## 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-I, France; *A. Schuetze,* ACT

*Author :Dr Pierre Collignon , PD2-I*

*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 CrWAlN 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 Si3N4. 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 $10^{-4}$. 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 $SiO_2$, 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 $SiO_2$. 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 1015 cm-3eV-1 level[2]. Our technique has additional advantage: this method is tough for sample charging problem, opening chance to measure various isulating 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 Reseach, 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)[1]. 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 α-Mn and β-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 α-Mn and β-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 $Fe_{0.5}Mn_{0.5}$, $Ni_{0.5}Mn_{0.5}$, $Co_{0.25}Mn_{0.75}$, and $Cr_{0.4}Mn_{0.6}$ 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 $Fe_{20}Ni_{20}Co_{20}Cr_{20}Mn_{20}$ 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.

## 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) 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

HoIn various industrial applications, friction and wear reduction by diamond-like carbon (DLC) can be severly affected by the presence of zinc-dialkyldithiophosphate (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[1].

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.

[1] 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 $Y_2SiO_5$ Environmental Barrier Coatings***, Byung-Koog Jang,* Kyushu University, Japan

Silicon-based ceramics such as SiC/$SiC_f$ 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 enginesbecause 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, $Y_2SiO_5$EBCs have been deposited by plasma spray technique as protection layer of SiC substrate from oxidation and steam corrosion. $Y_2SiO_5$ 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 $Y_2SiO_5$ 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 $Y_2SiO_5$ coatings showed increasing tendency with an increase in isothermal heat-treatment time.In addition, the hardness and elastic modulus of$Y_2SiO_5$ coatingswere 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 600ºC and 800ºC 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 $Si_3N_4$ 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 <10-16 m3/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 proprieties 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 $H_2O$ and $O_2$by using reactive MD simulation.

The sliding simulation model is shown in a supplementary document (SD) Fig.1. To investigate the effects of $H_2O$ and $O_2$, we prepared the following three models: $H_2O$ model, $O_2$ model and $H_2O$+$O_2$ model. $H_2O$ molecules, $O_2$ molecules and both $H_2O$ and $O_2$ molecules were placed at the DLC/Fe sliding interface of $H_2O$ model, $O_2$ model and $H_2O$+$O_2$ 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, $H_2O$+$O_2$ model < $O_2$ model < $H_2O$ model. In $H_2O$ model, $H_2O$ 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 $O_2$ model $O_2$ molecules reacted with the Fe surface, forming chemically inert layer, thereby prevented atomic-scale adhesive wear (SD Fig.2(b)) [2]. Moreover, in $H_2O$+$O_2$ model, in addition to the above roles of $H_2O$ and $O_2$, the reaction of $H_2O$ 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 $H_2O$ and $O_2$ play the different role to reduce atomic-scale wear. Moreover, when $H_2O$ and $O_2$ 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 unparallel 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 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 $FeNiCoCrMnS_2$ exhibits superior OER activity with exceptionally low overpotential of 199, 246, 285, and 308 mV at current densities of 10, 100, 500 and 1000 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 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.

## 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 it 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 Al2O3 films, and on the outer side by depositing Ta2O5 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 $Al_2O_3$ 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 $Al_2O_3$-polymer hybrid layer as thin gas barrier films. Filling of the free volumes of polymers at the subsurface region with $Al_2O_3$ 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 thins layers with the infiltration depth in the nanometer ranges while $Al_2O_3$ could not infiltrate into PFA and PS films. The selectivity of $Al_2O_3$ infiltration into polymer films was employed to prepare stretchable gas encapsulating films by encapsulating individual segments of 144 Ca dots by $Al_2O_3$-PET hybrid films on a PFA polymer substrate. Regardless of bending and stretching, it exhibited extremely low gas barrier properties with WVTR of $<10^{-7}$ $gm^{-2}day^{-1}$. 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, σ, 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 $Fe_2O_3$ (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 σ'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.

References

1. C. R. Brundle and B. V. Crist, J. Vac. Sci. Tech A, 38(4) Jul/Aug 2020; doi:10.1116/1.5143897
2. P. S. Bagus, C. J. Nelin, C. R. Brundle, B. V. Crist, N. Lahiri, and K. M. Rosso, Phys. Chem. Chem. Phys., 2022, **24**, 4562-4575.

**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($HfO_2$ and $SiO_2$) 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 $HfO_2$ and $SiO_2$ while the total thickness of the insulator is equal. As a result, the higher the $HfO_2$ 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. $HfO_2$ 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 sp3/sp2 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 $ZrO_2$ 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 $O_3$ ALD, each using reactants such as $H_2O$ (or other oxidants), $O_2$ plasma, and $O_3$. We systematically and comparatively investigated thermal ALD and PE-ALD $ZrO_2$ using a widely used precursor of $CpZr(NMe_2)_3$. We observed that Zr-Cp and Zr-$N(CH_3)_2$ have different degrees of ligand exchange, which leads to different surface-reaction with reactants. The weak oxidizing power of $H_2O$ showed difficulties on breaking the Zr-Cp bond, while the $O_2$ 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 $ZrO_2$ film, leading to superior film properties such as roughness (RMS 0.293 nm) and film density (5.8 g/cm$^3$). In contrast, the case of $H_2O$ 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 $ZrO_2$ process with Cp-containing Zr precursor.

