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

Thin Films - Materials I

Moderator: Ryo Toyoshima, The University of Tokyo

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

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

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

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

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

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

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

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

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

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

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

Thin Films - Characterization

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

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

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

[1] Toyoshima, R. et al. J. Phys. Chem. C 2021, 125, 4540–4549.

[2] Toyoshima, R. et al. J. Phys. Chem. Lett. 2022, 13, 8546–8552.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

References [1] Kern et al, Handbook of Thin Film Deposition Process and Techniques, 2, 11-43 (2001). [2] Woochool Jang et al, Physica Status Solidi, 212, 2785-2790 (2015). [3] F. Koehler, IOP conference Series: Materials Science and Engineering, 41, 012006 (2012). [4] Stacey F. Bent et al. Materials Today, volume 17, number 5 (2014).

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

As the semiconductor industry advances towards complex multilayered devices with smaller features, area-selective atomic layer deposition (AS-ALD), a bottom-up method, has gained significant interest for its capability to enable precise and self-aligned deposition within specified areas, i.e., the growth areas. In this study, we primarily utilized small molecular inhibitors as vapor-phase deactivating agents to non-growth areas, due to their small size, high volatility, and ease of process integration into 3D structured devices. More particularly, this AS-ALD methodology is advantageous for manufacturing high aspect ratio SiO_2/SiN structures in V-NAND, where the reduction in tier size leads to cell-to-cell crosstalk between vertically downscaled SiO_2/SiN stacks. To mitigate this issue, it is essential to apply

AS-ALD of SiO_2 thin films on SiO_2 surfaces while preventing deposition on SiN surfaces. For this purpose, we employed a vapor-dosing process using silane-based small molecule inhibitors that chemo-selectively adsorb on -NH terminated surface groups of the SiN surface. Moreover, to further improve deposition selectivity, we periodically introduced a post-atomic layer etching step with atomic scale fidelity after a certain number of ALD SiO_2 cycles, which effectively removed SiO_2 moieties from the SiN surfaces. Finally, we achieved a deposition selectivity greater than ~10 nm on blanket SiO_2 and SiN substrates. The approach we present here contributes to the advancement of the manufacturing process for next-generation bottom-up 3D nanofabrication.

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

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

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

TF-TuP-7 UV Light Extinction Imaging Method for Monitoring Inkjet-Printed Organic Layer in Thin Film Encapsulation Process*, **Jun Young Hwang**, Jun Ho Yu, Heui Seok Kang,* Korea Institute of Industrial Technology, Republic of Korea*; Dal Won Lee, Gyu-Young Yun,* LG Electronics, Republic of Korea*; Seong Woo Lee,* Poongsan System Co., Ltd., Republic of Korea

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

TF-TuP-8 Room–Temperature Ferromagnetism Observed in Graphene Oxide Fabricated by AFM Lithography*, Bae Ho Park,* Department of Physics, Konkuk University, Republic of Korea*; **DaYea Oh**,* Deparment of Physcis, Konkuk University, Republic of Korea*; Duk Hyun Lee,* Department of Physics, Konkuk University, Republic of Korea*; Wondong Kim,* Korea Research Institute of Standards and Science, Republic of Korea*; Jun Woo Choi,* Center for Spintronics, Korea Institute of Science and Technology, Republic of Korea

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

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

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

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

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

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

Thin Films - Bio- and Medical-related
Moderator: Seo-Hyun Lee, Hanyang University

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Thin Films - Processing
Moderator: Christopher Muratore, University of Dayton

7:40pm **TF2-TuE-7 Guided Combinatorial Synthesis, High-Throughput Materials Characterization and Machine Learning Methods Expedite the Discovery of Improved Pt-Au Thin Films***, **David Adams**, Troy Shilt, Rishabh Kothari, Kyle Dorman, Cari Martinez, Catherine Sobczak, Sadhvikas Addamane, Manish Jain, Frank DelRio, Mark Rodriguez, Brad Boyce, Remi Dingreville,* Sandia National Laboratories

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

which spans large ranges of binary stoichiometry and deposition atomistics.

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

resistivity vary with film stoichiometry and process parameters.

