

## Thin Films

### Room Naupaka Salons 4 - Session TF-MoM

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

**Moderator:** Toshiyuki Taniuchi, The University of Tokyo

8:00am **TF-MoM-1 Characteristics of ZrO<sub>2</sub> Films Atomic-Layer-Deposited Using Cp-Zr(NMe<sub>2</sub>)<sub>3</sub>: Effects of Oxidant and Deposition Temperature**, *Wan Oh, W Lee, S Choi, Y An, C Lee, S Wi, H Kim*, Sungkyunkwan University, Republic of Korea

The ZrO<sub>2</sub> thin films have been actively used as a dielectric material in various nanoelectronic devices, such as transistors and memories. In achieving excellent electrical performance, uniformity, and step coverage, atomic layer deposition (ALD) is the most perfect method. Consequently, development of the ALD ZrO<sub>2</sub> process itself as well as dielectric engineering (nanolaminating or alloying with other dielectrics) have been largely researched to lower the leakage current while taking advantage of its relatively high dielectric constant [1].

In this study, the ALD ZrO<sub>2</sub> thin films were deposited using Cp-Zr(NMe<sub>2</sub>)<sub>3</sub> as a Zr precursor, and the effects of oxidant (H<sub>2</sub>O, O<sub>3</sub>) and deposition temperature (200-300°C) on their electrical properties were systematically studied. Metal-insulator-metal capacitors were fabricated and their electrical properties, such as capacitance and leakage current, were evaluated. In addition, the physical properties of the ZrO<sub>2</sub> thin films were compared by examining them using transmission electron microscopy, atomic force microscopy, and X-ray diffractometry. Lastly, the ALD ZrO<sub>2</sub> films were applied to a stacked structure of ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>, which has been popularly used in memory devices and their electrical properties were evaluated.

[1] D. Panda and T.-Y. Tseng, *Thin Solid Films* 531, 1 (2013).

8:20am **TF-MoM-2 Enantioselective Catalyst on Oxide Support: Study of the Chemical Nature of Tartaric Acid on Rutile TiO<sub>2</sub>(110) by XPS and HREELS**, *Gregory Cabailh, E Meriggio*, Sorbonne Université, France; *R Lazzari*, CNRS, France; *C Méthivier*, Sorbonne Universitévier, France; *V Humblot, X Carrier*, Sorbonne Université, France

#### 1. Objectives :

Chiral molecules play a vital role in the biochemistry of living organisms, justifying the essential challenge of controlling enantioselectivity in several fields such as the pharmaceutical and agrochemical industry. Heterogeneous asymmetric catalysis for the synthesis of enantiopure chiral compounds is a tool of choice for its many economic and ecological benefits. Several techniques have been developed, including the modification of a metal surface by an organic chiral inducer. Nevertheless, the number of systems developed successfully remains limited. Unlike monocrystalline metal surfaces, very little is known on the role of the oxide support in catalysts based on supported metallic nanoparticles. The control of the role of the oxide support and the chiral inducer is based on the knowledge of the interactions at the molecular level between the three parties involved in the reaction: the oxide, the metal nanoparticles and the chiral inducer, represented in this work by TiO<sub>2</sub> single crystals, nickel nanoparticles (NPs) and tartaric acid (TA). A model approach is used here, where TA molecules and NPs are deposited by evaporation in an ultra-vacuum environment and then characterized by surface analysis techniques.

#### 2. Results :

The chemical state of TA is characterized by X-ray Photoemission Spectroscopy (XPS) and High Resolution Electron Energy Loss Spectroscopy (HREELS). TA is first deposited on single crystals of Cu (110) and Au (111), on which the chemical nature of TA is well known, in order to obtain reference XPS spectra. By analyzing the C 1s and O 1s spectra, the presence of monotartrate adsorbed species (COO<sup>-</sup> / COOH) is demonstrated on copper, while the molecules are in the bi-acid form (COOH / COOH) on gold. The comparison of these results with the data recorded on rutile TiO<sub>2</sub>(110) (in particular the energy differences between the C1s peaks) and complementary HREELS measurements allow to conclude that TA is adsorbed as monotartrate on TiO<sub>2</sub> in analogy with other carboxylic acids. In addition, the organization and the nucleation point on the surface can be observed by scanning tunneling microscopy (STM). TA is finally deposited on the Ni / TiO<sub>2</sub> system at different coverage rates and studied by XPS and

STM to characterize the interaction between the three parties of the system.

8:40am **TF-MoM-3 The Study on Flash Light Sintering Characteristics of Printed Copper Pattern Electrodes with Respect to their Width and Interval**, *Yong-Rae Jang, H Kim, C Ryu, Y Hwang*, Hanyang University, Seoul, Korea

In this work, copper nano/micro-ink screen-printed on a polyimide (PI) substrate, were sintered by flash light irradiation. To find out the effects of the pattern width and interval between copper patterns on the flash light sintering characteristics, analytical thermal transfer simulation was conducted by finite difference method, where the temperature of the substrate and electrodes during the flash light irradiation could be predicted. The copper nano/micro-ink was printed with different widths and intervals and sintered via flash light. The flash white light irradiation conditions such as pulse duration, frequency, and number of pulses were optimized on each pattern sizes. To investigate the macrostructure of the copper pattern, optical microscope and alpha step were used. The microstructures of the copper pattern were observed using scanning electron microscope (SEM). Also, in-situ resistance monitoring was conducted to find the tendency of the sintering characteristics according to the Cu printed pattern. From the study, it was confirmed that the heat generated in the copper pattern by flash light irradiation, was dramatically increased as the pattern width becomes wider and the pattern interval becomes narrower. It is noticeable that the flash light irradiation condition should be designed considering the size of the pattern due to pattern dependent heat transfer phenomena.

9:00am **TF-MoM-4 High Throughput XPS Surface Analysis of Novel Materials Generated by a Combinatorial Approach**, *J Counsell, S Coultas*, Kratos Analytical Ltd., UK; *David Surman, C Moffitt*, Kratos Analytical Inc.

Combinatorial approaches have been widely used to discover new material phases for many years, allowing rapid exploration of composition-structure properties in complex material systems<sup>1</sup>. The mapping of chemical properties such as oxidation state and alloying as a function of composition is an integral part of understanding the underlying physical and chemical properties. Here we apply combinatorial techniques for preparation of model systems to be characterised by X-ray photoelectron spectroscopy (XPS). Two diverse sample sets have been characterised by high throughput XPS - ternary alloy formation post thin-film deposition and polymer microarrays for biomaterial screening.

Ternary metal compounds are used in a wide range of applications; as high-performance alloy materials and electronic semiconductors. We have examined a range of thin-films of first-row transition metals co-deposited on Si wafers to form a matrix of ternary alloys. The surface composition was analysed with XPS to determine the stoichiometric mixing for different alloy compositions and the extent of oxidation and chemical bond formation during deposition. Further analysis of large datasets allows the user to determine areas of particular interest and performance for further investigation – leading to more detailed bulk/surface comparison studies by destructive and non-destructive depth profiling techniques.

Combinatorial methods are also exploited for screening of functional biomaterials. The surface composition of a series of printed polymer microarrays are analysed with XPS to correlate differences in surface chemistry with specific biological performance. This high throughput method allows for library databases to be created for parallel screening of a wide range of polymer blends.

Workflow and data-handling will be discussed for the two different systems. Data visualisation through XPS processing is also described for large datasets generated during these analyses.

1. C. J. Long, J. Hatrick-Simpers, M. Murakima, R. C. Srivastava, I. Takeuchi, V.L. Karen and X. Li, *Rev. Sci. Inst.*, 78, 072217, 2007.

9:20am **TF-MoM-5 Semiconductor Nanowire Y-Junction Arrays Grown by MBE**, *Esteban Cruz-Hernandez*, CIACYT, Universidad Autonoma de San Luis Potosi, Mexico

#### INVITED

Energetically unstable crystalline surfaces, among their uses, can be templates for the self-assembling of semiconductor structures at the nanometric level. Highly uniform structures such as quantum wires can now be fabricated from the self-assembly of nanometric facet arrays produced by using high-index substrates and epitaxial techniques such as Molecular Beam Epitaxy (MBE) [1]. However, the self-assembling of more complex nanostructures such as Y-junctions (produced by the union of two semiconductor nanowires) is a more complex problem. In MBE the growth process is carried out under non-equilibrium conditions, then the nonlinear

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evolution processes (such as step-bunching, meandering instabilities, and coarsening) that produce a very rich variety of surface morphologies have to be understood to precisely control the self-assembly of such complex nanostructures.

The control on the assembly of semiconductor Y-junctions could have great potential in technological applications (for example, in nanoelectronics as quantum logic gates) and one-dimensional physics exploration. Until very recently, related works on nanometric Y-junctions have been based on carbon nanotubes and graphene [2, 3], but not with semiconductor crystalline materials. In this contribution we report on the high-order and two-dimensional mechanisms in the MBE growth of GaAs on high-index GaAs substrates, which allow the formation of a regular alternating pattern of bifurcated nanowires [4] with suitable dimensions to form a Y-junction electron gas device.

[1] E. Cruz-Hernandez, S. Shimomura, and V. H. Mendez-Garcia, *Appl. Phys. Lett.* **101**, 073112 (2012).

[2] Zhen Yao, Henk W. Ch. Postma, Leon Balents, and Cees Dekker, *Nature* **402**, 273 (1999).

[3] A. Jacobsen, I. Shorubalko, L. Maag, U. Sennhauser, and K. Ensslin, *Appl. Phys. Lett.* **97**, 032110 (2010)

[4] R. Mendez-Camacho, M. Lopez-Lopez, V. H. Mendez-Garcia, D. Valdez-Perez, E. Ortega, A. Benitez, A. Ponced and E. Cruz-Hernandez, *RSC Adv.* **7**, 17813 (2017).

## 10:20am TF-MoM-8 Controllable Bandgap Design in (2+1) D Colloidal Photonic Crystals, *Lijing Zhang*, Dalian University of Technology, China

Photonic crystals (PCs) are artificial periodic dielectric materials with the characteristic of photonic bandgap (PBG), which can control the behavior of photons in a similar manner as what semiconductors do for electrons. (2+1) D photonic crystals, as a novel photonic crystal structure, possess unique advantages in both structural tenability (control in single layer level) and optical property (PBG broadening and deepening) compared with traditional 1D, 2D and 3D photonic crystals. However, the fabrication of high quality (2+1) D photonic crystals is still a big challenge, which greatly limit the systematic study on its optical property. Here we present a simple strategy to achieve (2+1) D photonic crystal with enhanced crystalline integrity by layer-by-layer deposition of annealed colloidal crystal monolayers. By simply manipulating the diameter of PS spheres, arrangement type and repetition period of the colloidal monolayers, flexible control in structure and stopband position of the (2+1) D photonic crystals (including superlattice and heterostructure) have been realized. The optical properties of the resulting (2+1) D PCs with different lattice constants were systematically studied and a universal photonic stopband variation rule was proposed, which makes it possible to program any kind of stopband structure as required. The superlattice structure exhibits fine control in PBG position and obvious PBG resonance enhancement. While dual- or multi-stopbands and ultra-wide stopband can be achieved by fabricating heterostructures. This work may afford new opportunities for delicate engineering photonic bandgap materials. Furthermore, we explored their fluorescence (FL) enhancement ability based on their special bandgap effect and demonstrate their application in heavy metal ion detection. A multiple heterostructure photonic crystal (MHPC) with super-wide stopband improved the limit of detection of Cr(VI) to 0.2ppb. and may find significant applications for augmenting FL intensity in chemical and biochemical sensing, imaging, disease diagnosis, and environmental monitoring.

## 10:40am TF-MoM-9 Effects of Interface on Proton Ordering in Heteroepitaxially Grown Ice Films, *Toshiki Sugimoto*, Institute for Molecular Science, Japan

INVITED

Materials with a strongly correlated and highly frustrated degree of freedom have potential for exhibiting dramatic and unusual responses to external stimuli. In the case of common water ice, protons in the hydrogen-bond network are strongly correlated and highly frustrated under the Bernal-Fowler-Pauling ice rules. The ubiquity of water ice makes it essential to clarify the fundamental physicochemical properties of the strongly correlated many-body proton system. It is, however, extremely difficult to directly access the local configuration of protons and their ordering dynamics through traditional experimental approaches. Moreover, the strongly correlated protons inevitably lose ergodicity at low temperature. These problems prevent us from fully understanding cooperative thermodynamic and electric responses of the many-body protons to external stimuli at the low temperature.

To open up a new route to unveil hidden exotic properties of many-body protons in ice, we have investigated a possibility of interface-induced ferroelectric proton ordering by focusing on heteroepitaxially grown crystalline-ice films on metal substrates as model systems [1-3]. We have used recently developed phase-resolved sum-frequency generation (SFG) vibrational spectroscopy in an ultrahigh vacuum chamber [4]. The Im  $\chi^{(2)}$  SFG vibrational spectra ( $\chi^{(2)}$ : the second-order nonlinear susceptibility) exhibits positive and negative sign for OH oscillators with H-up and H-down orientation, respectively. Thus, heterodyne-detected SFG has a great advantage to directly observing local configuration of protons that cannot be investigated by other traditional experimental methods.

Recently, we have demonstrated that the adsorbed first-layer water molecules prefer an net-H-down configuration on model platinum substrate: Pt(111) [1,3]. The coverage dependence of the Im  $\chi^{(2)}$  SFG spectra in the hydrogen-bonded OH stretching regions clearly reveals that the H-down proton ordering in the first layer is significantly pinned by the Pt(111) substrate and is subsequently propagated to the overlayer during the multilayer film growth. Temperature dependent SFG measurement revealed that such a ferroelectric proton ordering is thermodynamically stable and has an extremely high critical temperature of  $\sim 175$  K [1,3], which is more than twice as large as that of ferroelectric bulk ice XI ( $T_c \sim 72$  K). In addition to these results, I will discuss our recent challenges on the interface engineering for modulation of the ferroelectric proton ordering.

[1] *Nature Phys.* **12**,1063(2016);[2,3] *Phys.Rev.B* **96**,115405(2017); **97**,075410 (2018); [4] *Phys.Rev.Lett.* **117**,186101(2016).

## Thin Films

### Room Naupaka Salons 4 - Session TF-MoE

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

5:40pm **TF-MoE-1 Synthesis and Characterization of Novel Nitride Semiconductor Thin Films**, *S Bauers, A Holder, S Lany, Andriy Zakutayev*, National Renewable Energy Laboratory

Nitride thin films have proven to be an invaluable class of materials with a broad range of uses. Examples include transition metal (TM) nitride rocksalts used as hard-wearing industrial and decorative coatings, and semiconducting III-N wurtzites with exceptional optoelectronic properties. We used high-throughput experimental and computations tools to investigate new inorganic ternary nitrides that have previously received very little attention. Specifically, we focused on heterovalent II-IV-N analogues to well-known III-N nitrides, most of which had not been reported in crystallographic databases.

Thin films of Mg-TM-N (TM=Ti, Zr, Hf, Nb, Mo) have been made by combinatorial sputtering, which has allowed for rapid investigation of how film stoichiometry and growth conditions affect properties. Most of the Mg-based ternary compounds form as rocksalt derived structure, with the transition metal in the high valence state. In each case, the heterovalent ternary space provides for tunable properties, characterized by composition-dependent metallic to semiconducting transition. When grown Mg-rich, the materials exhibit semiconducting visible-range optical absorption onsets and mobilities near  $1 \text{ cm}^2/\text{Vs}$  – quite high as for nanocrystalline thin films. The calculated indirect bandgaps are in the visible - near IR range (0.9-2.4 eV), and the calculated static dielectric constants are large (30-80).

Finally, the lattice parameters fall within the range of existing nitrides, suggesting compatibility with established growth techniques and possibility for epitaxial integration of these materials into functional nitride devices. This structural compatibility, along with the tunable properties, make these new nitrides promising materials for various electronic applications

6:00pm **TF-MoE-2 Rheology Behavior and Flash Light Sintering Characteristics of Cu/Ag hybrid-ink for Multi-layered Flexible Printed Circuit Board (FPCB) Application in Printed Electronics**, *Ji-Hyeon Chu, S Joo, H Kim*, Hanyang University, Seoul, Korea

For decades, global printed circuit board (PCB) market has been continuously expanded due to increasing demand of smart devices. Also, PCB became smaller and thinner than before, which resulted in multi-layered flexible printed circuit board (FPCB). Conventionally, multi-layered FPCB was manufactured through a photolithography method. However, the photolithography method has serious drawbacks, such as long tact time, use of toxic chemicals, and high cost. Therefore, a printed electronics technique was considered as an alternative technique, which consists of three simple processes: printing, sintering, and inspection. This technique enables fabrication of electronic devices with short process time, low cost, and environmentally friendliness. Once this technique is combined with a flash light sintering method, it can be a powerful process for the fabrication of multi-layered FPCB. The flash light sintering method uses xenon lamp that irradiates intensive white light, various nano/micro materials can be sintered in a few milliseconds under room temperature and ambient condition. However, there is no study considering printability and sinterability of inks in multi-layered PCB with via-holes. Therefore, in this work, rheological property and flash light sintering characteristics of Cu/Ag hybrid-ink were simultaneously investigated for multi-layered FPCB application. Cu/Ag hybrid-inks were fabricated with various epoxy content, then the fabricated inks were printed on via-hole formed in polyimide substrate to analyze printing characteristics according to the rheology of ink. The printed Cu/Ag hybrid-ink was subsequently sintered by using flash light sintering method with various irradiation conditions including irradiation energy, pulse number, and pulse duration. The sintered Cu/Ag hybrid-inks were characterized using a scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). From these results, it was found that the Cu/Ag hybrid-ink with optimal ratio of epoxy binder content showed high printability, and the optimized multi-pulse flash light irradiation condition (irradiation energy:  $7 \text{ J}/\text{cm}^2$ , and pulse duration: 1 ms, off-time: 9 ms and pulse number: 20) exhibited high conductivity (pattern:  $9.52 \mu\Omega/\text{cm}$ , via-hole:  $12.69 \mu\Omega/\text{cm}$ ) and high adhesion strength (5B) with well-sintered morphology.

