $10^{-3}$  S/cm at  $\varphi=0.2$ . X-ray photoemission spectroscopy (XPS) indicates deleterious metal-insulator interface states which increase the conductivity of the insulator in the region surrounding the metal islands. For Mo- $\text{SiN}_x$  sputtered in Ar,  $\text{MoSi}_2$  forms due to N vacancies in the  $\text{SiN}_x$ . By sputtering the Mo- $\text{SiN}_x$  films in an Ar/H/N environment, the N vacancies and  $\text{MoSi}_2$  formation are mitigated, as shown by optical bandgap and XPS measurements. As desired,  $\sigma$  is reduced by 3-4 orders-of-magnitude for  $\varphi < \varphi_c$ . Additionally, annealing the GM films increases the island sizes/separations, as shown by in-situ TEM annealing. Increased island separation weakens the effects of interface regions, and  $\sigma$  can be reduced  $>6$  orders-of-magnitude when  $\varphi < \varphi_c$ . Based on this work, precise control of the interface chemistry and island morphology will be crucial for controlling the conduction mechanisms in future GMs.

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