**TF-WeP-7 High Performance Amorphous Oxide Semiconductor Thin-film Transistors with $HfO_2/Al_2O_3$ 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 $SiO_2$ exhibits excellent insulating properties and uniformity, the doped Si and thermally grown $SiO_2$ are generally used as a gate electrode and a gate insulator in the conventional AOS TFTs, respectively. However, the thermally grown $SiO_2$ 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 $HfO_2/Al_2O_3$ gate insulator deposited by low temperature atomic layer deposition (ALD). Because $Al_2O_3$, 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 $HfO_{-2}$ 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 $HfO_2/Al_2O_3$ gate insulator. The $Al_2O_3$ gate insulator and $HfO_2$ insulator buffer were deposited on a heavily doped p-type Si substrate by low temperature ALD at 120 ℃ using tri-methyl-aluminum (TMA), tetrakis [ethyl-methyl-amino] hafnium (TEMAHf) and $H_2O$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 $10^{-3}$ Torr. After depositing the channel layers, annealing was performed using a hot plate at 250 ℃ for 1h. The fabricated TFTs were analyzed with a semiconductor parameter analyzer (Elecs Co. EL423).

Fig. 2 shows (a) output curves and (b) transfer curves of IZO TFTs with $HfO_2/Al_2O_3$ gate insulator. The electrical properties of the fabricated TFTs exhibited 6.02 cm$^2$ / Vs of carrier mobility ($\mu_{sat}$), 1.18 x $10^6$ 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 $HfO_2/Al_2O_3$ gate insulator by varying the thickness of insulator, the thickness ratio of $Al_2O_3$ and $HfO_2$, 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).

**References**

[1] FINŠGAR, Matjaž. Time-of-flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy study of 2-phenylimidazole on brass. Rapid communications in mass spectrometry, 2021, vol. 35.

[2] FINŠGAR, Matjaž. The influence of the amino group in 3-amino-1,2,4-triazole corrosion inhibitor on the interface properties for brass studied by ToF-SIMS. Rapid communications in mass spectrometry, 2021, vol. 35.

[3] FINŠGAR, Matjaž. Advanced surface analysis using GCIB–$C_{60}^{++}$-tandem-ToF-SIMS and GCIB-XPS of 2-mercaptobenzimidazole corrosion inhibitor on brass. Microchemical journal, Volume 159, December 2020, 105495

**TF-WeP-9 Temperature Dependence of Dielectric Function for $WSe_2$**, *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, $WSe_2$ 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, $WSe_2$ 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 $WSe_2$ are needed. Although there are a few studies on the dielectric functions, systematic study on temperature dependence of critical points (CPs) of monolayer $WSe_2$ has not been reported, yet. In this work, we report the dielectric function of monolayer $WSe_2$ 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 $WSe_2$ 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 $\varepsilon$ 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 $A^-$, and a superposition of biexciton emission (*AA*) with defect-bound exciton emission (*L*1). 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 $WSe_2$.

**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 $sq^{-1}$), together with superior flexibility. Addtionally, 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 efficieny, 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. $Ge_2Sb_2Te_5$ (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 [1,*], C.J. Negrete [1, 2], Wesley Hung [1], Kevin R. Anderson [1], Jeremy B. Gan [3], Corey R. Grice [4]

[1] Department of Mechanical Engineering, California State Polytechnic University, Pomona, 3801 W Temple Avenue, Pomona, CA 91768, USA.

[2] Citrus College, 1000 W Foothill Blvd, Glendora, CA 91741, USA.

[3] Department of Chemical and Biomolecular Engineering, The University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095, USA.

[4] Center for Materials & Sensor Characterization, College of Engineering, The University of Toledo, 1700 N Westwood Ave, University of Toledo, Toledo, OH 43606-3390, USA

* Correspondence: Tel. +01-909-869-2388; Email: yxgan@cpp.edu (Y.X.Gan)

**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 ofextremely low heat development and no mechanical force on the substrate during the coating process. This 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 $cm^{-2}$, and excellent electrochemical stability at different constant current densities of 10 and 100 mA $cm^{-2}$ 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 $TiO_2$ 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 $TiO_2$ 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 $TiO_2$ 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 $TiO_2$ 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 (Tio2) Thin Film by Sol-Gel Method**, ***Moniruzzaman Syed***, *J. Gibson, D. White,* LeMoyne-Owen College

Titanium dioxide ($TiO_2$) multilayer thin films (2-layers) have been deposited on glass substrate by using Sol-Gel technique. $TiO_2$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 $TiO_2$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 $N_2/O_2$ 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.