6:20pm **TF-MoE-3 Synthesis and Characterization of Pt-Ag Alloyed Thin Films Deposited using Inverted Cylindrical Magnetron Sputtering with a Configurable Target Assembly**, *Saxon Tint*, Johnson Matthey Inc.; *G Taylor*, Rowan University; *E Burkholder*, Johnson Matthey Inc.; *J Hettinger*, Rowan University; *S Amini*, Johnson Matthey Inc.

Cylindrical magnetron sputtering cathodes, which sputter from the surface of cylindrical targets, were first described by Penfold and Thornton in the mid 1970's. They described cathodes that can be built in either post (sputtering outwards) or inverted (sputtering inwards) geometries. Inverted cylindrical magnetrons (ICM) can be used to efficiently and uniformly coat wires, extended objects, and complex geometries for a variety of industrial and medical applications. ICM targets are typically manufactured by roll-forming a flat sheet of a metal or an alloy into a cylinder. However, the mechanical characteristics of some materials preclude this method. An example of this is observed in platinum (Pt) - silver (Ag) alloys that are too brittle to roll-form, thus an alternative target assembly must be used. This work will focus on a systematic study using a configurable target assembly to deposit Pt-Ag alloyed thin films by inward sputtering from an inverted cylindrical cathode for their use as antibacterial/antimicrobial coatings on orthopedic and dental implants. The target assembly comprised of hollow Pt and Ag rings which were stacked in various configurations in order to vary the composition of the final Pt-Ag films. Additionally, varying chamber pressure and cathode power were used to study their effect on film composition and film stress. Finally, film compositional uniformity was investigated throughout the height of the target assembly, which is of particular interest considering the large variation in the size of orthopedic and dental implants ranging from around one to several centimeters in length.

6:40pm **TF-MoE-4 Surface and Interface Imaging by Ultrahigh Resolution Laser-based Photoemission Electron Microscopy**, *Toshiyuki Taniuchi*, The University of Tokyo, Japan; *S Shin*, The University of Tokyo, AIST-UTokyo OPERANDO-OIL, Japan

INVITED

Photoemission electron microscopy (PEEM) is an imaging method based on a cathode objective lens, which enables non-scanning and relatively high-resolution imaging of photoelectrons emitted from sample surfaces. With ultraviolet light sources, PEEM is one of the suitable techniques for chemical and magnetic nano structures because threshold photoemission yields are very sensitive to chemical and magnetic properties. However the spatial resolution of PEEM is limited by space charge effect in use of pulsed photon sources as well as aberrations in the electron optics. We have developed the Laser-PEEM system with combination of the continuous wave (CW) laser and the aberration-corrected PEEM instrument to achieve the spatial resolution better than 3 nm. In this talk, we first show that the use of continuous wave laser has a capability to overcome such a limit due to the space charge effect. Using this technique, we have demonstrated structural and magnetic imaging using the Laser-PEEM with circular and linear dichroism. As another use case, we also show carrier-selective imaging on two-dimensional electron gases (2DEGs) at oxide surfaces and interfaces. Since threshold photoemission gives selective detection of their surface carriers, we successfully observed the imaging of 2DEGs at the oxygen-deficient surfaces and interfaces of SrTiO<sub>3</sub>. By using magnetic circular dichroism, we have found that the 2DEGs of SrTiO<sub>3</sub> surfaces show room-temperature ferromagnetism. Besides threshold photoemission using ultraviolet light sources is expected to have very large probing depth due to less electron scattering in materials. Using this technique we have also succeeded in visualization of chemical states of buried nanostructures. Since this technique enables us to observe changes in chemical and magnetic structures during operations without removing capping layer or top electrodes, We expect that it can be applied not only to non-destructive observations but also *operando* measurements.

7:40pm **TF-MoE-7 All Photonic Annealing of Solution based Indium-Gallium-Zinc-Oxide Thin Film Transistor with Printed Ag Electrode via Flash White Light combined with Deep-UV Light**, *Chang-Jin Moon, H Kim*, Hanyang University, Seoul, Korea

Recently, Indium-Gallium-Zinc-Oxide (IGZO)-based thin film transistor (TFT) has received significant attention due to high electrical mobility, optical transparency and flexibility in next generation display field. Despite of these benefits, IGZO-based TFTs have disadvantage that the film is formed on the substrate through expensive vacuum deposition process. To solve this problem, solution-process of IGZO semiconductor were attempted at room temperature. However, high temperature annealing process was indispensably required. Using light annealing system such as deep-UV, laser and flash light irradiation, the process temperature applied to the

annealing of IGZO could be significantly reduced. However, the manufacturing process of the IGZO-based TFT still involves deposition process under vacuum condition because metal-based electrode (source, drain) on the IGZO layer is fabricated by a deposition process.

In this study, all photonic annealing process of IGZO-based TFT was conducted via flash white light combined with deep-UV irradiation method for high performance TFT. Through solution-process using IGZO precursor solution and Ag ink, the TFT was made on heavily-doped Silicon wafer covered with thermally grown silicon dioxide. The IGZO semiconductor layer was coated on silicon dioxide using spin coating system and Ag electrode was printed on phonic-annealed IGZO layer by screen printing method. In order to optimize the flash light irradiation condition for annealing process, flash light irradiation energy was varied from 70 J/cm<sup>2</sup> to 130 J/cm<sup>2</sup> for IGZO, from 40 J/cm<sup>2</sup> to 60 J/cm<sup>2</sup> for Ag electrodes, respectively. The electron transfer property and several performances such as field effect mobility on saturation region, threshold voltage, subthreshold swing and on-off ratio of all photonic-annealed TFT were measured and calculated using parameter analyzer. Based on various channel lengths of Ag electrode, the contact resistance between IGZO and Ag was derived through transmission line model (TLM). The cross-sectional microstructure of interface on TFT was observed using scanning electron microscope. As a comparative case, the TFT structure was annealed by conventional thermal process. Finally, it was found that the flash light annealed IGZO with Ag electrodes shows similar performance compared to that fabricated by thermal process. The photonic annealing process of solution based IGZO TFT with printed Ag electrode using flash light combined with deep-UV light is expected to open a new path in the IGZO TFT field.

8:00pm **TF-MoE-8 Carbon-nanotube Dispersed Ga<sub>2</sub>O<sub>3</sub>Films for UV Transparent Electrodes Fabricated by Molecular Precursor Method, Tohru Honda, Y Takahashi, R Yoshida, C Mochizuki, H Nagai, T Onuma, T Yamaguchi, M Sato, Kogakuin University, Japan**

Light extraction is a crucial issue for UV LEDs. For realization of their high efficiencies, absorption in electrode should be reduced. Transparent conductive oxide (TCO) is one of the candidates. In this case, very wide bandgap (VWBG) oxides are required for its realization. Generally, VWBG oxides are known as "insulator." Thus, these materials selection is limited. On the other hand, carbon nanotube (CNT) has a good electric conductivity and its diameter is several nanometers. This means that a transparency in CNTs depend on Rayleigh scattering and a high light transparency will be expected for CNT dispersed VWBG oxides. In this paper, the fabrication of CNT dispersed Ga<sub>2</sub>O<sub>3</sub>films by molecular precursor method [1], which is one of the chemical solution methods, is reported. Their transparent properties and conductive properties are also discussed.

The Ga<sub>2</sub>O<sub>3</sub>precursor solution was prepared as follows [1]. The 3.65 g (12.5 mmol) of ethylenediamine-N, N, N', N'-tetraacetic acid (EDTA) and 5.00 g (12.5 mmol) of Ga(NO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O (n = 7–9) [calculated as Ga(NO<sub>3</sub>)<sub>3</sub>·8H<sub>2</sub>O] were added to 30 mL of pure water at 80°C, and the solution was stirred for 1 hour, and then cooled to room temperature (RT). The white powder (abbreviated as Ga-edta complex) precipitated from the solution was collected on a paper filter under reduced pressure and air-dried. The precursor solution was prepared by a reaction of 1.34 g (3.55 mmol) of Ga-edta complex with 0.51 g (3.91 mmol) of dibutylamine in 10 g of ethanol. The solution was refluxed for 0.5 h, and then cooled to RT. The Ga concentration for the precursor solution was adjusted to 0.3 mmol g<sup>-1</sup>. CNT solution of ethanol solvent (CNT; 0.0583 mmol g<sup>-1</sup>). The solutions were then mixed with the CNT solution. The 100 mL of solution was coated on quartz glass substrate by spin-coating method, and the films were dried in air at RT for 10 min and were then thermally treated using a tubular furnace in an Ar gas flow of 1.0 L min<sup>-1</sup> at 600°C for 30 min. Thickness of the resultant CNT doped Ga<sub>2</sub>O<sub>3</sub>films were about 100 nm.

The transparencies of the films are over 80% in UV spectral regions longer than a wavelength of 300 nm. The typical resistivity of a CNT-dispersed Ga<sub>2</sub>O<sub>3</sub>film is 2 × 10<sup>-2</sup>Ω·cm. The results indicate that the CNT-dispersed VWBG oxides have a potential for the application of UV transparent oxides.

[1] H. Nagai and M. Sato, in *Heat Treatment— Conventional and Novel Applications, Heat Treatment in Molecular Precursor Method for Fabricating Metal Oxide Thin Films*, ed. Dr. F. Czerwinski (InTech, Rijeka, 2012).

## Thin Films

### Room Naupaka Salons 4 - Session TF-TuM

#### Innovations in the Development of Multifunctional Thin Films

**Moderator:** Jolanta Klemberg-Sapieha, Polytechnique Montréal

##### 8:00am TF-TuM-1 Anion Interactions with Vapour Deposited Conducting Polymers, *Drew Evans*, University of South Australia, Australia

Conducting polymers offer several key advantages over their inorganic counterparts, such as mechanical flexibility, transparency, and material abundance, which can enable low-cost fabrication and novel applications such as printed and flexible electronics. The conducting polymer poly(3,4-ethylenedioxythiophene), PEDOT, is one material which displays (among others) high electrical conductivity [1], enhanced thermal conductivity [2], good electrocatalytic performance [3], as well as thermoelectric behaviour [4]. Enhancing the properties of PEDOT has been achieved through Vapour Phase Polymerisation (VPP), an oxidative polymerization process under vacuum conditions. We report that VPP PEDOT shows interesting interactions with anions, in some examples almost specific ion effects [5]. For example, the uptake of anions from an aqueous solution into electrochemically reduce PEDOT is highly dependent on the anion itself. More interestingly is nitrate is specifically absorbed by PEDOT when present in a mixed electrolyte solution [6]. This selective absorption is hypothesised to originate from anion- $\pi$  interactions, in part validated by MD simulations [5]. Such interactions, relating to both chemistry and structure, lead to interesting opportunities in energy storage as well as (agricultural) sensing.

References:

[1] Fabretto MV, et al. "Polymeric material with metal-like conductivity for next generation organic electronic devices", *Chem. Mater.* 24, pp. 3998-4003, 2012.

[2] Weathers A, et al. "Significant Electronic Thermal Transport in the Conducting Polymer Poly(3,4-ethylenedioxythiophene)", *Adv. Mater.* 27, pp. 2101-2106, 2015.

[3] Vucaj N, et al. "Vapor Phase Synthesis of Conducting Polymer Nanocomposites Incorporating 2D Nanoparticles", *Chem. Mater.* 26, pp. 4207-4213, 2014.

[4] Bubnova O, et al. "Semi-metallic polymers", *Nat. Mater.* 13, pp. 190-194, 2014.

[5] Rudd S, et al. "Charge transport and structure in semimetallic polymers", *J. Polym. Sci. B* 56, pp. 97-104, 2018.

[6] Rudd S, et al. "Selective uptake and sensing of nitrate in poly(3,4-ethylenedioxythiophene)", *Sci. Rep.* 7, pp 16581, 2017.

##### 8:20am TF-TuM-2 Decorative Electro-magnetic Transparent Metal-semiconductor Thin-films for Consumer Electronics, *Bastian Stoehr, E Charrault, D Evans*, University of South Australia, Australia; *F Lacroix*, ENSCBP - Bordeaux INP, France; *J Parks*, University of Bath, United Kingdom; *P Murphy, C Hall*, University of South Australia, Australia

Electro-magnetic (EM) transparent decorative coatings with a metallic appearance are highly desirable for military, automotive and communication applications. More specifically, they are advantageous as decorative coatings for consumer electronics. Such coatings will enable device to device communication with minimal attenuation of the signal. This will allow devices to save energy and result in increased battery life.

Inherently, a metallic thin-film, e.g. aluminium, interferes with EM radiation rendering it unsuitable for these applications. Hence, to create multifunctionality, aluminium was alloyed with semiconductors in order to manipulate its EM transparency, whilst maintaining the decorative properties of the metal thin film. One challenge for these coatings is to maintain their desired properties during thermal events, either during manufacturing into a final device or as a result of environment conditions during use.

Metal-semiconductor thin films have the inherent advantage that the optical and electrical properties of the thin film can be manipulated in multiple ways.<sup>1</sup> The properties of the thin films can be controlled not only by changing the alloy composition (type and amount of semiconductor), but also by varying the deposition parameters. We report the influence of deposition parameters and thin film composition on the EM transparency, as well as the optical properties of these coatings.

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We also report on their response to thermal stress. The optical and electrical properties of these thin films have been studied for relevant process temperatures of up to 240 °C. Their properties were analyzed and compared post processing. It was revealed that after processing the thin films at relevant temperatures, the properties changed. Interestingly, the magnitude and direction of change was dependent on the type of semiconductor used. Possible mechanisms include oxidation, phase changes, grain formation, grain size changes and changes along grain boundaries. This information will be used to select composition and process properties so that aluminium-semiconductor alloys can be used in a number of applications.

1. Kawaguchi, T., Tahara, K. & Saga, T. Radio wave transmitting decorative member. (2008).

##### 8:40am TF-TuM-3 Applications of Polarized Neutron Scattering for Development of Novel Functional Heterostructures, *Valeria Lauter*, Oak Ridge National Laboratory, USA

New functionality often arises at the mesoscale where defects, interfaces, and non-equilibrium structures are formed [1]. Probing the internal structure morphology and spin structure in thin films and nanostructured materials via Polarized Neutron Reflectometry (PNR) is a type of experiments addressing not only a kind of "surface visualization" or integration over the whole sample size. PNR is a tool providing depth resolved information and establishes a direct and precise correlation between local interfacial characteristics and global physical properties and delivers the most exhaustive and detailed information on the 3-dimensional structure of thin films and hidden interfaces on enormous length scale [2]. In this talk I will present a spectrum of experiments performed at the Magnetism Reflectometer at the Spallation Neutron Source, that covers multiple scientific areas, e.g. new generation of heterostructures based on integrating topological insulators (TIs) with conventional materials to induce ferromagnetic interactions with symmetry breaking at the interface [3], tunnel barriers in hybrid organic/metallic spin-valve structures, asymmetric block-copolymer/nanoparticle composite structures. The specific details will be presented.

Research at Oak Ridge National Laboratory's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, and the US Department of Energy, by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory.

[1] From Quanta to the Continuum: Opportunities for Mesoscale Science, a report from the Basic Energy Sciences Advisory Committee (2012)

[http://science.energy.gov/~media/bes/pdf/reports/files/From\\_Quanta\\_to\\_the\\_Continuum\\_rpt.pdf](http://science.energy.gov/~media/bes/pdf/reports/files/From_Quanta_to_the_Continuum_rpt.pdf)

[2] V. Lauter, H.J.C. Lauter, A. Glavic, B. Toperverg, "Reflectivity, Off-Specular Scattering, and GISANS Neutrons," book chapter in Reference Module Material Science Elsevier, 2016

[3] F. Katmis, V. Lauter, F. Nogueira, B. Assaf, M. Jamer, P. Wei, B. Satpati, J. Freeland, I. Eremi, D. Heiman, P. Jarillo-Herrero, J. Moodera, "Achieving high-temperature ferromagnetic topological insulating phase by proximity coupling", *Nature* 2016, **533**, 513

##### 9:00am TF-TuM-4 Oxygen-Free Palladium/Titanium Coating, a Novel Non-Evaporable Getter Coating with an Activation Temperature of 133 °C, *T Miyazawa*, SOKENDAI, Japan; *M Kurihara, S Ohno*, Yokohama National University, Japan; *N Terashima, Y Natsui, H Kato*, Hirosaki University, Japan; *Y Kato*, Irie Koken Co., Ltd., Japan; *A Hashimoto*, National Institute for Materials Science, Japan; *T Kikuchi, Kazuhiko Mase*, KEK, Japan

We developed a novel non-evaporable getter (NEG) coating with an activation temperature as low as 133 °C, that is, a palladium/titanium coating with extremely low oxygen concentration (oxygen-free Pd/Ti coating) (Fig. 1) [1]. The substrate was coated with Ti, and then overcoated with Pd using sublimation under ultra-high vacuum conditions. The morphology and surface elemental composition of the Pd/Ti thin film were investigated with electron microscopes and X-ray photoelectron spectroscopy, respectively. The thicknesses of Ti and Pd films were approximately 1.3  $\mu\text{m}$  and 50 nm, and the Ti film was completely overcoated by the Pd film. Ti and oxygen were found to be negligible on the oxygen-free Pd/Ti surface. The oxygen-free Pd/Ti coating was applied to formed bellows. The bellows was successively baked at 133 °C for 12 h, 176 °C for 3.5 h, and 200 °C for 3.5 h. After sealing off a turbomolecular pump from the vacuum system containing the bellows, the pressure reached values of  $4.6 \times 10^{-6}$  Pa,  $1.7 \times 10^{-7}$  Pa, and  $6.1 \times 10^{-8}$  Pa, respectively (Fig. 2). The pumping speeds of the bellows were estimated to be 0.028, 0.23, and 0.23  $\text{L s}^{-1}$ , respectively. These results demonstrate that oxygen-

free-Pd/Ti deposition can be used as a new NEG coating for vacuum systems with a baking temperature of 133 °C or higher. Oxygen-free Pd/Ti coating was applied for a NEG pump that can be activated by baking at 150 °C for 12 h [2].

## References

[1] T. Miyazawa, M. Kurihara, S. Ohno, N. Terashima, Y. Natsui, H. Kato, Y. Kato, A. Hashimoto, T. Kikuchi, and K. Mase, *J. Vac. Sci. Technol. A*, in press.

[2] T. Kikuchi, T. Miyazawa, H. Nishiguchi, K. Mase, *AIP Conf. Proc.*, submitted.