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

future study and reveal strategies for improved deposition.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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TF-WeP-10 Synthesis and Characterization of Mo and W Compounds for Disulfide Materials*,* ***Sunyoung Shin****, Chang Gyoun Kim, Taek-Mo Chung, Bo Keun Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

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

TF-WeP-11 Creating Multiple Catalytic Sites for Enhanced CO_2 Photoreduction Activity Through Synergistic Catalysis of MIL-TiO_2-PI Hybrids*, **Lipei Ren**, Han Wang,* Deakin University, Australia, China*; Milad Laghaei,* Deakin University, Australia, Iran (Islamic Republic of)*; Shuaifei zhao, Lingxue Kong,* Deakin University, Australia

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

TF-WeP-12 Synthesis of Novel Yttrium and Lanthanide Precursors and Fabrication of La_2O_3 Thin Films Through High-Temperature ALD*, **Yongmin Go**, Bo Keun Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Tae joo Park,* Hanyang University, Korea

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

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

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

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

Thin Films - Properties

Moderator: Tetsuhide Shimizu, Tokyo Metropolitan University

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

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

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

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

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

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

Thin Films - Materials II

Moderator: Diana Berman, University of North Texas

7:40pm **TF2-WeE-7 On the Growth of Cubic Boron Nitride Thin Films Using High-Power Impulse Magnetron Sputtering***, **Tetsuhide Shimizu,** Hayate Nagakura,* Tokyo Metropolitan University, Japan*; Yuuki Tokuta,* Tokyo Metropolitan Industrial Technology Research Institute, Japan*; Ivan Fernandez,* Nano4Energy, Spain*; Robert Boyd,* Linköping University, Japan*; Daniel Lundin, Ulf Helmersson,* Linköping University, Sweden **INVITED**

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

8:20pm **TF2-WeE-9 Physical Properties of Pure Vanadium Nitrides Thin Films***, **Marjorie Cavarroc**, Julien Neyrat,* Safran, France*; Dylan Marquez, Dominique Michau, Angéline Poulon-Quintin,* ICMCB, France

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

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

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

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

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

Thin Films - Plasma and Etching-related
Moderator: Gregory S. Herman, Argonne National Laboratory

8:20am **TF1-ThM-2 Reactive Ion Etching of InGaZnO using HFC-based Gas and Chamber Cleaning***, **Sang Jin Lee**, Jong Woo Hong,* Sungkyunkwan University, Republic of Korea*; Yu Gwang Jeong, Hee Min Cho, Da Woon Jung, Yun Jong Yeo,* Samsung Display, Republic of Korea*; Dong Woo Kim, Geun Young Yeom,* Sungkyunkwan University, Republic of Korea

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

8:40am **TF1-ThM-3 Eco-Friendly Dry-Cleaning of Silicon Dioxide Deposition Chambers using a Cylinder-Type Remote Plasma Source with NF_3/N_2 Mixtures***, **Won Kyun Yeom**, Hong Sung Gil,* Sungkyunkwan University, Republic of Korea*; Guen Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

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

9:00am **TF1-ThM-4 Innovative Fluorite-Based High-Entropy Oxide: A Novel Electrocatalyst for All-Vanadium Redox Flow Batteries***, **Chen-Hao Wang**,* National Taiwan University of Science and Technology, Taiwan **INVITED**

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

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

Key findings include:

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

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

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

Thin Films - Surface Modifications
Moderator: Hyo-Chang Lee, Korea Aerospace University

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

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

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

In order to minimize surface losses in resonant and optical applications highly smooth surfaces are required. Characterization of the glassblown samples before glassblowing and after revealed a two-fold improvement in surface roughness, from 0.4 nm Sa down to 0.23 nm Sa. Such improvements in surface roughness are attributed to viscous flow of the glass layer and the associated surface tension forces. The glassblowing creates an effect analogous to “stretching out” the angstrom-level wrinkles on the surface, lowering the surface roughness.

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

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

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

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

Annealing of a sapphire m-plane (1-100) substrate produces a nano-meter-scale faceted structure with alternating r- and S- planes [1]. It has been confirmed that (111)- oriented ZnTe layers with a single domain were grown by molecular beam epitaxy on sapphire S-plane (1-10-1) substrate, which was confirmed by the X-ray diffraction pole figure measurement. One domain ZnTe(111)/S-plane sapphire aligned layer structure was also confirmed from the layer grown on the r- and S- nanofaceted sapphire substrate (Fig.1(a)). With a 17.66° off of the r- and S-nanofacet substrates, (110)-oriented ZnTe thin films were grown on the substrate [2]. (111)-oriented ZnTe layers were preferentially grown on the S-plane of the nanofacet structure, but the diffraction peaks from twinned (-1-1-1) ZnTe were also confirmed (Fig.1(b)). The off-angle of the substrate caused the reduction of the surface area ratio of the S-plane surface and increased the r-plane, resulting in an increase in the number of growth nuclei on the r-plane.

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

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

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

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

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

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

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

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

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

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Author Index

Bold page numbers indicate presenter