## 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 wasperformed 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 x $10^{17}$ $cm^{-3}$. 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. Phyik 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), TiCl4 with NH3 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 H2S pulse between TiCl4 and NH3 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 H2S 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.

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 opto-electronics 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 $Ar/O_2$ 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 $VSe_2$**, *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 $VSe_2$ 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 $BaTiO_3/CoFe_2O_4/BaTiO_3$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 biphase system with robust ferroelectric and ferromagnetic response at room temperature would be ideally suitable for microelectronic and memory devices and spintronic applications.Multiferroic magnetoelectric $BaTiO_3$-$CoFe_2O_4$-$BaTiO_3$ (BTO/CFO/BTO) heterostructures thin films were synthesized by pulsed laser deposition (PLD) on Pt(111)/$TiO_2$/$SiO_2$/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 $BaTiO_3$-$CoFe_2O_4$-$BaTiO_3$ (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 (Ps ~ 99.86 $\mu C/cm^2$), magnetization (Ms ~ 51.48 $emu/cm^3$) and a strong magnetoelectric coupling coefficient of~274 mV/cmOe at a bias feld 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 Irisson,* 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.

## 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/$WS_2$ 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 ($WS_2$) and molybdenum disulfide ($MoS_2$) 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/$WS_2$ heterostructures with different interlayer angles. This allows observing typical mini gaps reported in 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/WS2). 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 tetraphenyldibenzoperiflanthene (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, weuse 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

$Al_xCe_{100-x}$ 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 $Al_{50}Ce_{50}$ target. The crystal structure, phase fraction, film morphology, and temperature-dependent coefficients of thermal expansion (CTE) are all correlated to the $Al_xCe_{100-x}$ 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 $Al_{11}Ce_3$ intermetallic phase has a nearly constant CTE of ~$1.5x10^{-5}$/°C within the temperature range studied (25-550°C).To confirm the thin film $Al_{11}Ce_3$ results, bulk stoichiometric $Al_{11}Ce_3$ 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. $SiO_x$ hosted 70% of two-level system (TLS) losses, with only 24% associated with $NbO_x$. Although TLS losses dominated decoherence, 39% of loss did not show the expected TLS power dependence [1]. $NbO_x$ hosted 68% of non-TLS losses, with only 17% associated with SiOx. 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].

[1] Müller et al, 'Towards understanding two-level-systems in amorphous solids: insights from quantum circuits', Rep Prog Phys, 2019.

[2] Siddiqi, 'Engineering high-coherence superconducting qubits', Nat Rev Mat, 2021

[3] Altoë et al, 'Localization and mitigation of loss in niobium superconducting circuits' PRX Quantum 3, 2022.

[4] Sheridan et al, 'Microscopic Theory of Magnetic Disorder-Induced Decoherence in Superconducting Nb Films', arXiv 2111.11684, 2021.

[5] Harrelson et al, 'Elucidating the local atomic and electronic structure of amorphous oxidized superconducting niobium films', APL 2021.

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 applicate 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 $cm^{-1}$ was observed, which was corresponding to in-plane six-membered ring vibration of *h*-BN. From these results, it can be said that we succeed in to synthesize *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 Magnetronsputtered 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 necessarydosage 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 cytocompatibility 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 Li2CO3 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.

[1] D. Haffner, C. Zamponi, et al. (2015) BioNanoMat 16:19-22 [2] C. Volkmann, T. Bschor, S. Köhler (2020) Front. Psychiatry 11:377

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. Kmieciak, 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 ($\varphi$), GMs are insulating; at high $\varphi$, metallic. In the insulating regime, conduction occurs by electron tunneling and capacitive transport between metal islands. The percolation threshold ($\varphi_c$) is the metal volume fraction indicating the transition between insulating and metallic regimes. A sharp conductivity ($\sigma$) knee at $\varphi_c$, with $\sigma$ increasing 4-6 orders-of-magnitude with $\Delta\phi \approx 0.1$ indicates a low-defect insulating matrix surrounding metal islands at $\varphi<\varphi_c$ and a conductive metallic film with limited insulator inclusions at $\varphi>\varphi_c$. Such 4-6 orders-of-magnitude changes in $\sigma$ at $\varphi_c$ are seen for Au- and Ag-based GMs with $\sigma$ as low as $10^{-6}$ S/cm at $\varphi$=0.2. However, most other GMs exhibit 1-3 orders-of-magnitude $\sigma$ changes at $\varphi_c$ and comparatively high $\sigma$ ($10^{-2}$-$10^{-4}$ S/cm) at $\varphi$=0.2. Despite decades of research on GMs, the variations in $\sigma$ for 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 $SiN_x$.[1] 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 ~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-$SiN_x$ sputtered in Ar, $MoSi_2$ forms due to N vacancies in the $SiN_x$. By sputtering the Mo-$SiN_x$ films in an Ar/H/N environment, the N vacancies and $MoSi_2$ 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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1. SJ Gilbert *et al* 2022 J. Phys.: Condens. Matter **34** 204007

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