9:20am **TF-TuM-5 Droplet assisted Growth and Shaping (DAGS): A Broadly Applicable Method for Chemical *in situ* Shaping of Complex Polymeric Nano and Microstructures**, *Stefan Seeger, G Artus, N Saddiqi*, University of Zurich, Switzerland

The synthesis of nano and microstructures is an emerging field in chemistry and materials science. They can be made from a large variety of materials, for example metals, semi-metals, or polymeric substances. Usually, these particles exhibit a simple shape.

Some years ago, we have presented the synthesis of silicone nano filaments in particular for surface coatings. Now, we have shown a mechanism, called **Droplet assisted Growth and Shaping (DAGS)** explaining how these one-dimensional growths can be explained. Based on this synthesis scheme we are able to synthesize silicone nanoparticles of different shapes depending on the reaction conditions at room temperature from gas phase and liquid phase. Some of these structures exhibit a shape complexity which goes clearly beyond wires and filaments. Very recently, we could show that the mechanism of this synthesis is applicable not only to silicone structures but also to other chemical compounds. For example we have synthesized Germanium oxide and Aluminumoxide nanostructures. For these structures we have used Germaniumchloride and Tributyl-Aluminum. The procedure for all of them is identical, does not require high temperature, pressure or other cost increasing conditions. The shape of the structures depend on the grade of humidity in the gas phase during the reaction.

In this presentation, we will give an overview about the synthesis and process reaction conditions allowing the directed growth of nano and microstructures of complex shape.

## References

G. R. J. Artus, S. Jung, J. Zimmermann, H. P. Gautschi, K. Marquardt, S. Seeger, *Adv. Mater.* **2006**, *18*, 2758

Stojanovic, S. Oliveira, M. Fischer, S. Seeger, *Chem. Mater.* **2013**, *25*, 2787

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

9:40am **TF-TuM-6 Low Temperature Nitridation of Hafnia with Low Density of N-O Bonds**, *J Torres-Ochoa, O Cortazar-Martinez, M Mayorga-Garay, A De Luna Bugallo, Y Chipatecua-Goday, O Ceballos-Sanchez, D Silva-Cabrales, F Corona-Davila, J Raboño-Borbolla*, CINVESTAV-Unidad Queretaro, Mexico; *Alberto Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico, México

The nitridation of hafnia is attractive because it improves its dielectric properties and minimize its crystallization. The thermal budget employed might be large when nitridation is carried out through rapid thermal annealing [1]. Ultraviolet-assisted nitridation might be carried out at lower temperatures; however, N-O species dominates the N 1s spectrum [2], affecting the dielectric quality. These species are also present when the nitridation is carried out through decoupled-plasma processing [3] and can only be removed through high-temperature annealing.

We have developed a low-temperature nitridation process that minimize the formation of N-O species. It also minimizes the formation of a hafnium silicate interface layer in hafnia/Si structures [4]. It is based on remote-plasma employing a gas-mixture. The structure of the multilayer films was characterized through ARXPS, and the effect on the dielectric properties through I-V and C-V curves.

[1] S.Y. Son, P. Kumar, J.S. Lee, R.K. Singh, High efficiency nitrogen incorporation technique using ultraviolet assisted low temperature process for hafnia gate dielectric, *Appl. Phys. Lett.* **92** (2008). doi:10.1063/1.2892040.

[2] K. Ramani, C.R. Essary, V. Craciun, R.K. Singh, UV assisted oxidation and nitridation of hafnia based thin films for alternate gate dielectric applications, *Appl. Surf. Sci.* **253** (2007) 6493–6498. doi:10.1016/j.apsusc.2007.01.027.

[3] G. Saheli, W. Liu, C. Lazik, Y. Uritsky, M. Bevan, W. Tang, P. Ma, E. Venkatasubramanian, S. Bobek, P. Kulshreshtha, C.R. Brundle, Characterization of film materials in wafer processing technology development by XPS, *J. Electron Spectros. Relat. Phenomena.* (2018). doi:10.1016/j.elspec.2018.03.007.

[4] P.G. Mani-Gonzalez, M.O. Vazquez-Lepe, A. Herrera-Gomez, Aperture-time of oxygen-precursor for minimum silicon incorporation into the interface-layer in atomic layer deposition-grown HfO<sub>2</sub>/Si nanofilms, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **33** (2015) 010602. doi:10.1116/1.4904496.

10:20am **TF-TuM-8 Fundamental Properties of Transition-metal Nitrides: Materials Design Strategies for Extreme Properties**, *Joe Greene*, Linköping University, Sweden, University of Illinois at Urbana-Champaign **INVITED**

Transition-metal (TM) nitrides exhibit an enormous range of properties and offer a smorgasbord of opportunities for materials scientists. Cubic TM nitrides have wide single-phase compound fields that can be exploited. We show results for vacancy hardening in 3d Group-IV TiN<sub>x</sub>(001) and Group-V VN<sub>x</sub>(001); the hardness H (and resistivity ρ) of epitaxial layers increases, while the elastic modulus E and the relaxed lattice constant decreases linearly, as x is decreased from 1.0 to 0.67 and 0.80, respectively. In contrast, H(x), E(x), and ρ(x) for 5d Group-V TaN<sub>x</sub>(001) remain constant due primarily to the presence of isoelectronic antisites. Strong electron/phonon coupling in VN<sub>x</sub> results in thermal conductivity at room temperature and above being dominated by electronic contributions.

All Group-IV TM nitrides, TiN, ZrN, and HfN, are very good metallic conductors with room-temperature resistivities of 12–14 μΩ-cm. 3d Group-III ScN(001) is a transparent semiconductor with an indirect Γ-X gap of 1.3 eV. Reflectivity measurements from Sc<sub>1-x</sub>Ti<sub>x</sub>N(001) layers show TiN is strongly reflecting up to the reflectance edge at ħω<sub>e</sub> = 2.3 eV, while ScN is transparent, and ω<sub>e</sub> ∝ x<sup>0.5</sup> for the alloy. ZrN is intermediate with ħω<sub>e</sub> = 3.04 eV. Thus, hard decorative coatings can be obtained with a wide palette of colors.

Superconducting transitions T<sub>c</sub> for the Group-IV TM nitrides range from 10.4 K for ZrN to 9.18 K for HfN to 5.35 K for TiN. For comparison, superconductivity is not observed for the Group-IV rare-earth (RE) nitride CeN. These results are consistent with electron/phonon coupling parameters of 1.11 (ZrN), 0.82 (HfN), 0.73 (TiN), and 0.44 (CeN). The acoustic phonon modes soften monotonically with increasing cation mass; optical mode energies remain approximately constant for the TM nitrides, but are significantly lower for the RE nitride due a lower interatomic force constant.

The extreme range of materials properties available in TM nitrides and related systems can be enhanced through the formation of self-organized superhard nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanopipes.

An issue with hard ceramic films, however, is that they are typically brittle, leading to failure by crack formation and propagation. We show several approaches to obtaining TM nitride layers that are both hard *and* ductile (i.e., tough). IV-VI and V-VI alloys, e.g. Ti<sub>1-x</sub>W<sub>x</sub>N and V<sub>1-x</sub>Mo<sub>x</sub>N, exhibit dramatic delocalization of electron density leading to a more ductile response to shear stress while exhibiting increased hardness under tensile and compressive loading. Vacancy-induced toughening is also observed in under-stoichiometric (V,Mo)N<sub>x</sub> alloys.

11:00am **TF-TuM-10 Surface Reactions of Metal and Metal Oxides on Hybrid Perovskite Materials for Optoelectronics Applications**, *J Cazares-Montañez, M Martinez-Puente, R Garza-Hernández, E Martínez-Guerra*, CIMAV-Monterrey, Mexico; *M Quevedo-Lopez*, University of Texas at Dallas; *Francisco Aguirre-Tostado*, CIMAV-Monterrey, Mexico

Hybrid perovskites (HPV) have recently emerged as highly efficient optoelectronic materials and are currently being intensively investigated as alternative active layer materials for photodetectors, light-emitting diodes, laser devices, sensors and X-ray detectors, among others. Since HPV are direct band gap materials with high optical absorption coefficients (~ 10<sup>5</sup>cm<sup>-1</sup>) the majority of publications have been dedicated to hybrid organic-inorganic solar cells with certified efficiencies over 20%. However the realization of a long-lasting device implies the understanding of chemical and structural stability of HPV materials and their interface with electron and hole transport layers (ETL and HTL, respectively). This presentation will show detailed XPS analyses of the chemical stability of the transition metal and transition metal oxides with ABX<sub>3</sub> hybrid perovskites for A=MethylAmmonium (MA), B=Pb, and X=Cl, I, and Br. HTL/HPV interface is not trivial as the reactivity of halogen group elements

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forms an unstable high resistance interlayer at the charge transport layer interface compromising the optimum operation of the device. The electrical characterization and work function measurements will be discussed and correlated to the chemistry and crystalline structure of the materials of interest.

11:20am **TF-TuM-11 Thin-Film Alchemy: Engineering Oxide Films to Unleash their Hidden Properties**, **Darrell G. Schlom**, Cornell University  
**INVITED**

Guided by theory, unparalleled properties—those of hidden ground states—are being unleashed by engineering oxides at the atomic level. This engineering includes strain engineering, dimensional confinement, and defect engineering. Using these thin-film tricks, materials that are not ferroelectric or ferromagnetic in their unstrained state can be transmuted into ferroelectrics, ferromagnets, or materials that are both at the same time. Similarly, new tunable dielectrics with unparalleled performance have been created. Our studies reveal details about the microscopic growth mechanism of these phases, which are relevant to preparing multicomponent oxide heterostructures with atomic precision. A new era for engineering functional oxide thin films for electronics is upon us: oxides by design. This work was performed in collaboration with the coauthors listed in the references below.

C.H. Lee, N.D. Orloff, T. Birol, Y. Zhu, V. Goian, E. Rocas, R. Haislmaier, E. Vlahos, J.A. Mundy, L.F. Kourkoutis, Y. Nie, M.D. Biegalski, J. Zhang, M. Bernhagen, N.A. Benedek, Y. Kim, J.D. Brock, R. Uecker, X.X. Xi, V. Gopalan, D. Nuzhnyy, S. Kamba, D.A. Muller, I. Takeuchi, J.C. Booth, C.J. Fennie, and D.G. Schlom, "Exploiting Dimensionality and Defect Mitigation to Create Tunable Microwave Dielectrics," *Nature* **502** (2013) 532–536.

C.H. Lee, V. Skoromets, M.D. Biegalski, S. Lei, R. Haislmaier, M. Bernhagen, R. Uecker, X.X. Xi, V. Gopalan, X. Martí, S. Kamba, P. Kužel, and D.G. Schlom, *Appl. Phys. Lett.* **102** (2013) 082905.

Y.F. Nie, Y. Zhu, C.-H. Lee, L.F. Kourkoutis, J.A. Mundy, J. Junquera, P. Ghosez, D.J. Baek, S. Sung, X.X. Xi, K.M. Shen, D.A. Muller, and D.G. Schlom, "Atomically Precise Interfaces from Non-Stoichiometric Deposition," *Nat. Commun.* **5** (2014) 4530.

V. Goian, S. Kamba, N. Orloff, T. Birol, C.H. Lee, D. Nuzhnyy, J.C. Booth, M. Bernhagen, R. Uecker, and D.G. Schlom, "Influence of the Central Mode and Soft Phonon on the Microwave Dielectric Loss near the Strain-Induced Ferroelectric Phase Transitions in  $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ ," *Phys. Rev. B* **90** (2014) 174105.

A.M. Hagerstrom, X. Lu, N.M. Dawley, H.P. Nair, J. Mateu, R.D. Horansky, C.A.E. Little, J.C. Booth, C.J. Long, D.G. Schlom, and N.D. Orloff, "Sub-Nanosecond Tuning of Microwave Resonators Fabricated on Ruddlesden-Popper Dielectric Thin Films," *Adv. Mater. Technol.* (2018) 1800090. <https://doi.org/10.1002/admt.201800090>

N.M. Dawley, E.J. Marksz, A.M. Hagerstrom, M.E. Holtz, G.H. Olsen, J. Zhang, C.J. Long, J.C. Booth, C.J. Fennie, D.A. Muller, N.D. Orloff, and D.G. Schlom, "Applying Chemistry to Make Today's Best Tunable Millimeter Wave Dielectric even Better" (unpublished).

# Tuesday Afternoon Poster Sessions, December 4, 2018

## Thin Films

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

#### Thin Films Poster Session I

Moderator: Darrell G. Schlom, Cornell University

**TF-TuP-1 Oxidation Behavior of Sputtered NiFe<sub>2</sub> Coating on Ferritic Stainless Steel for SOFC Interconnect Application, *Shujiang Geng, F Wang*, Corrosion and Protection Division, Shenyang National Laboratory for Materials Science, Northeastern University**

Ferritic stainless steels are confronted with several problems during operation in SOFC cathode working condition such as the spallation of the oxide scale and cathode Cr-poisoning, leading to significantly degradation of the cell performance. To solve these problems, NiFe<sub>2</sub> alloy coating has been deposited on SUS 430 ferritic stainless steel via magnetron sputtering method. Electrically conductive NiFe<sub>2</sub>O<sub>4</sub> spinel coatings were thermally developed on the steels from the sputtered NiFe<sub>2</sub> coatings in air at 800°C. Initial oxidation behaviors of NiFe<sub>2</sub> coated bare and pre-oxidized steels were investigated for understanding the conversion process from the alloy coating to spinel. The phase structure and composition of coated steels after oxidation were characterized with XRD and SEM/EDS.

The oxidation kinetics analysis of the first 60min exposure demonstrated rapid mass gains were observed during the beginning 5-10 min for the coated bare and pre-oxidized steels, followed with slightly increase. The XRD and SEM/EDS results indicated Fe was preferentially oxidized resulting in un-reacted Ni residue in the coatings during the rapid mass gains stages. Scale formed on the coated bare steel presented multilayered structure, primarily consisting of a top Fe<sub>2</sub>O<sub>3</sub> layer followed with NiFe<sub>2</sub>O<sub>4</sub> layer and NiO layer. During the first 10 min, un-reacted Ni region beneath the NiO layer was decreasing with time. Cr-rich oxide was detected at the interface of scale/steel after 30min exposure. Similar scale structure was observed on the coated pre-oxidized steel except Cr-rich layer at scale/steel interface consistently. Compared with the coated bare steel, the bigger defect gap between columnar-grains in NiFe<sub>2</sub> coating on pre-oxidized steel serving as channel for oxygen inward diffusion will presumably provide higher oxygen capacity in coating, which accelerated Ni consumption during oxidation. Chromia layer formed after pre-oxidation treatment acted as a barrier to block Cr outwards diffusion into the alloy coating at the beginning of oxidation. Scales on both coated steels were well-bonded to steel substrate with a few tiny pores distributing discretely. The oxidation mechanisms were discussed.

**TF-TuP-2 Effects of Bias Voltage on the Structure and Corrosion Properties of Thick Cr Coatings Deposited Using Cathodic Arc Ion Plating, *Jung-Hwan Park, Y Jung, D Park, H Kim, B Choi, Y Lee, J Yang*, Korea Atomic Energy Research Institute**

After the Fukushima Daiichi nuclear accident, the major issue of nuclear researchers has been an improvement in the oxidation resistance under beyond-design accident conditions. Therefore, accident tolerant fuel (ATF) has been widely studied, which has high-temperature oxidation resistance. For the development of ATF claddings, several advanced cladding materials that have high-temperature oxidation resistance have been proposed, including advanced stainless steels, Mo alloys, and SiC/SiCf composites. However, they require changes in the engineering design of the reactor cores. An alternative approach to improving safety is to fabricate a cladding with a protective coating. A protective coating that has a high oxidation resistance also improves the corrosion performance during normal operation. Several coating materials have previously been suggested, including SiC, FeCrAl, TiN, TiAlN and Cr. Among the candidate materials for protective coating, Chromium coatings are well known for their high hardness, good corrosion, and wear resistance. In our previous work, Cr coating deposited on a zircaloy-4 cladding by cathodic arc ion plating was investigated to evaluate the corrosion protection of zircaloy-4 cladding in a high-temperature steam environment. Compared to pristine Zircaloy-4, Zircaloy-4 with a Cr layer exhibited superior oxidation resistance. However, an oxygen-stabilized alpha zirconium ( $\alpha$ -Zr(O)) layer, which was formed through oxygen diffusion, was observed after a high-temperature steam oxidation test.

In this study, we tried to optimize the ion plating conditions to reduce the inward oxygen diffusion. Cr coatings were deposited on a Zircaloy-4 tube using arc ion plating at various substrate bias voltages. The effects of the substrate bias voltage on the corrosion behavior of arc ion plated Cr films has been investigated. We also investigated the relationships among the

substrate bias voltage, physical properties, and corrosion resistance for Cr coated zircaloy-4. The internal stress was measured using an iso-inclination method with an x-ray diffractometer at room temperature. A high-temperature steam oxidation test at 1473 K was executed.

**TF-TuP-3 Graphite Tribofilm Extracted from Base Oil by Self-Oxidizing Coating: A Highway for Friction and Wear Reduction, *Lina Yang*, State Key Laboratory of Superhard Materials, Department of Materials Science and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China., China; *K Zhang*, State Key Laboratory of Superhard Materials, Department of Materials Science and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China, China**

Tailoring sliding interface is a vital pathway to minimize friction and wear, commonly, either fluid layers or solid tribofilms have been employed. Herein, the lubricating effects from both ones are combined via in situ formation of graphite tribofilm extracted from PAO base oil (without additives) when introduced catalytic TiN coating enabled by solute Ag atoms (super-hard nature). In this way, superior tribological properties with ultralow friction coefficient at 0.075 and wear rate at  $2.28 \times 10^{-11}$  mm<sup>3</sup>/Nm can be obtained. Better yet, the incorporation of solute Ag atoms into TiN structure could induce a charge depletion state and active surface self-oxidation to a special Ag<sub>2</sub>O/TiO<sub>2</sub> composite, as demonstrated by electron localization function (ELF) and XPS. Different from traditional metal catalysts, such metallic oxides from solid solution structure are suggested to dominant this catalyst and extraction action. Besides, the direct transfer of part of electrons from the unstable charge structure to oil molecules further ensures the catalytic effect. This study highlights the crucial role of solid solution coating in catalyzing and extracting tribofilms from lubricating oil, which would be a new insight towards a more efficient lubricating system.

**TF-TuP-4 Solute Ag Atom Incorporated into TaN with Excellent Tribological Property and Robust Antibacterial Activity, *Ping Ren, M Wen*, State Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun 130012, People's Republic of China, China**

Nowadays, designing transition metal nitrides (TMN)-based films deposited on Ti-6Al-4V substrates with enhanced wear-resistance, anti-bacteria and a reduced friction represents urgent challenge for various application including bistoury scalpel, medical catheter, door handle and kitchen utensils et al. Generally, incorporating higher content (> 10 at.%) of antibacterial metallic phase (i.e. Cu, Ag) into TMN matrix to form the TMN/metal nanocomposite film has been considered as an effective approach to achieve improved toughness and antibacterial activity. However, in this system, hardness and wear rate are highly sensitive to soft metal content and can be significantly worsened. Herein, we provide a new strategy to introduce few solute Ag atoms (~ 3.08 at.% Ag) into TaN lattice to form a Ta-Ag-N solid solution structure, simultaneously achieving superhard (~ 40 GPa) yet high toughness, and improved wear-resistance, coupled with remarkable decrease in friction relative to Ag-free TaN film and TaN/Ag nanocomposition film with the same Ag content. In addition, the solid solution Ta-Ag-N film exhibits the excellent antimicrobial activity on *Escherichia coli* tested by measuring the diameters of the bacteriostasis circles. Obviously, introduction of few solute Ag atoms into TMN may open a new window to improve the comprehensive properties including hardness, toughness, friction, wear-resistance and anti-bacterial.

**TF-TuP-5 Influence of Ag Content on the Tribological Properties of MoNbN-Ag Coatings at Elevated Temperature, *K Zhang*, State Key Laboratory of Superhard Materials, Department of Materials Science, Key Laboratory of Automobile Materials, MOE, and Jilin University, Changchun, People's Republic of China, People's Republic of China; *Xuan Dai*, State Key Laboratory of Superhard Materials, Department of Materials Science, Key Laboratory of Automobile Materials, MOE, and Jilin University, Changchun, People's Republic of China, China; *M Wen*, State Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun, People's Republic of China, China; *W Zheng*, State Key Laboratory of Superhard Materials, School of Materials Science and Engineering and Key Laboratory of Automobile Materials, MOE, Jilin University, Changchun, People's Republic of China**

In recent years, with the increasingly fierce and vigorous development of aviation technology, aerospace engine, as the "crown jewel of the aviation industry", has been constantly improving its requirements of technology and performance. Because the aerospace engines always work in high



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temperature environment, it is necessary for materials to have reliable tribological performance at high temperature. However, high temperature lubrication is still a considerable challenge for the tribology field, and it results that the damage and failure of motor components are always caused by high temperature friction. Here, a reduced friction coefficient from 25 to 800 °C was achieved successfully in MoNbN-Ag coating with tailoring Ag content. The deposited MoNbN coating is a ternary fcc-solid solution, and the transformation from solute Ag atoms to precipitate metal Ag can be realized through the increasing of Ag content. The reduced friction coefficient can be ascribed to silver, molybdenum and niobium reacted with oxygen at elevated temperatures and create lubricious phases molybdenum oxide, niobium oxide, silver molybdate and silver niobite film on the coating. Amusing, compared with Ag in the form of precipitation in MoNbN coating, when silver exists in the form of solid solution, it has a lower friction coefficient at 25-450 °C and a similar friction coefficient at 450-800 °C. In which, it's attributed to the contribution: solute Ag can activate easier self-oxidation forming  $Ag_2O$  and  $MoO_3/Nb_2O_5$  on the surface, which is beneficial for formation of  $Ag_2Mo_4O_{13}/AgNbO_3$  during sliding at medium and low temperatures, thereby reducing friction.

**TF-TuP-6 High rate Reactive Sputter-deposition of  $WO_3$  Films by using Two Different Deposition Methods, Yoji Yasuda, Y Hoshi,** Tokyo Polytechnic University, Japan

Tungsten oxide ( $WO_3$ ) is well known as a functional material with excellent gasochromic, electrochromic, and photocatalytic properties. Nano-structured  $WO_3$  films prepared by glancing angle sputter deposition and high-rate gas flow sputtering were reported by Horprathum et al. and Oka et al., respectively. We have already reported that high-rate deposition of  $WO_3$  films at a deposition rate ( $R_D$ ) of more than 100 nm/min can be achieved by pulsed dc planar magnetron sputtering (PMS). However, poor gasochromic film was obtained near the center area of the substrate. This was due to bombardment by high energy negative oxygen ions that are sputtered from a target surface to the substrate surface during sputter-deposition. This ion bombardment is expected to be completely suppressed if the facing-target type low damage sputtering system (FTS) used for the deposition process.

In this study, we deposited  $WO_3$  films using two different sputtering methods (a PMS and an FTS system), and compared the structure and properties of the resulting films. Typical sputtering conditions are presented in the poster session.  $R_D$  of more than 120 nm/min was easily realized with an increase in the sputtering voltage above 700 V. A typical  $WO_3$  film obtained by PMS exhibited inhomogeneous gasochromic properties that depended on the location on the substrate, and films with excellent gasochromic properties were only obtained at the corner of the substrate. It was also found that the nonuniformity of the films can be improved by altering the angle of incidence of the particles on the substrate and relaxing the impact.

In contrast, uniform films were easily obtained by FTS. Details will be presented in the poster session.

**TF-TuP-7 Initial Growth of Pentacene Thin Film on Si(001) Substrate, Takayuki Suzuki, K Yagyu, H Tochiyama,** Fukuoka University, Japan

Initial growth process of the pentacene molecules on the clean Si(001)-2x1 substrate were investigated by Scanning Tunneling Microscopy (STM) at room temperature (RT). The pentacene molecules were deposited onto the clean Si(001) surface held at RT, using a quartz crucible. We found that the wetting layer forms first by increasing the amount of the deposited pentacene molecules before starting the formation of the first layer, which is not crystalized, but disorder, where the molecules adsorb flatly. It does not have any ordered domain structure. The first pentacene layer that is crystalized with the standing-up pentacene molecules grows on the disordered wetting layer by increasing the deposited amount of the molecules more. The first layer consists of three domains at least, which have different crystal structures from each other: the ' $\alpha$ ', the ' $\beta$ ' and the ' $\gamma$ ' domains. Among them, the ' $\beta$ ' domain has a new pentacene crystal structure that can form only on the first layer. The first layer does not have a dendritic shape at least at a field of view of 2  $\mu m$ . Second pentacene layer starts to form on top of the first layer by increasing the deposited amount more again, before the first layer completely covers the substrate surface. In contrast, the second layer has only single domain. The all other crystal structures found in the present study except for that of the ' $\beta$ ' domain, are similar to those of the four polymorphs reported previously [1]. Moreover, we investigated electronic properties of the various pentacene layers by the I-V measurements. The pentacene layers are semiconducting with a gap of about 4 eV from -1 eV to +3 eV.

Reference

[1] M. Kitamura, Y. Arakawa, J. Phys.: Condens. Matter 20, 184011 (2008), and references therein.

**TF-TuP-8 Thermal Stability of Atomic Layer Deposition Precursors, Kyuyoung Heo, J Son, G Jung,** Korea Research Institute of Chemical Technology, Republic of Korea; *W Lee,* Korea Research Institute of Chemical Technology, Republic of Korea, Republic of Korea

The development of high-k dielectric precursors for advanced semiconductor applications requires molecular engineering and chemical tailoring to obtain specific physical properties and performance capabilities. Some high-k precursors such as organometallic precursors for atomic layer deposition (ALD) that have metal atoms bound to cyclopentadienyl, are stored at a sufficiently high temperature due to their low volatility and consumed through continuous deposition for a commercial semiconductor process. In this case, thermal degradation slowly occurs due to storage at a high temperature for a long time, which causes deterioration of physical properties and reliability of the thin film. However, a technique for assessing the reliability of precursor has been undeveloped and thus causing the development of new precursors to be delayed. In this study, we have developed a reliability evaluation method for cyclopentadienyl tris(dimethylamino) zirconium [ $CpZr(NMe_2)_3$ ] through accelerated thermal degradation test under severe environmental conditions in a short period of time. To evaluate the lifetime of precursor, we have investigated the thermal stability and degradation mechanism of precursor by using analysis of NMR and mass and viscosity measurements.

**TF-TuP-9 Growth Behavior and Film Properties of Titanium Dioxide by Plasma-Enhanced Atomic Layer Deposition with Discrete Feeding Method, Heungseop Song, D Shin, J Jeong, H Park, D Ko,** Yonsei University, Korea, Republic of Korea

Titanium dioxide ( $TiO_2$ ) has emerged as an attractive dielectric material for electronic devices such as memory and thin film transistors due to its high dielectric constant and high thermal stability or its role as an important constituent of multi-metal oxide systems.  $TiO_2$  thin films can be fabricated in many ways, such as physical vapor deposition, chemical vapor deposition and spin coating. Among these growth methods, plasma-enhanced atomic layer deposition (PE-ALD) technology becomes one of the most promising methods for nanoscale thin film deposition because of its advantage of conformal growth, precise control of the film thickness and relatively low substrate temperature. However, most PE-ALD  $TiO_2$  processes show a low growth-per-cycle (GPC) of less than 1.0 Å, making them difficult for mass production. T. Park et al. reported the steric hindrance caused by the physical size and proximity of the neighboring parts of the precursor (or partially decomposed) molecule during precursor feeding time and introduced a "discrete feeding method" (DFM) of the metal precursor as a solution for improved GPC of  $HfO_2$  film [1]. In this presentation, we report the growth behavior of  $TiO_2$  film with the DFM-applied and the conventional ALD growing method, using tetrakis-dimethylamido-titanium [ $Ti(NMe_2)_4$ ], as a Ti precursor. Our work focused on improving both physical and electrical properties of the film as well as increasing its growth rate through DFM application. In our experiments,  $TiO_2$  films were deposited on Si (100) substrates at 250 °C. Spectroscopic ellipsometry (alpha-SE model, J. A. Woollam Co. Ltd.) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific Inc., U.K) were examined to compare GPC. As a result, the GPC of the DFM group was increased by 18% compared to that of the conventional method group and the GPC difference from the ellipsometry measurement results of the two groups was also in agreement with the XPS analysis. In addition, we performed a wet etch rate test using 25: 1 HF chemical to compare the physical properties of the thin films and confirmed that the DFM group had a wet etch rate close to 6% of the wet etch rate for the conventional group. This confirms that the denser film was formed when DFM was applied, which was also consistent with the finding of the difference in Ti density observed through Rutherford backscattering spectrometry analysis. We expect that these differences in physical film properties would affect dry etch selectivity and consequently result in better dry etch selectivity compared to  $SiO_2$  that has been most widely used in the semiconductor industry.

[1] T. Park et al., Chem. Mater. 2011, 23, 1654-1658.

# Tuesday Afternoon Poster Sessions, December 4, 2018

**TF-TuP-10 Properties of nm Scale Tungsten Thin Film Deposited using Inductively Coupled Plasma Assisted Sputtering, Soojung Lee, T Kim, B Jeong, C Song, J Byun, J Kim, Y Ji, G Yeom, Sungkyunkwan University, Republic of Korea**

As the device width is reduced under 10 nm due to the high integration of semiconductor devices, resistivity of metallization line is significantly increased due to the decrease of the device width. Copper (Cu) is the most commonly used for metallization owing to the low resistivity and high conductivity. However, Cu metallization is known to show the limitation for the nm thickness due to the size effect linked to the long electron mean free path (EMFP) of 39nm. Also, the reliability of Cu is degraded as device operating temperatures and current densities are increased with each technology node. Since W has a smaller EMFP of 19nm, it is expected to reduce the size effect as it goes to nm dimension. Furthermore, W has a very high melting temperature of 3673K, there is a possibility to replace Cu for future metallization material for the metal thickness lower than tens of nm. In this study, ICP assisted sputtering of W has been investigated for lower resistivity of nm scale W film. An internal-type coil antenna has been used for a high ionization, and a DC sputter system has been used for the deposited W thin film. When the characteristics of W thin film deposited with and without ICP assistance were investigated, the decrease of the W thin film resistivity was decreased and, regardless of substrate heating, the deposition rate was increased due to the increase of plasma density. By using high density plasma, we could get dense structure of W thin film at low temperature. Using the XRD, the decrease of  $\beta$  peak which is A-15 structure and the increase of  $\alpha$  peak which is bcc structure at both room temperature and 673K were observed with ICP-assisted sputtering. It means ICP assistance influence the decrease of the W thin film resistivity. In addition, analyzing with XPS, the O content in the W thin film which has great influence on the resistivity of W thin film was decreased with increasing the ICP power. As a result, the feasibility of tungsten deposited by ICP assisted sputtering as a next-generation metal interconnect material was investigated.

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**TF-TuP-11 A New High Wear-resistant Conductive Coating Based on Transition Metal Nitrides with Solid Solution Structure, Yuankai Li, C Hu, State Key Laboratory of Superhard Materials, Key Laboratory of Automobile Materials of MOE, and School of Materials Science and Engineering, China**

High wear-resistant conductive coatings have recently attracted increasing interest owing to their technological importance in the fields of high-speed railways, artificial joints and electrode materials. However, wear-resistance and conductivity of materials are a dilemma from the perspective of structures and chemical bonds. Thus, developing ideal wear-resistant conductive coatings remains a significant challenge. Here, we propose a novel strategy to design wear-resistant conductive coatings: a transition metal nitride is selected as a base, and its wear-resistance and electrical conductivity are simultaneously improved by doping transition metals or noble metals to form a solid solution structure. The new strategy is demonstrated to be practically feasible and effective by two experiments: doping tantalum and silver into hafnium nitride films. Doping with tantalum and silver can improve wear-resistance and conductivity of hafnium nitride films due to the formation of solid solution structures. The conductivity and wear-resistance of the silver precipitated Hf-Ag-N supersaturated solid solution are higher than those of the Hf-Ta-N solid solution, which is attributed to not only the solid solution strengthening effect but also the effects of precipitate silver including the precipitation strengthening, self-lubrication and additional conductivity enhancement. Combining a series of experiments with first-principle calculations and Drude-Lorentz fitting, we have proved that the formation of solid solution structures can achieve both wear-resistance and conductivity enhancement, apart from well-known strength enhancement. This work provides new insights in designing hard, wear-resistance yet high-conductivity coatings.

**TF-TuP-13 Tribo-mechanical and Tribo -corrosion Properties of Thin-on-thick Duplex PVD/HVOF Coatings, Jolanta Klemberg-Sapieha, F Pougoum, J Qian, L Martinu, Polytechnique Montréal, Canada; Z Zhou, K Li, City University of Hong Kong; R Schulz, Institut de recherche d'Hydro-Québec**

The tribo-mechanical, corrosion and, in general, multifunctional performance of metallic substrates can be significantly enhanced by applying a thin-on-thick duplex coating architecture. Specifically, in a very promising system consisting of a High Velocity Oxy-Fuel (HVOF) coating followed by a Physical Vapor Deposition (PVD) coating, the hard thick HVOF layer provides the load carrying capacity of the soft substrate, while the top

dense thin PVD film improves the wear and corrosion resistance. In the present work, pure Fe<sub>3</sub>Al coatings and composite Fe<sub>3</sub>Al:BN coatings (~300  $\mu$ m), with a hardness between 4.3 and 12.8 GPa, were prepared on SS304 substrates by HVOF. The top thin PVD layer of diamond like carbon (DLC, 1~2  $\mu$ m) has been prepared by pulsed DC magnetron sputtering. The tribo-mechanical and tribo -corrosion properties of the DLC/SS304, DLC/Fe<sub>3</sub>Al/SS304 and DLC/Fe<sub>3</sub>Al:BN / SS304 coating systems were then compared. Application of the DLC layer on top of the HVOF coating allowed one to decrease the friction coefficient from 0.7 to <0.1, and to significantly enhance the wear resistance. Particularly, the DLC/Fe<sub>3</sub>Al:BN system exhibits the lowest wear rate of  $8 \times 10^{-8}$  mm<sup>3</sup>/N<sup>-1</sup>.m<sup>-1</sup>. The corrosion resistance of the DLC/Fe<sub>3</sub>Al system was increased by 3 orders of magnitude. The wear, corrosion, and tribo -corrosion mechanisms are discussed in detail.

## Thin Films

### Room Naupaka Salons 4 - Session TF-TuE

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

**Moderator:** Lars Hultman, Linköping University

##### 5:40pm TF-TuE-1 Effects of Ar:N<sub>2</sub> gas ratio on TiN and TiAlN Thin Films Synthesized via RF Magnetron Sputtering, *Jason Audrey Licerio, A Alibadbad, M Vasquez*, University of the Philippines, Philippines

There is a growing interest in using titanium nitride (TiN) and titanium aluminum nitride (TiAlN) as a hard coating in recent years because of their high hardness, low friction coefficient, and good wear and oxidation resistance. Lifetime of machining tools significantly increase when coated with these transition metal nitrides. Radio frequency (RF) magnetron sputtering was used to synthesize the films. In this study, the Ar:N<sub>2</sub> ratio of synthesized TiN and TiAlN films were varied and characterized using a single target magnetron. That is, thin film growth is achieved using either a Ti target or 1:1 TiAl composite target. Argon:nitrogen (Ar:N<sub>2</sub>) partial pressure ratios were varied at 9:1, 8:2, and 7:3 to grow the TiN and TiAlN films. Scanning electron microscope (SEM) images of TiN showed rough, 'pyramid-like' grains. Higher N<sub>2</sub> content resulted in more compact grains. The TiAlN films formed were dense 'cauliflower-like' grains. Cross-sectional SEM images showed both films having columnar structure with increasing grain diameter as N<sub>2</sub> content is increased. Energy dispersive x-ray spectroscopy mapping of TiN showed over-stoichiometric TiN<sub>x</sub>. TiAlN maps showed almost 1:1 Ti:Al ratio but an abundance of N, confirming the formation of TiAlN<sub>x</sub> films. X-ray diffraction (XRD) results of TiN showed presence of (111), (220), and (311) TiN crystallographic planes. Decreasing N<sub>2</sub> content in the system resulted in the increase in intensity of (111) and (220) planes while increase in N<sub>2</sub> resulted in broadening of (111) plane. TiAlN XRD results showed formation of (111), (200), and (220) peaks. Increasing N<sub>2</sub> enhances the (220) peak. The 80:20 Ar:N<sub>2</sub> ratio resulted in increase of (200) peaks. The performance of drill bits coated with TiN showed three-fold increase in number of holes drilled while TiAlN films showed a two-fold increase as compared to that of uncoated drill bits. This work succeeded in the synthesis of TiN and TiAlN films and improving drill bit performance.

##### 6:20pm TF-TuE-3 Formation Mechanism of Tribofilm of Silicon Carbide under Water Lubrication: Molecular Dynamics Simulation, *Fumiya Nakamura, Y Wang, N Miyazaki, Y Ootani, N Ozawa, K Adachi, M Kubo*, Tohoku University, Japan

Water lubrication has the characteristic of low environmental burden. It is known that silicon carbide (SiC) shows low friction coefficient due to the formation of a tribofilm by chemical reaction at sliding interfaces under water lubrication. Thus, understanding of the chemical reaction mechanism is essential to improve friction characteristic for practical use and application. However, it is difficult to observe directly such a complicated phenomenon including friction and chemical reaction by experiments. Therefore, in this study, molecular dynamics (MD) simulation using reactive force field, which can simulate chemical reaction, was conducted to analyze the structure and formation mechanism of tribofilm in the friction process of amorphous SiC under water environment.

In the simulation, we used a model in which amorphous SiC ball and disk were rubbed in water (See supplementary document (SD) Fig.1). The SiC ball was slid on the SiC surface with nominal pressure of 0.5 GPa and sliding speed of 100 m/s.

During the friction, the surface wears as the SiC ball and the SiC disk come into contact with each other. Silica (SiO<sub>2</sub>) particle and hydrocarbon were confirmed as wear debris. It was also observed that the SiO<sub>2</sub> particles dissolved in water and forms colloidal silica. Firstly, we investigated the changes in number of water molecules and Si-O-Si and C-H bonds during the friction (See SD Fig. 2, Fig.3). It was found that the number of water molecules decrease continuously while the number of Si-O-Si and C-H bonds increase correspondingly. This result indicates that hydrolysis reaction of SiC (SiC + H<sub>2</sub>O → Si-OH + C-H) occurs at the sliding interface. Next, we investigated the change in the number of Si and C contained in the wear debris (See SD Fig. 4). We found that the number of Si in the debris was always larger than that of C in the debris. This result indicates that the Si atoms are easily dissolved from the SiC surface as SiO<sub>2</sub> particle, whereas the C atoms tend to remain on the SiC surface. The distribution of C, Si, H, and O atoms except H<sub>2</sub>O molecules shows that the C and H atoms

were concentrated on the surface of the SiC disk and SiC ball (See SD Fig. 5, Fig. 6). On the other hand, the Si and O atoms were dissolved in water, forming the colloidal silica. Meanwhile, the Si and O atoms also located between the SiC disk and SiC ball. This fact indicates that the colloidal silica prevent the contact of the surfaces, leading to low friction. Thus, we concluded that colloidal silica, which is produced by the hydrolysis reaction of SiC surface, lowers the friction of SiC in water lubrication.

##### 6:40pm TF-TuE-4 Recent Advances in Surface Engineering, *Ivan Petrov*, Linköping University, Sweden, Frederick Seitz Materials Research Laboratory, University of Illinois

**INVITED**  
Surface Engineering (SE) is the science and technology of improving the surface properties of materials for protection in demanding contact conditions and aggressive environments. SE also encompasses engineering new multi-functional surface properties, such as electrical, optical, thermal, chemical, and biochemical properties. It involves multiple or hybrid processes which include substrate modification and deposition of overlayers in complex architectures. These processes enhance adhesion and optimize composition or microstructure to enhance protective properties coupled with other functionality. The substrates may be of complex shapes, like metal-cutting tools and automotive or aerospace components, and range in size from micrometers, such as in MEMS or NEMS devices, to meters, such as in architectural glass. The applications are wide-ranging, and include, for example, control of friction, wear-resistance, corrosion-resistance, thermal-barrier coatings, decorative coatings, bioimplants, antimicrobial layers, web-coatings, and thin films with engineered electrical and optical responses. Areas of scientific interest range from first-principle atomistic studies of new materials, to scientific and technological advances in synthesis methods, structural and chemical characterization techniques, property measurements, and performance characterization of surface-engineered parts. I will highlight a few selected SE advances from the past three years which include: complex SE architectures for joint-replacement implants [1], duplex coating for superior wear resistance of Ti alloy compressor blades or landing gear components [2], fracture-resistant thin-film metallic glass [3] and non-stick syringe needles[4]. TiB<sub>x</sub> thin films grown from compound TiB<sub>2</sub> targets by magnetron sputter deposition are typically highly over-stoichiometric due to differences in Ti and B preferential ejections angles and gas-phase scattering during transport. I will describe two methods to control of the B/Ti ratio in sputter deposited titanium diboride coatings, involving preferential ionization of sputter-ejected Ti atoms [5,6]. The ability to obtain stoichiometric TiB<sub>2</sub> films is a prerequisite to obtaining high-quality epitaxial transition metal diboride layers. Overall, Surface Engineering continues to be a vibrant interdisciplinary field in the area of interest of AVS.

<sup>1</sup> P Hovsepian et al, J. Mat. Sci: Mater Med (2016) 27:147

<sup>2</sup> D Goldbaum et al, Surf. Coat. Technol. 291 (2016) 264

<sup>3</sup> CC Yu et al, APL MATERIALS 4, 116101 (2016)

<sup>4</sup> JP Chu et al, Scientific Reports 6:31847

<sup>5</sup> I Petrov et al, J. Vac. Sci. Technol. A 35 (2017) 050601

<sup>6</sup> B Bakhit et al, J. Vac. Sci. Technol. A 36 (2017) 030604

##### 7:40pm TF-TuE-7 Influence of Defect Structures in MoS<sub>2</sub> Tribo-film Generated from MoDTC at DLC/DLC Interface on Friction Behavior: A Molecular Dynamics Simulation, *Masahiro Saito, N Miyazaki, Y Ootani, N Ozawa, M Kubo*, Tohoku University, Japan

MoDTC friction modifier for engine oil is well known to reduce friction under boundary lubrication where friction surfaces locally contact each other. MoDTC decomposes during friction and then, tribo-film of 2D-MoS<sub>2</sub> layers oriented at sliding interface is formed from the decomposition products of MoDTC, leading to low friction [1]. It is well known that the effect of MoS<sub>2</sub> largely depends on sliding condition. However, understanding of the dependency is not sufficient because of the difficulty of *in situ* observation at the sliding interface although sliding condition optimization is important to improve friction property. As one cause of this dependency, it is considered that the defect structure in MoS<sub>2</sub> tribo-film has some influence on friction. Thus, in order to investigate influence of defect structures in MoS<sub>2</sub> tribo-film generated from MoDTC at sliding interface on friction behavior, we performed molecular dynamics simulation by using reactive force field (ReaxFF), which takes into account the chemical reactions.

In the simulation, we prepared models in which some MoS<sub>2</sub> layers are sandwiched between two diamond-like carbon (DLC) substrates because DLC is a coating material used in engine cylinders. Here, we investigated

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the influence of the defects by comparing the friction behavior of the MoS<sub>2</sub> layers with and without defect structures. As the defect structures, we considered grain boundary structures in the MoS<sub>2</sub> layer and a distorted layer structure in which layers unoriented at the interface. In order to simulate friction process, one DLC substrate was fixed and the other was slid at 100 m/s with 3 GPa of a contact pressure.

The friction simulation the model without defect showed that the contact surface of DLC and MoS<sub>2</sub> was the sliding interface. The simulation the model with grain boundaries showed that the contact surface of MoS<sub>2</sub> and MoS<sub>2</sub> was the sliding interface since C-S bonds were formed between DLC and MoS<sub>2</sub> around grain boundaries. In addition, the MoS<sub>2</sub> layers with grain boundaries showed higher friction force because the grain boundaries in neighboring MoS<sub>2</sub> layers interact each other. The simulation the model with distorted layer structure showed that the MoS<sub>2</sub> edge adhered to DLC since C-S and Mo-C bonds were formed between DLC and MoS<sub>2</sub>. The shear stress acting on the unstable MoS<sub>2</sub> edge accelerated the chemical bond formation. In summary, we found that interactions between MoS<sub>2</sub> grain boundaries and formation of chemical bonds between MoS<sub>2</sub> and DLC sliding surface around defect are significant frictional resistance.

[1] J. Graham et al., *J. Tribol.*, 44 (2001) 4

8:00pm **TF-TuE-8 Diamond-like Carbon Thin Film Deposition using Low-energy Ion Beams**, *A Cuevas, M Ramos, A Catapang, Magdaleno, Jr. Vasquez*, University of the Philippines, Philippines

Diamond-like carbon (DLC) is a metastable form of carbon that has characteristics similar to diamond. High hardness, low wear rate, and chemically inert are some desirable properties of DLC that find a host of industrial applications. Diamond-like properties are greatly dictated by sp<sup>2</sup>/sp<sup>3</sup> ratio of hybridized carbon and hydrogen atoms that are present in the DLC matrix. High sp<sup>3</sup> content in DLC can be achieved when carbon ion energy incident on a substrate is in the range of 100 eV. In this work, we developed a two-electrode ion source system capable of extracting broad ion beams with mean ion energies around 100 eV. The ion reservoir is made of stainless steel with permanent magnets around the cylindrical body to realize a multicusp configuration. Quiescent plasma was produced using 0.3 mm dia tungsten wires as hot cathodes. Acetylene (C<sub>2</sub>H<sub>2</sub>) was used as the carbon source with argon (Ar) as background gas. Doping was also done by introducing nitrogen (N<sub>2</sub>) gas into the system. Retarding potential analyzer measurements suggest the successful generation of tunable broad ion beams with mean energies around 100 eV and current densities of around 10<sup>-6</sup> A/cm<sup>2</sup>. The dissociation of Ar/C<sub>2</sub>H<sub>2</sub> and Ar/C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub> plasma were obtained using a residual gas analyzer. The mass spectra of the Ar/C<sub>2</sub>H<sub>2</sub> ion beam showed the presence of mostly hydrocarbon radicals such as C<sub>2</sub>H<sub>2</sub><sup>+</sup>, C<sub>2</sub>H<sup>+</sup>, CH<sup>+</sup>, as well as heavier C<sub>x</sub>H<sub>y</sub><sup>+</sup> radicals and monatomic carbon and Ar. For Ar/C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub> ion beam, CN radicals, monatomic and diatomic N were also observed. Compositional analyses of the films via Raman spectroscopy revealed the successful growth of DLC with sp<sup>3</sup> content of up to 80%. Energy-dispersive x-ray spectroscopy measurements show up to 10% doping implying the successful and uniform incorporation of N in the DLC matrix. Improvement in adhesion was also observed for N-doped DLC films. X-ray photoelectron spectral measurements suggest the presence of sp<sup>2</sup> and sp<sup>3</sup> on the surface which supports the subplantation growth scheme of DLC. X-ray diffractometry suggests the presence of diamond and graphite phases in a generally amorphous films. Surface analyses employed using scanning electron microscopy showed good conformity of the DLC films with increasing thickness upon the subsequent increase in C<sub>2</sub>H<sub>2</sub> content. Hardness testing via nanoindentation show acceptable hardness values of around 8 GPa. These films may find applications in tribological coatings.

8:20pm **TF-TuE-9 A Study on Copper/Silver Core-shell Microparticles with Silver Nanoparticles Hybrid Ink and its Sintering Characteristics with Flash Light for High Oxidation Resistance**, *Jong-Whi Park, Y Jang, H Kim*, Hanyang University, Seoul, Korea

In this study, a silver(Ag) coated copper(Cu) core-shell microparticles ink were fabricated and screen-printed on Polyimide(PI) substrates. It was sintered via flash light sintering technique. Flash light irradiation condition (i.e. pulse duration, irradiation energy) was optimized to obtain high conductivity and good oxidation resistance characteristics of Ag coated Cu core-shell pattern. To increase the packing density of the electrodes and its oxidation resistance, Ag nanoparticles(NPs) were added to Cu/Ag core-shell microparticles (MP) ink. To determine optimal amount of the Ag NPs, the hybrid ink having different mass ratios of the Ag NPs and Cu/Ag core-shell MP were fabricated and tested. The sheet resistance of the hybrid ink was measured using the four-point probe method. To analyze the sintering

behavior and degree of oxidation of hybrid pattern, a scanning electron microscope (SEM) was used. To demonstrate the mechanism of the sintering process on hybrid ink, multiphysics COMSOL simulation and temperature monitoring was conducted. As a result, hybrid pattern sintered with flash light showed excellent oxidation resistance (resistance increase rate in 300°C for 5 hours: 54.34 %), and high electrical conductivity (9 μΩ-cm).

## Acknowledgments

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## Thin Films

### Room Naupaka Salons 4 - Session TF-WeM

#### Nanostructural and Surface Morphological Evolution: Experiment and Theory

**Moderator:** Andres De Luna Bugallo, CINVESTAV-Unidad Queretaro, Mexico

8:00am **TF-WeM-1 Nanostructure and Morphological Evolution During Thin Film Growth of Metals and Silicides Using Real-time Diagnostics**, **Gregory Abadias**, *C Furgeaud*, Institut Pprime, CNRS-Université de Poitiers, France; *B Krause*, KIT, Germany; *A Jamnig*, Institut Pprime, CNRS-Université de Poitiers and IFM Linköping University, Sweden; *K Sarakinos*, Linköping University, Sweden; *J Colin*, *L Simonot*, *A Michel*, *C Mastail*, Institut Pprime, CNRS-Université de Poitiers, France

**INVITED**

Thin metallic films deposited on Si are still largely used in many technological areas, such as microelectronics, catalysis, architectural glazing or plasmonics. In the case of high-mobility metals on weakly interacting substrates (e.g. Ag on SiO<sub>2</sub>), the growth proceeds in a 3D fashion, known as Volmer-Weber. The control of islands size and shape at the beginning of growth is vital for many applications as the characteristic length scales and physical attributes of ultrathin films are mostly set-in during the coalescence stage.

By employing a panel of *in situ* and real-time diagnostics, we could obtain valuable insights on the thin film growth dynamics, as well as stress evolution, in a variety of sputter-deposited metallic systems (Ag, Cu, Au, Pd and Mo). More particularly, the characteristic thickness of film percolation and film continuity can be determined from a combination of real-time electrical resistivity and wafer curvature measurements. This will be highlighted for the case of Ag and Cu deposited on amorphous carbon as a function of deposition rate *F* and deposition temperature *T<sub>s</sub>*.

We will also provide examples on how chemical alloying or interface reactivity can affect the growth morphology and stress evolution of Ag and Cu films. Growth monitoring was performed *in situ* by employing either surface differential reflectance spectroscopy or spectroscopic ellipsometry. We will show that strategies based on interfacial or alloying design can be efficiently employed to manipulate growth and obtain ultra-thin, ultra-smooth, continuous layers.

Finally, we will discuss the case of silicide formation during growth of metal layers with lower adatom mobility (e.g. Mo) on silicon. By coupling simultaneously X-ray diffraction, X-ray reflectivity and wafer curvature during sputter-deposition of metal layers on amorphous Si, information about thickness-dependent crystalline phases, texture, grain growth and microstrain can be gained. This will be demonstrated for Mo/Si and Pd/Si systems. A complex nanostructure formation is uncovered from these synchrotron studies, pointing out to different silicide formation mechanisms and subsequent structural development.

8:40am **TF-WeM-3 Seeding and Growth of Metallic Ultra-thin Film Deposited on Amorphous Polymeric Substrates**, **Jitesh Hora**, *D Evans*, *E Charrault*, *P Murphy*, Future Industries Institute, University of South Australia, Australia

**Abstract:** In order to add a new functionality to materials, applying thin film coatings is among one of a feasible route. Ultra-thin films deposited by physical vapor deposition techniques on plastic substrates have found significant roles in a variety of industrial applications like in electronics, automotive, etc. [1] This is due to their attractive properties such as high electrical conductivity and transparency, light weight, mechanical flexibility and so forth.[1] There are challenges involved for deposition of a film on polymers, like limitation related to the deposition temperature, due to the low thermal stability of the polymers and to control the formation of cracks on coating due to mechanical stress and environmental effects like the effect of humidity and moisture uptake [2]. In order to overcome the challenges, also to minimise the material use and to get the same functionality as that from thick film, there is a fundamental need to understand the seeding and growth of films deposited by physical vapour deposition technique on different polymeric substrates (stiff and flexible) by exploring the effect of compliance of substrates. This research work aims to understand the structure-property relationships of an ultra-thin film (UTF) on different amorphous polymeric materials. Investigating the structure-property relationships of these advanced materials will lead to an understanding of the link between the growth and seeding with the effect of substrates nature and its effect on composite material properties. In this

work, we present the effect of amorphous polymeric substrate mechanical properties on seeding and growth of ultra-thin metallic film deposited using magnetron sputtering, (DC) technique. When same material is deposited under similar conditions on different compliant polymeric substrates we observed different coating growth morphology.

#### Acknowledgments

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#### References

[1]. J. Hora, C. Hall, D. Evans, and E. Charrault, (2017), Inorganic Thin Film Deposition and Application on Organic Polymer Substrates. *Advanced Engineering Materials*, 2017.1700868.

[2]. N. Bradley, J. Hora, C. Hall, D. Evans, P. Murphy, and E. Charrault, Influence of post-deposition moisture uptake in polycarbonate on thin film's residual stress short-term evolution. *Surface and Coatings Technology*, 2016. 294: p. 210-214.

9:00am **TF-WeM-4 In situ Studies of Surface Morphological Evolution During Indium Nitride Growth by Atomic Layer Epitaxy**, **Charles Eddy, Jr.**, *N Nepal*, *S Rosenberg*, U.S. Naval Research Laboratory; *V Anderson*, Sotera Defense Solutions; *J Woodward*, U.S. Naval Research Laboratory; *C Wagenbach*, Boston University; *A Kozen*, U.S. Naval Research Laboratory; *Z Robinson*, College at Brockport - SUNY; *L Nyakiti*, Texas A&M University; *S Qadri*, U.S. Naval Research Laboratory; *M Mehl*, U.S. Naval Academy; *K Ludwig*, Boston University; *J Hite*, US Naval Research Laboratory

Nitride semiconductors have had significant commercial success, but full bandgap engineering of these materials is prohibited by the high temperatures used in conventional growth methods. Recently, we have developed a growth method –low temperature atomic layer epitaxy (ALEp) – that has empirically produced crystalline semiconductor films with properties comparable to those from conventional growth processes, but at roughly half the growth temperature [1,2]. This has eliminated miscibility gaps in ternary III-N semiconductor films and enabled the realization of full bandgap engineering from 0.7 eV to 6.1 eV.

Despite these empirical successes, the fundamental mechanisms involved in ALEp are unknown and the full promise of the method unrealized. To obtain such enabling knowledge we have employed synchrotron-based grazing incidence small angle x-ray scattering (GISAXS) to study the low temperature atomic level processing (ALP) of GaN substrate surfaces for epitaxy and ALEp nucleation and growth of InN on said surfaces. GISAXS allows real-time, in situ monitoring of the surface morphology during these processes.

In this presentation, we will introduce the GISAXS method and the apparatus we have developed to conduct in situ GISAXS measurements of the aforementioned ALP and ALEp processes. We monitor the evolution of GaN substrate surface morphology during a series of low-temperature ALPs including: gallium flash off (GFO), hydrogen plasma clean, and nitrogen plasma nitridation. We learn that the optimum surface results from a GFO conducted at 500° C for only 10 cycles followed by a hydrogen plasma clean. Further, we learn that conventional plasma nitridations are detrimental to smooth surface evolution. When employed to study ALEp InN nucleation and growth, GISAXS data, coupled with Porod[3] and 2D Fourier Transform analysis, affords a clear picture that the growth proceeds by island nucleation and growth and not by the conventionally accepted layer-by-layer growth associated with atomic layer deposition. We have monitored the evolution of island nucleation density, island spacing, island shape and island size as a function of key ALEp growth parameters. We observe that the islands are generally tens of nm or less in size and evolve from a spherical mound shape to a cylindrical shape. Finally, we will present the variations between 2D and 3D growth modes with growth parameter variations that provide insights on process modifications to promote higher quality electronic materials growth.

1. Nepal et al., *Cryst. Growth and Des.*, 13, 1485 (2013)

2. Nepal et al., *Thin Solid Films* 589, 47 (2015).

G. Porod, *Kolloid Z.*, 124, 83 (1951).

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9:20am **TF-WeM-5 Nanostructured Material Surface and Thin Film Interface Characterization by X-ray Photoelectron Spectroscopy**, *Jisheng Pan*, Institute of Materials Research and Engineering, A\*STAR (Agency for Science, Technology and Research), Singapore

It is well known that X-ray photoelectron spectroscopy (XPS) is a very powerful tool for understanding the nature of solid surfaces. Although many newly developing tools with high spatial resolution play important role in the analysis of individual nanostructured features of materials XPS is still considered as an essential tool for understanding several important aspects of nanostructured materials that cannot easily be observed using other techniques. However, the question of how the nanostructured material features impact XPS data have been heavily debated in the scientific community, which limits its application in characterization of nanostructured materials. For example, there is consistent observation of cluster-size-dependent binding energy (BE) shifts. But there is substantial disagreement over the assignment of these shifts to initial or final state effects. As a result, the measured PES data can't directly match to the electronic property of clusters because among the initial and final state effects, only the initial state effect involves information of changes in the electronic structure before photoemission, and hence is directly related to nanostructured material properties and is relevant for understanding other chemical process and reactions. In the first part of the presentation, I will talk to you the issues raised specifically for XPS analysis of nanostructured materials and followed by the method to overcome limitations through some examples of application of XPS to study nanostructured materials. In the second part, band energy alignment of different material interfaces such as semiconductor/semiconductor, metal/semiconductor, metal/insulator, semiconductor/insulator, 2D material interfaces determination by XPS will be presented. The performance of any type of hetero-junction device is determined by band energy alignment (band offsets) of material interfaces which form the hetero-junction. Therefore, accurately determining heterojunction band offsets and tuning them to a desired application would have an obvious impact on the optimization of the devices. The effects of chemical shift, differential charging, band bending and photoemission final state on the XPS measurement accuracy and reliability will be discussed.

9:40am **TF-WeM-6 Sputter Epitaxy via Inverse Stranski-Krastanov Growth Mode: A Method of Single Crystal Growth beyond Lattice Matching Condition**, *Naho Itagaki, D Yamashita, K Kamataki, K Koga, M Shiratani*, Kyushu University, Japan

Success in semiconductor devices has been limited thus far because of lattice-mismatch problems between growth layers and substrate. Here, we report on a new method of single crystal growth beyond lattice matching condition, sputter epitaxy via "inverse Stranski-Krastanov (SK) growth mode". Regarding heteroepitaxy on large lattice mismatched substrates, there are two primary modes by which thin films grow: 1) Volmer-Weber (VW: island formation) mode and 2) Stranski-Krastanov (SK: layer-plus-island) mode. In both modes, crystal growth ends up in formation of three-dimensional (3D) island (Fig. S1), making fabrication of single crystalline films challenging. On the other hand, in "inverse" SK mode, 3D islands are initially formed, and subsequent growth of 2D layers occurs on the 3D islands (Fig. S1 (c)). This 3D-2D transition, which is just opposite to the 2D-3D transition in SK mode, is caused by introducing impurity atoms into the growth atmosphere during the initial stage of crystal growth. In this study, we demonstrate the inverse SK growth of ZnO films on 18%-lattice mismatched sapphire substrates, where nitrogen is employed as impurity.

First, 3D island layers of 10 nm thickness were deposited by  $N_2/Ar$  sputtering. Next, 2D layers of 1  $\mu m$  thickness were deposited on the 3D island layers by  $O_2/Ar$  sputtering.

We have successfully grown ZnO single crystals on sapphire substrates via inverse SK mode. XRD and AFM analyses revealed that the 3D island layers consist of nm-sized islands with high crystal quality (Fig. S2 (a)). Since the strain induced by the lattice mismatch is relaxed through the island formation, smaller islands have lower density of misfit dislocation, resulting in high crystal quality. In a conventional method, however, such small islands hardly grow because of the cost of additional surface energy due to the increased surface area. Therefore, we consider that the role of nitrogen is to reduce the surface energy through the adsorption on the island surface, taking the advantages of its active but ZnO-insoluble natures. In fact, our calculation indicates that nitrogen addition leads to 4-nm-sized island growth owing to the lowered surface energy (Fig. S3). Furthermore, we found that after cessation of  $N_2$  supply, crystal grains that grow originating from the 3D islands rapidly coalesce to form 2D layer, and eventually grow in a layer-by-layer (2D growth) fashion (Fig. S2 (b)).

We believe that our findings on this growth mode will offer new opportunities for designing materials with unprecedented properties.

This work was supported in part by JSPS KAKENHI 18H01206 and NTT collaborative research.

10:20am **TF-WeM-8 Self-organized Nanostructure Formation in Functional Nitride Alloy Thin Films – Playing Games with Physical Metallurgy**, *Lars Hultman*, Linköping University, Sweden **INVITED**

This presentation reviews a multitude of tricks that can be used to promote self-organized nanostructuring in materials. These are used to enhance mechanical and electronic properties for transition metal and group-III nitride alloy thin films prepared by physical vapor deposition. The structural design is obtained by surface- and bulk-driven phase transformation in metastable TiAlN, ZrAlN, HfAlN, TiSiN, MoVN, VWN, and InAlN model systems, and analyzed by XRD, HREM, FIB, APT, and phase field modeling. *Ab initio* calculations are employed to assess phase stability and decomposition behavior from lattice mismatch and electronic band structure effects. The concept of age hardening in transition metal nitride alloys is reviewed for isostructural model systems. Spinodal decomposition is thus established for TiAlN by the formation of cubic-phase nm-size domains in a checker-board-pattern of TiN and AlN at temperatures corresponding to cutting tool operation. 2-D-nanolabyrinthine structuring in ZrAlN is obtained from with intergrowth of non-isostructural phases c-ZrN/w-AlN:  $\{110\} \parallel \{11-20\}$  interfaces. Superhardening in TiN/Si<sub>3</sub>N<sub>4</sub> nanocomposites takes place due to Si segregation forming a few-monolayer-thick SiN<sub>x</sub> phase, which is a vacancy-stabilized cubic-SiN<sub>x</sub> layer. A hardness maximum at 34 GPa – short of ultrahard – is observed in TiN/SiN<sub>x</sub>(001) superlattices at the epitaxial-to-amorphous thickness-limit for the SiN<sub>x</sub> layers. Thermodynamically-driven Si segregation in c-Ti<sub>1-x</sub>Si<sub>x</sub>N is proven in atom probe tomography on the sub-nm scale using <sup>15</sup>N isotopic substitution to resolve mass spectral overlap between Si and N. For In<sub>x</sub>Al<sub>1-x</sub>N, we report curved-lattice epitaxial growth of nanospirals with controllable chirality as well as core-shell nanorod formation. Finally, the possibility to intercalate atomic layers of Au in non-Van-der Waals nanolaminated Ti<sub>3</sub>SiC<sub>2</sub> (MAX phase) is demonstrated.

11:00am **TF-WeM-10 Effect of Atomic Layer Deposition Grown VO<sub>2</sub> Film Morphology and Crystallinity on Opto-Electronic Phase Transition.**, *Jason Avila*, ASEE postdoc fellow; *M Currie, B Downey, V Wheeler*, Naval Research Laboratory

VO<sub>2</sub> is a promising material for a variety of opto-electronic applications due to its metal-to-insulator phase transition occurring near room temperature. Atomic layer deposition (ALD) is an advantageous technique to deposit VO<sub>2</sub> due to its excellent conformality and ability to deposit thin films at low temperatures allowing for growth on a variety of substrates and device architectures. Such conformality is especially useful for complex optical devices with non-planar structures such as waveguides or diffraction gratings. There is, however, no current ALD method for direct growth of crystalline VO<sub>2</sub>, therefore post deposition annealing is required to achieve crystallinity. In this study, we examine the impact of annealing conditions on the resulting phase, crystallinity, composition, morphology, and metal-to-insulator transition of as-grown amorphous ALD VO<sub>2</sub> films on sapphire. By controlling annealing conditions such as temperature, time, and O<sub>2</sub> pressure, this study demonstrates a control over film morphologies and phase transition properties of the VO<sub>2</sub> film. One such example is decreasing the VO<sub>2</sub> film roughness by an order of magnitude by changing the annealing temperature by 100 °C, which simultaneously improves the hysteresis of the metal-to-insulator film transition. Through these efforts, the structure-property relationship of VO<sub>2</sub> will be revealed, which can then provide a guide for tailoring of optimal film properties for specific electronic and optical applications.

11:20am **TF-WeM-11 Relationship between Relaxation ratio and growth temperature of GaInN by RF-MBE**, *Yusuke Nakajima, T Honda, T Yamaguchi, T Onuma*, Kogakuin University, Japan

Full-color micro-LED displays [1] requires a monolithic integration of blue, green and red LEDs. In this case, realization of GaInN-based red LEDs with high efficiencies is one of the technical issues. One of the difficulties of these fabrications is due to lattice mismatch between GaN and GaInN layers as the indium composition is increased [2]. At present, the GaInN substrate is still in the research stage. Thus, fabrication of GaInN underlying layers is one of the technique to overcome the lattice-mismatch problems. The lattice-relaxed underlying layers are required for the red LEDs. On the other hand, the lattice relaxation requires the generations of threading dislocations (TDs). These points show the GaInN underlying layers require

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the lattice relaxation and reduction of TDs. We consider that growth temperature is an important parameter in GaInN growth.

In this paper, lattice relaxation in GaInN layer growth by RF-MBE with different growth temperature is reported. Their photoluminescence (PL) spectra are also discussed. The growth temperatures were fixed at 520, 540, 560, 580 and 600 ° C. The indium compositions were of grown layers 25±5%. The lattice relaxations of these layers were estimated using the patterns of reciprocal space mapping in X-ray diffraction (RSM).

GaInN layers on GaN templates were grown by RF-MBE. GaN templates were grown by MOVPE. The growth time was 60 minutes. The thickness of all grown layer was approximately 0.4µm. The RSMs show that the high relaxation was observed from the low-temperature grown layer nevertheless indium compositions were constant of 25%. On the other hand, PL peaks were shifted towards higher energy side as a function of growth temperature. These mean that the high indium segregation will be occurred in the layers grown at low temperature. Detailed relaxation ratio depended on growth temperature will be discussed.

## Acknowledgment

The authors would like to thank Spring-8, Dr. Sasaki and Takahasi of QST and Profs. Nanishi and Araki of Ritsumeikan University for their help with the experiments.

[1] Jacob Day *et al.*, Appl. Phys. Lett. **99**, 031116 (2011).

[2] S.Shinji *et al.*, Appl. Phys. Lett **6** 111004(2013).

11:40am **TF-WeM-12 The Effect of Interface Structure on MgO/Al/MgO Multilayer Photocathodes**, *Jeff Terry, Z Lee, L Spentzouris*, Illinois Institute of Technology

Early research and development of photocathode material was based on characterizing compounds with low work function and high quantum efficiency. Recent theoretical and experimental work has shown that the metal-insulator junctions can give rise to changes in the band structure at the interface, which in turn leads to a change in work function and quantum efficiency.

In addition to concerns about work function and quantum efficiency, many modern photoinjector designs also require low beam emittance. Beam emittance is an intrinsic property of the photocathode, therefore it is important to be able control the growth and quantify the factors that lead to such growth. Nemeth [Phys. Rev. Lett. **104**, 046801 (2010)] used DFT to model metal- insulator multilayer junction. The model indicate that it is possible to reduce the emittance of the photoemitted beam. Velazquez *et al* [Appl. Surf. Sci. **360**, 762 (2016)] has demonstrated that the work function of lab grown thin film multilayers had trends that match the theory. However the model predicted an exponential decrease of work function, but experimental measurements suggests a linear decrease.

It has been suggested that the surface roughness of the lab grown thin film multilayers might be the main cause of the discrepancy. Our multilayer then films are synthesized using Pulsed Laser Deposition. We have developed growth methodology to systematically control the surface roughness. We characterize these interfaces with photoelectron spectroscopy, Kelvin-probe measurements, and quantum efficiency measurements. We track these measured changes with the interface roughness to better understand the role of chemistry at the interfaces.

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[5] S. Pratiyush *et al.*, Appl. Phys. Lett. **110**, 221107 (2017).

## Thin Films

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

#### Thin Films Poster Session II

**Moderator:** Ivan Petrov, University of Illinois at Urbana-Champaign

**TF-WeP-2 Effect of Modulation Structure on the Microstructural and Mechanical Properties of TiAlSiN/CrN Thin Films Prepared by HiPIMS Process,** *H Liu*, Institute of Advanced Wear & Corrosion Resistant and Functional Materials, Jinan University, China; *F Yang*, Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan; *Y Tsai*, Department of Materials Engineering, Ming Chi University of Technology, Taiwan; **Chi-Lung Chang**, Department of Materials Engineering, Ming Chi University of Technology, Taiwan, Taiwan, Republic of China

The TiAlSiN/CrN multilayer coatings were deposited on silicon Si (100) substrates and cemented carbide (WC-10 wt.%, Co) substrates at 80°C using both metallurgical TiAlSi alloy target and Cr target, with varying modulation period ( $\Lambda$ ) from 27 nm to 2 nm, by reactive high power impulse magnetron sputtering technique (HiPIMS). The modulation structure characteristics of the TiAlSiN/CrN multilayer was first investigated, and then the microstructure evolution and mechanical properties of TiAlSiN/CrN coatings with decreasing modulation period ( $\Lambda$ ) were analyzed by TEM, SEM, XRD, Scratch test, Rockwell hardness and nanoindenter. It was found that the grain size of TiAlSiN/CrN multilayer increased with a decreasing modulation period ( $\Lambda$ ). The hardness and elastic modulus of the multilayer reached their maximum when  $\Lambda$  is about 8.5 nm. The hardness,  $H_3/E^*2$  ratios and critical loads LC in scratch test showed an initial increase, followed by a decrease with a decreasing modulation period ( $\Lambda$ ). The modulation period ( $\Lambda$ ) at 8.5 nm exhibited the highest hardness,  $H_3/E^*2$  ratios and critical loads.

**TF-WeP-3 Effect of  $\alpha$ -(Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> Overgrowth on MSM-Type  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> Ultraviolet Photodetectors Grown by Mist CVD,** *Kenichiro Rikitake*, *T Yamaguchi*, *T Onuma*, *T Honda*, Kogakuin University, Japan

Ultraviolet (UV) photodetectors using high Al content AlGaN have been studying towards applications such as flame detection, sterilization and so on [1]. However, the growth of high-quality AlGaN with increased Al content required for UV photodetector has difficulty in epitaxy. Therefore, we have been focusing on corundum-structured gallium oxide ( $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>) as an alternative material.  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> has a wide bandgap of 5.3 eV, and the bandgap engineering is possible in whole composition range of (Al, Ga, In)<sub>2</sub>O<sub>3</sub> alloys [2, 3]. A  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> based UV photodetector has been shown to have high responsivity [4], and Al<sub>2</sub>O<sub>3</sub> deposition on  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> for surface passivation has been reported [5]. In contrast,  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> detector has so far not yet been reported.

In this study, a metal-semiconductor-metal (MSM)-type UV photodetector using  $\alpha$ -(Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is fabricated by mist CVD.

1- $\mu$ m-thick unintentionally doped  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> film was grown on *c-plane* sapphire substrate by mist CVD. Ga acetylacetonate was used as a source material for this mist CVD growth, and it was solved in deionized water with a small amount of hydrochloric acid. The concentration of Ga was 0.05 mol/L. It was followed by 20-50-nm-thick (Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> growth using Al and Ga acetylacetonate as source materials. Then,  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>-based MSM-type photodetector was fabricated by employing Ni (50 nm)/Au (100 nm) pads as Schottky electrodes.

Figure 1 shows XRD  $2\theta$ - $\omega$  scan profile. (0006) $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and (0006) $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> diffraction peaks were observed.  $2\theta$ - $\omega$  and  $\phi$  scan profiles indicate growth of single crystalline epitaxial film. As shown in Fig. 2, the full-width at half maximum of the X-ray rocking curve for (0006) $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> diffraction peak is 39.8 arcsec. The absorption coefficient  $\alpha$  was determined by optical transmittance measurements. Then,  $(\alpha h\nu)^2$ - $h\nu$  plots give bandgap energy of 5.3 eV. Figure 3 shows photo-responsivity of the MSM-type photodetector. Increase in responsivity above the bandgap energy of 5.3 eV was successfully observed. Maximum photo-responsivity was estimated to be 1.0 A/W. However, the photo-responsivity decreased in the energy range between 5.6 and 5.8 eV due to surface effect of the  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> film. Surface effect on MSM-type UV photodetectors using  $\alpha$ -(Al<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>O<sub>3</sub> on  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> structure will be shown at the conference.

[1] A. Yoshikawa *et al.*, Jpn. J. Appl. Phys. **55**, 05FJ04 (2016).

[2] N. Suzuki *et al.*, J. Cryst. Growth **401**, 670 (2014).

[3] S. Fujita and K. Kaneko, J. Cryst. Growth **401**, 588 (2014).

[4] T. Oshima, T. Okuno and S. Fujita, Jpn. J. Appl. Phys. **46**, 7217 (2007).

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**TF-WeP-4 Continuous Dielectric Function of Monolayer MoSe<sub>2</sub> for Temperature Range from 31 to 300 K by Spectroscopic Ellipsometry,** *Tae Jung Kim*, *H Park*, *V Le*, *H Nguyen*, *X Nguyen*, *Y Kim*, Kyung Hee University, Republic of Korea

Molybdenum diselenide (MoSe<sub>2</sub>) is a layered material with strong in-plane bonding and weak out-of-plane interactions like many transition metal dichalcogenides (TMDCs). These interactions lead to exfoliation into two-dimensional layers of single unit cell thickness. MoSe<sub>2</sub> is well known as one of TMDCs that has a potential substitute for silicon or organic semiconductors in high-tech transistors, sensors, and photodetectors. Several works reported the dielectric function of monolayer MoSe<sub>2</sub> at low and room temperatures by using spectroscopic ellipsometry (SE). However, in order to apply properly for device applications, the dielectric function of monolayer MoSe<sub>2</sub> had better be well known for continuous temperature.

In this work, monolayer MoSe<sub>2</sub> is formed by selenization of MoO<sub>3</sub> which is fabricated on a sapphire substrate by using pulsed-laser sputtering. We report dielectric function parametric model (DFPM) of optical properties of MoSe<sub>2</sub> over the energy range of 0.74 to 6.42 eV and the temperature range from 31 to 300 K that measured by SE. We could clearly observe the existence of twelve critical point ( $A'$ ,  $A^0$ ,  $B_1$ ,  $B_2$ ,  $C_a$ ,  $C_b$ ,  $E$ ,  $F$ , and  $E_{I-IV}$ ) structures. The parameters were extracted by fitting the spectra with the reconstruction from twelve dispersive oscillators at each measured data. The dependence of temperature is achieved from the model parameters that are fitted by polynomial and then the dielectric functions of MoSe<sub>2</sub> for continuous temperature is determined. These results are expected to be useful in design and understanding in applied device technologies based on MoSe<sub>2</sub>.

**TF-WeP-5 Formation of Microwire Arrays with Dot Structure on Sol-gel Derived Cu<sub>2</sub>O Surfaces by Thermal Annealing,** *Katsuhiro Uesugi*, *K Matsumoto*, *W Ikesugi*, *Y Nakata*, *Y Hoshiyama*, *K Obara*, *H Fukuda*, Muroran Institute of Technology, Japan

Cu<sub>2</sub>O is recognized as the most promising p-type oxide semiconductor because of its desirable optical properties in the visible region and high Hall mobility. It has been widely studied for the applications such as gas sensors, solar energy conversion, photocatalyst, and photosynthesis. Although Cu<sub>2</sub>O films can be synthesized by using chemical- and physical-deposition methods and thermal oxidation of metallic Cu surfaces, nanomicroscale modifications on the surfaces are important to improve the surface reaction rate of the photoelectrodes. In this study, the self-assembled growth of Cu<sub>2</sub>O microwire arrays with dot structures was performed on the sol-gel derived Cu<sub>2</sub>O films by thermal annealing.

A metal precursor solution was prepared by the mixing of copper (II) acetate monohydrate and monoethanolamine in 2-propanol at 50 °C. After thin films were deposited on glass substrates, they were annealed in the furnace at 270 °C for 40 min. Cu<sub>2</sub>O(111) peak was observed by the X-ray diffraction measurement of the samples. A lot of wires spread through from dot structures were observed on the surfaces. A typical structure of the wires was 1.6  $\mu$ m in width and 200-340  $\mu$ m in length. The number of the wires was proportional to the circumference of the dot, and 10-100 wires per one dot were formed. Although the wires were isotropically grown from the isolated dot, the wire arrays were formed between neighboring dots. The lateral fusion of the wires did not occur, and the wire grown from the different dots was connected directly and formed the microwire array structures. These results suggest that the surface diffusion of the atoms during the thermal annealing was promoted to the parallel direction of the wires.

**TF-WeP-6 Surface Plasmon Excited on Metallic-Glass Nanotube Arrays for Surface-Enhanced Raman Scattering Applications,** *Yi-Chi Lu*, National Taiwan University of Science and Technology, Taiwan, Republic of China; *H Ho*, *C Hsueh*, National Taiwan University, Republic of China; *J Chen*, National Taiwan University of Science and Technology, Republic of China; *J Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China

Metallic glass (MG) is a new class of alloys with the amorphous structure and unique characteristics, including high strength, smooth surface, absence of grain boundaries, and corrosion resistance. MG materials can exhibit a plastic-like flow property at temperatures between glass transition ( $T_g$ ) and crystallization ( $T_c$ ). It has been reported that Au-based MGs possess negative dielectric constants and could be used as plasmonic materials. Furthermore, with a low  $T_g$  temperature of Au-based thin-film MGs (TFMGs), large dimensions of nanostructures can be thermally



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imprinted in air [1]. Both measurements and simulations have shown that designed nanostructures were suitable for surface-enhanced Raman scattering (SERS) applications. In addition, in the absence of grain boundaries in amorphous TFMGs, damping due to increased scattering at grain boundaries does not occur, and SERS could be improved. In addition to the thermal imprint method, the metallic glass nanotube (MGNT) array on Si has been successfully fabricated by a widely-used lithography and sputter deposition process for very large-scale integration [2]. Like other nanostructured surfaces, MGNT array surfaces show water repelling and attracting properties. In this presentation, as-prepared nanotubes are 500-800 nm tall and 500-800 nm in diameter and they are used for the SERS property evaluations. The MG alloys selected include Pd-, Ti-, and Zr-based systems. The characterization results are obtained and will be discussed in the presentation. Hence, our result shed lights on the possibility of MGNT array for plasmonic applications.

## References

[1] Cheng Wang, Li-Wei Nien, Hsin-Chia Ho, Yi-Chen Lai, and Chun-Hway Hsueh, Surface plasmon excited on imprintable thin-film metallic glasses for surface-enhanced Raman scattering applications, *ACS Appl. Nano Mater.*, 1 (2018), 908–914.

[2] J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, Metallic glass nanotube arrays: preparation and surface characterizations, *Materials Today*, 21 (2018), 178-185.

**TF-WeP-7 Study on Characteristics of the REBCO Thin Film Superconducting Wire according to the Thickness and Properties of the Wire's Stabilization Layer, Ho-Ik Du, S Yang, H Jeong,** Chonbuk National University, Republic of Korea

To protect REBCO layers that are weak against thermal impact after quenching, REBCO thin-film superconducting wires are manufactured with a complex structure of a substrate layer (metal), a superconducting layer (ceramic), and a stabilizing layer (metal). The stabilizing layer is positioned at the outermost layer of the REBCO thin-film superconducting wire to cover the REBCO superconducting layer, and is made mainly of Ag. The stabilizing layer normally protects the REBCO superconducting layer from thermal stress.

Therefore, in this paper, a REBCO thin film superconducting wire was fabricated by depositing materials with different specific resistance values (Ag) on REBCO thin-film superconducting wire, using the "RF Sputtering Deposition Method" with micro-range thicknesses to form a outer layer. Then the fabricated REBCO thin film superconducting wire were subjected to basic characteristics tests (measurement of their temperature distribution according to their changing resistance) and over-current transport- current tests to investigate their phase transition. Finally, the results of the basic characteristics tests and the over-current transport-current tests were analyzed to present the applications of superconducting power application devices of the REBCO thin film superconducting wire according to the thickness and properties of the wire's stabilization layer.

**TF-WeP-8 Arginine and Aspartic Acid on Cu(110) to Predict RGD Adsorption, Vincent Humblot, R Totani, C Methivier,** LRS - CNRS Sorbonne Université, France; *H Cruguel,* INSP - CNRS Sorbonne Université, France; *C Pradier,* LRS - CNRS Sorbonne Université, France

Peptides are versatile molecules, whose properties can be conveniently tailored through genetic engineering and chemical functionalization. For this reason they are employed as building blocks for functional materials with applications in nanotechnology, medicine and biotechnology [1].

The knowledge of amino acids (peptides subunits) adsorption processes on metallic surfaces is mandatory to implement peptides and proteins in these applications, but also to collect information on the obtained functional materials and to control the biointerfaces behavior [2].

In this work, we examined the interaction mechanisms of aspartic acid and arginine, the main components of the polypeptide RGD (arginine-glycine-aspartic acid), with a Cu(110) single crystal surface. The molecular films have been obtained by means of an electrospray ionization source (ESI) [3]: with respect to the traditional Knudsen cells, ESI allows an adsorption from an aqueous solution at room temperature, avoiding the high sublimation temperatures and all molecular damages related to them [4].

The chemical state and the anchoring points of the molecules on the surface have been investigated with X-ray Photoelectron Spectroscopy (XPS) and Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-RAIRS). Scanning Tunneling Microscopy (STM) furnished complementary information about the structures of the adlayers.

We show that the adsorption occurs differently for the two molecules: via the amine reactive groups for arginine and via both the carboxylate and the amine reactive groups for aspartic acid. In accordance, they self-assemble in a very different way:

- Aspartic acid creates islands of dimers showing a 2D pattern whose unit cell is disorientated from the crystallographic axes,
- While arginine assembles in line along the Cu [001] direction.

Thus, for arginine the molecule-substrate interactions dominate on long-range distances, influencing the molecular arrangement along one of the crystallographic axis. Conversely, for aspartic acid and, intermolecular interactions are predominant and are responsible for the dimerization process and the creation of extended 2D arrays.

[1] Costa et al., *Surf. Sci. Reports*, **2015**, 70, 449-553

[2] Barlow et al, *Surf. Sci. Reports*, **2003**, 50, 201-341

[3] C. Méthivier, V. Humblot, C.-M. Pradier, *J. Phys. Chem. C*, **2016**, 120 (48), 27364-27368.

[4] C. Méthivier, H. Cruguel, D. Costa, C.-M. Pradier, V. Humblot, *Langmuir*, **2016**, 32 (51), 13759–13763.

**TF-WeP-10 Improvement of Pumping Characteristics of Oxygen-Free Palladium/Titanium Non-Evaporable Getter (NEG) Coating Based on Removal of Carbon Contamination, Tetsuya Miyazawa,** SOKENDAI, Japan; *Y Kano, Y Nakayama,* Tokyo University of Science, Japan; *K Ozawa,* Tokyo Institute of Technology, Japan; *T Kikuchi, K Mase,* KEK, Japan

Non-evaporable getter (NEG) coatings are widely used for accelerators because they are ideal for maintain ultrahigh vacuum (UHV), and are oil free, magnetic-field free, vibration free, economical, and energy saving. Recently, we have developed a new NEG coating for pumping H<sub>2</sub> and CO, and named it as oxygen-free Pd/Ti coating. In oxygen-free Pd/Ti coating Ti thin film is deposited and overcoated by Pd thin film under clean UHV conditions in the range of 10<sup>-7</sup>–10<sup>-8</sup> Pa [T. Miyazawa, M. Kurihara, S. Ohno, N. Terashima, Y. Natsui, H. Kato, T. Kikuchi, and K. Mase, *J. Vac. Sci. Technol. A*, in press.]. When the oxygen-free Pd/Ti thin film is exposed to the atmosphere, the Pd surface is contaminated with organic compounds to some degree, resulting in a decline of the pumping speeds. In the present paper, we report removal of the carbon contamination and improvement of the pumping speeds of the oxygen-free Pd/Ti thin film using UHV or O<sub>2</sub> annealing. Unannealed, UHV annealed, and O<sub>2</sub> annealed (annealed under O<sub>2</sub> pressure of 1.3 × 10<sup>-4</sup> Pa) oxygen-free Pd/Ti thin films were analyzed with X-ray photoelectron spectroscopy using synchrotron radiation. The carbon coverage of the unannealed sample was estimated as 0.90 ML. On the other hand, the carbon coverages of UHV annealed and O<sub>2</sub> annealed samples were estimated as 0.41 and 0.10 ML, respectively. The pumping speed of the oxygen-free Pd/Ti for H<sub>2</sub> and CO after baking under O<sub>2</sub> pressure of 1.3 × 10<sup>-4</sup> Pa was improved by a factor of 3.7 and 16.3 in comparison with UHV baking, respectively [T. Miyazawa, Y. Kano, Y. Nakayama, K. Ozawa, T. Kikuchi, and K. Mase, in preparation.].

**TF-WeP-11 Development of a New NEG Pump Using Oxygen-Free Pd/Ti Thin Film that can be Activated by Baking at 150 °C for 12 h, T Kikuchi,** KEK, Japan; *T Miyazawa,* SOKENDAI, Japan; *H Nishiguchi,* Baroque International Inc., Japan; *Kazuhiko Mase,* KEK, Japan

Non-evaporable getter (NEG) pumps are widely used in synchrotron radiation facilities because they are free of oil, evaporation, sputtering, sublimation, magnetic field, and vibration as well as economical, compact, lightweight, and energy efficient. However, conventional NEG pumps have the following drawbacks: 1) decreased pumping speed after repeated venting-activating cycles; 2) relatively high activation temperature (typically 450 °C for 10 min when ZrVFe alloy is used, and typically 180 °C for 24 h when TiZrV film is used); and 3) a dedicated power supply is

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required. In order to overcome these disadvantages, we developed a new NEG pump with a DN 160 conflat flange using a new NEG material, i.e., oxygen-free Pd/Ti thin film, for evacuating residual H<sub>2</sub> and CO (Fig. 1) [1]. After baking at 150 °C for 12 h, the pumping speeds of the NEG pump were measured with the orifice method. Pumping speeds of 500–320, 370–260, 400–300, and 310–170 L s<sup>-1</sup> were estimated for H<sub>2</sub> after the first, second, third, and fourth venting–activating cycles in a pumped-quantity range of 0.01–10 Pa L. On the other hand, pumping speeds of 510–440, 590–470, and 880–690 L s<sup>-1</sup> were estimated for CO after the sixth, seventh, and eighth venting–activating cycles in a pumped-quantity range of 0.003–0.03 Pa L (Fig. 2). After baking at 150 °C for 12 h under O<sub>2</sub> pressure of 1.3 × 10<sup>-4</sup> Pa, pumping speeds of 680–240 L s<sup>-1</sup> and 900–470 L s<sup>-1</sup> were estimated for H<sub>2</sub> and CO, respectively (Fig. 2). The advantages of the new NEG pump are as follows: 1) it does not oxidize even after repeated venting–activating cycles; 2) it can be activated by baking at 150 °C for 12 h; 3) no dedicated power supply is required; 4) it is more economical than conventional NEG pumps because no electric feedthroughs are required; and 5) the pumping speeds can be improved by baking under O<sub>2</sub> pressure of 1.3 × 10<sup>-4</sup> Pa. The new NEG pumps are a suitable alternative to conventional NEG pumps or titanium sublimation pumps.

## Reference

[1] T. Kikuchi, T. Miyazawa, H. Nishiguchi, and K. Mase, AIP Conf. Proc., submitted.

## TF-WeP-12 The Effect of Cu Oxide Shell on the Flash Light Sintering of Cu Nanoparticle-ink on Si Wafer Substrate for Solar Cell Electrode, *Chunghyeon Ryu, J Chu, A Supriya, H Kim*, Hanyang University, Seoul, Korea

In this study, flash light sintering method of Cu nanoparticle (NP)-ink on Si wafer substrate and the effect of Cu oxide shell type and thickness on flash light sintering process were investigated. The Cu NPs were oxidized in a heat chamber and the oxidation temperature was varied from 100 °C to 300 °C. The Cu NP-ink was fabricated using the oxidized Cu NPs and the fabricated Cu NP-ink with was printed on Si wafer substrate using screen printing method. To sinter the printed Cu NP-ink, multiple pulsed flash light irradiation was employed. The flash light irradiation conditions were optimized to obtain a high electrical conductivity of Cu NP-ink. In order to characterize the microstructures, scanning electron microscopy (SEM) was performed. X-ray diffraction (XRD) was conducted to investigate the oxidation or reduction of oxidized Cu NPs. The thickness of Cu oxide shell was measured using transmission electron microscopy (TEM). The sheet resistance and thickness of sintered Cu NP-ink was measured to calculate the resistivity of sintered Cu NP-ink.

Finally, the Cu NP-ink was successfully sintered on Si wafer substrate using multiple pulsed flash light and it had a 15.42 μΩ·cm resistivity.

## Acknowledgments

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## TF-WeP-13 Realization of Three Optical States with High Contrast by Doping Nitrogen into Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, *Chaobin Bi, C Hu*, Jilin University, China

Phase change materials (PCMs) are widely used in non-volatile photonic applications due to the large optical contrast ( $\Delta R$ ) caused by phase transitions. However, only  $\Delta R$  between amorphous and metastable phase are used to achieve the modulation of two optical state, which limits the performance of the photonic device, such as the storage density of the optical disk, the multi-absorption band of the perfect absorber, and the channels of optical switch. Channels. And the  $\Delta R$  between metastable phase and the stable phase is too small to be considered as a third-order optical state. Therefore, it is necessary to develop new PCMs with three optical state of large  $\Delta R$ . Here, combined with experiments, theoretical calculations and Tauc-Lorentz model, we reveal the microscopic mechanism and propose a method to increase the  $\Delta R$  among the three phases. The results show that  $\Delta R$  is proportional to the change of material disorder and band gap before and after phase transition. On this basis, by introducing an appropriate amount of N (5.8%) into Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, the  $\Delta R$  between metastable and stable phase is significantly increased from 7% to 22%, exceeding the commercial requirement; meanwhile, the  $\Delta R$  between

amorphous and metastable phase is also increased from 20% to 37%, meaning that the tertiary optical state of large  $\Delta R$  is obtained. This study not only reveals the origin of  $\Delta R$ , but also provides new PCMs for research on improving the performance of photonic devices.

## TF-WeP-14 Self-Assembly of Nanocrystalline@amorphous Core-Shell Nanostructure in the TA-19 Alloy Film to Achieve High Strength, *M Wen, Meijia Wang, M Wu*, Jilin University, China

Improving the strength of alloy materials and simultaneously retaining high toughness are strongly desirable by various engineering applications. Nanocrystalline-amorphous dual-phase nanostructure consisting of nanocrystalline-cores encapsulated with amorphous-shells has been regarded as one of most effective routes to achieve high strength yet high toughness, which is better than either single-phase nanocrystalline alloys or single-phase metallic glasses because of reverse Hall-Petch effect or shear-band deformation. Herein, nanocrystalline@amorphous core-shell nanostructure has been successfully assembled in the sputtered TA-19 alloy film only by regulating bias voltages ( $V_b$ ), and then  $V_b$  induced microstructure and property evolution was further investigated by combined experiments of X-ray diffraction (XRD), atomic force microscope (AFM), scanning electron microscope (SEM), select electron diffraction (SAED), transmission electron diffraction (TEM) and nanoindentation. The results show that the bombardment of energy ions can promote formation of amorphous zones in TA-19 alloy film, successfully achieving ordered core-shell nanostructure at  $-120$  V of  $V_b$ , while single-phase nanocrystalline occurs at  $V_b = -40$  V and amorphous dominated structure appears at  $V_b = -200$  V. Maximum hardness value of 11.2 GPa achieves at  $V_b = -120$  V when the ordered core-shell nanostructure is formed with invisible shear bands around indenter, but more amorphous resulting in disappearance of core-shell nanostructure at  $V_b = -200$  V worsens hardness, accompanying with presence of obvious shear bands around indenter. This novel core-shell-like structure succeeded in achieving high strength or hardness by providing strong resistance to hinder movements of both grains and shear bands due large amount of nanocrystalline/amorphous interfaces. It is suggested that the  $V_b$  as a key factor controlling the core-shell-like structure of TA-19 films, which may provide a new strategy to improve mechanical properties of alloy films.

## TF-WeP-15 On the Deposition and Properties of Carbon-based Single- and Multilayer Systems Prepared by PLD, *René Bertram, D Haldan, S Weissmantel*, University of Applied Sciences Mittweida, Germany

The layer deposition technique Pulsed Laser Deposition (PLD) provides a feasible way to produce pure carbon films with a wide range of mechanical properties. These properties cover, depending on the deposition parameters, indentation hardness  $H_{IT}$  from 20 GPa to 60 GPa and indentation modulus  $E_{IT}$  from 300 GPa to 620 GPa what could be correlated with Raman spectra determined on these films. Thus, the ratio of the disordered and the graphitic peaks provides an efficient way to estimate the mechanical properties of the hydrogen free amorphous carbon films.

Furthermore, it will be presented, that a layered structure consisting of sublayers of alternating or continuously changing mechanical properties results in mechanically highly-resistant layer systems. In scratch tests, these multilayers show beside an excellent adhesion to various substrate materials, a significantly improved, very high cohesive breaking strength. In addition, by testing the abrasive wear of such coating systems against pc diamond suspension in calotte grinding and various ceramics and metals in tribological investigations superior durability was identified, surpassing conventional wear protection layers, in part, by 3 orders of magnitude.

These outstanding layer properties such as high hardness, elasticity, toughness and wear resistance show the great potential of such carbon-based coating systems, i.e. for application as wear protection coatings.

## TF-WeP-16 Microstructure and Phase Transformation Behavior of High Carbon M4 Steel Layers Prepared by Direct Energy Deposition Process, *Jong Bae Jeon, T Nam, G Park, H Jo, W Lee*, Korea Institute of Industrial Technology, Korea

Metal 3D printing has recently attracted attention as a new technology to replace existing processing processes because of its ability to directly produce complex shapes. Direct energy deposition method has potential to be used for remanufacturing, repairing, and surface modification of molds and broken parts, and recent studies have been carried out on the DED process of high carbon steels. However, due to the unique microstructural complexity of carbon steels, systematic understanding of microstructure and phase transformation behavior during the lamination process has not been systematically understood. Therefore, in this study, the

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microstructural characteristics and the phase transformation behavior of the thin layers fabricated by DED were studied. M4 steel powder was deposited on D2 steel base material and then the microstructure of the layers were characterized with SEM, EBSD and EDS. Through this study, it was found that the microstructure of DED processed layers dramatically differs from conventional bulk carbon steel. Especially, the nanocarbide formation and phase transformation behavior were different from those of conventional bulk materials. Therefore, this study suggests that understanding microstructure and phase transformation behavior during DED process is essential for controlling microstructures to obtain target properties of DED processed layers.

**TF-WeP-23 Development of Low-Emissivity Optical Filters Using Double Cannon Sputtering.** *Ramon Rodríguez Lopez, N Abundiz Cisneros*, Centro de Investigación Científica y de Educación Superior de Ensenada, México; *R Sangines de Castro, J Cruz Cardenas, R Machorro Mejia*, Universidad Nacional Autónoma de México, México

The implementation of Low emissivity (Low-E) filters in windows for buildings reduces energy costs employed to compensate the thermal interchange in the structure, hence saving up to 30% of the energy used to keep the building's temperature. The actual designs of these filters use a silver layer between two protective layers, which is expensive and can be easily oxidized when it gets in contact with the atmosphere, also when moisture reaches the thin silver layer, an agglomeration effect is produced due to the migration of the silver to the surface, causing peeling and losing its low emission property (Ando and Miyazaki, 1999).

The aim of this work is the construction of a Low-E filter made up of stack layers: glass/Si<sub>3</sub>N<sub>4</sub>/Al/Al<sub>2</sub>O<sub>3</sub>/Si<sub>3</sub>N<sub>4</sub>, with a high transmittance in the visible region > 80% and high reflectance in the infrared region. This filter has the novelty of employing aluminum (Al) instead of silver (Ag) as a reflector of IR to obtain a cheaper, efficient and durable Low-E filter. The Al is protected with silicon nitride (Si<sub>3</sub>N<sub>4</sub>) for hardness, high density, and high refraction index (Signore, et al, 2012), furthermore, alumina (Al<sub>2</sub>O<sub>3</sub>) is a protective layer for the aluminum, and that quality is exploited to enhance its durability.

The Low-E filter is grown using reactive magnetron sputtering technique with double cannon; the reason for this is to be able of synthesizing the whole stack without opening the chamber, hence of avoiding different layers interact with the atmosphere. With this procedure, we can ensure the intended optical properties of the filter. Plasma optical emission spectroscopy and in-situ spectroscopic ellipsometry are employed to find the optimal deposition conditions for each layer and also control and monitor the stack fabrication process for its reproducibility (Abundiz, 2013).

References:

Abundiz, N. (2013). Diagnóstico óptico de plasmas aplicado al crecimiento de películas delgadas. Centro de

Investigación Científica y Educación Superior de Ensenada, Ensenada, Baja California, México.

Ando, E., & Miyazaki, M. (1999). Moisture degradation mechanism of silver-based low-emissivity coatings. *Thin Solid Films*, 5.

Signore, M. A., Sytchkova, A., Dimaio, D., Cappello, A., & Rizzo, A. (2012). Deposition of silicon nitride thin films by RF magnetron sputtering: a material and growth process study. *Optical Materials*, 34(4), 632–638.

**TF-WeP-25 Investigation of CO<sub>2</sub> Sensing Efficiency and Mechanism Based on P-type MoS<sub>2</sub>.** *Kuan-Sheng Li, C Yang*, National Chiao Tung University, Republic of China; *C Wang*, National Synchrotron Radiation Research Center; *Y Tseng, S Chang*, National Chiao Tung University, Republic of China  
Two-dimensional materials have attracted tremendous attention due to their unique electronic structures, as well as extraordinary physical and chemical properties for sensing gas. In this work, we investigated the CO<sub>2</sub> sensing efficiency and sensing mechanism based on P-type MoS<sub>2</sub> which was doped with niobium (Nb). With a relatively high Nb dopant concentration, the sensor response showed decreased sensitivity, which could be attributed to a higher metallic NbS<sub>2</sub> ratio in the semiconducting MoS<sub>2</sub> film. Using in-situ x-ray absorption spectroscopy (XAS) and ambient-pressure x-ray photoelectron spectroscopy (ARXPS) techniques at national synchrotron radiation research center (NSRRC), we found that CO<sub>2</sub> acted as electron acceptor. However, the resistance of P-type MoS<sub>2</sub> would increase in sensor measurement, which was different from charge-transfer mechanism that acceptors would lower down the resistance of p-type semiconductor. The different behaviors between spectrum results and electric measurements may be the result of different sensing mechanism.

The dominated mechanism in this research could be intercalation mechanism which gas molecules intercalated into the structure and changed the conducting path. This work was financially supported by the "Center for the Semiconductor Technology Research" from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. Also supported in part by the Ministry of Science and Technology, Taiwan, under Grant MOST-107-3017-F-009-002.

**TF-WeP-26 Ion-beam Irradiation Induced Surface Chemical and Physical Modification of Polyethylene Glycol Film for Liquid Crystal Alignment.** *In Ho Song, J Lee, H Jeong, D Seo*, Yonsei University, Republic of Korea

The characteristics of ion beam (IB) irradiated polyethylene glycol (PEG) films were analyzed to determine their potential use as a liquid crystal (LC) alignment layer. The transmittance of the PEG films at various IB intensities was measured to verify the possibility of using it as an alignment layer. Anti-parallel cells with the PEG film were fabricated to examine the LC alignment characteristics. Perfectly dark cross-polarized microscopy images were obtained at an intensity of 700 eV, which indicates uniform LC alignment, and pre-tilt angle measurements supported this finding. X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) analyses were conducted to determine the effect of the IB irradiation on the PEG film on the surface modification. After exposure at an IB intensity of 700 eV where uniform LC alignment was achieved, remarkable chemical composition modification of the PEG film, including the reduction of C-O bonds that affected the uniform LC alignment, was observed via the XPS analysis. Furthermore, the AFM analysis revealed that low kurtosis value was obtained at this IB intensity. Therefore, we are convinced that the PEG films irradiated at this low IB intensity show potential as alternative alignment layer in LC applications.

**TF-WeP-27 Ultraviolet Nanoimprint Lithography for Homogeneous Liquid Crystal Alignment using Surface Wrinkling Driven by Ion-beam Irradiation.** *Dong Wook Lee, J Lee, H Jeong, D Seo*, Yonsei University, Republic of Korea

A simple and controllable surface wrinkling method was used to fabricate a 1-dimensional nanostructure. The structure was transferred to an ultraviolet cured polymer surface through ultraviolet nanoimprint lithography. The transferred 1-dimensional nanostructure of the ultraviolet cured polymer was used as an alignment layer in a liquid crystal display. The anisotropic geometry served as a guide for aligning liquid crystal molecules uniformly without defects. The liquid crystal cell based on the 1-dimensional UV-cured polymer exhibited high thermal stability above 180°C. The proposed 1-dimensional UV-cured polymer has advantages for advanced liquid crystal devices.

**TF-WeP-28 Fabrication of Au Atomic Junctions Using Artificial Intelligence Implemented on FPGA.** *Takuya Sakurai, Y Hirata, K Takebayashi, Y Iwata, J Shirakashi*, Tokyo University of Agriculture & Technology, Japan

Much progress towards artificial intelligence (AI) technique is due to the rapid growth of data size and accessibility in recent years. Thus, AI technique has been applied to many control systems. Meanwhile, feedback-controlled electromigration (FCE) has been employed to create atomic junctions with quantized conductance [1]. Previously, we have proposed ultrafast FCE system using field programmable gate array (FPGA) to adjust quantized conductances of Au atomic junctions [2]. Because of many experimental parameters in FCE procedure, it is difficult to optimize them by rules of thumb in control of quantum states. In this report, we investigated AI-assisted FCE system implemented on FPGA to immediately and precisely fabricate Au atomic junctions.

Au nanowires were fabricated using conventional electron-beam lithography and lift-off process. They were patterned on resist-coated SiO<sub>2</sub>/Si substrates using electron-beam lithography. Then, electron-beam evaporation of Ti (5 nm) and Au (20 nm) was carried out using a developed resist patterned as template.

AI-assisted FCE system is composed of four engines; learning, evaluation, inference and FCE engines. First, the feature values of conductance quantization obtained from previous experiments were stored in an initial database in learning engine. Then, FCE parameters were evaluated using cost function in evaluation engine. After the evaluation, FCE parameters were optimized by genetic algorithm (GA)-based selection methods in inference engine. Finally, FCE procedure using optimized experimental parameters was applied to Au nanowires in FCE engine. As a result, Au atomic junctions were fabricated by AI-assisted FCE procedure and the conductances of the junctions were successfully quantized at room temperature without catastrophic breaks of the structures. Furthermore,

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the FCE scheme was performed within an order of millisecond due to the use of FPGA. Therefore, these results imply that Au atomic junctions can be elaborately fabricated with improved controllability of quantized conductance using AI-assisted FCE implemented on FPGA.

## References

- [1] D. R. Strachan, D. E. Smith, D. E. Johnston, T.-H. Park, M. J. Therien, D. A. Bonnell, and A. T. Johnson, *Appl. Phys. Lett.*, **86**, 043109 (2005).
- [2] Y. Kanamaru, M. Ando, and J. Shirakashi, *J. Vac. Sci. Technol. B*, **33**, 02B106 (2015).

**TF-WeP-29 Electromigration-Induced Structural Modification of Series-Parallel-Connected Au Nanogaps**, *Koji Minami, S Tani, K Sakai, T Sato, M Ito*, Tokyo University of Agriculture & Technology, Japan; *M Yagi*, National Institute of Technology, Ichinoseki College, Japan; *J Shirakashi*, Tokyo University of Agriculture & Technology, Japan

We developed a simple and controllable nanogap fabrication method called "activation." This method is based on electromigration induced by Fowler-Nordheim (F-N) field emission current passing through the nanogaps. The F-N field emission current plays an important role in triggering the migration of atoms. By performing the activation, gap separations and tunnel resistances of the nanogaps are reduced because of the activated atoms that accumulated at the tips of nanogap electrodes. In this method, by only adjusting the applied current, we are able to control the structural properties of the nanogaps [1]. Previously, simultaneous tuning of the structural properties of series connected Ni nanogaps was achieved by using the activation [2, 3]. In this study, we investigated the application of the activation to the series-parallel-connected Au nanogaps for structurally defined, current-induced modification of nanogaps.

First, 2x1-6x6 series-parallel-connected Au nanogaps with the initial gap separation of 40-70 nm were fabricated with electron-beam lithography and lift-off processes. After the activation, the total resistance of the series-parallel-connected nanogaps became smaller than that before the activation. According to scanning electron microscope images, the current was passed through the narrower initial gaps within the series-parallel-connected nanogaps, and the separations of nanogaps were narrowed to less than 10 nm after the activation. Furthermore, we applied the activation to Au nanodots with interdot spacing of 30-50 nm placed between Au nanogap electrodes. As a result, the total resistances and the interdot spacing of Au nanodots were reduced by performing the activation. This tendency is quite similar to that of the series-parallel-connected Au nanogaps. These results clearly indicate that the structural properties of the series-parallel-connected Au nanogaps can be controlled simultaneously and precisely via the activation method. The understandings possibly imply that performing the activation to the series-parallel-connected nanogaps can be applicable to the shortest path problems.

## References

- [1] S. Kayashima, K. Takahashi, M. Motoyama and J. Shirakashi, *Jpn. J. Appl. Phys.*, Part 2 **46** (2007) L907.
- [2] M. Ito, M. Yagi, K. Morihara and J. Shirakashi, *J. Appl. Phys.*, **118** (2015) 014301.
- [3] M. Ito, K. Morihara, T. Toyonaka, K. Takikawa and J. Shirakashi, *J. Vac. Sci. Technol. B*, **33** (2015) 051801.

**TF-WeP-30 Oxygen Reduction Reaction Mechanism for N-doped Graphene Nanoribbons**, *Haruyuki Matsuyama, S Gomi, J Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

Recently, much attention has been devoted to the oxygen reduction reaction (ORR) on nitrogen(N)-doped graphene [1]. It has been theoretically revealed that N atoms prefer to be located near the edge of graphene [2,3]. The structure of graphene edge can be mainly classified into two types, armchair and zigzag edges. However, the effect of edge structures on ORR activity has not been fully understood.

We investigated the ORR activity for the N-doped graphene nanoribbons with armchair (N-ACGNRs) and zigzag (N-ZZGNRs) edges using first-principles calculations within the density functional theory. We used the computational hydrogen electrode model [3] to evaluate the maximum electrode potential ( $U_{max}$ ). ORR mainly proceeds in two pathways: For the two-electron ( $2e^-$ ) pathway,  $O_2$  molecule is reduced to  $H_2O_2$ , and for the direct four-electron ( $4e^-$ ) pathway, the final product is  $H_2O$ .  $H_2O_2$  for the  $2e^-$  pathway might corrode a carbon based electrocatalyst itself, leading to low durability. We also examined the selectivity with respect to these two pathways.

The calculation models are the N-ACGNRs and the N-ZZGNRs, in which a C atom is substituted by a N atom for each doping site from edge to in-plane. The reaction sites are set to C atoms adjacent to the N atom. We calculated the values of  $U_{max}$  for each doping site and reaction site for the N-ACGNRs and the N-ZZGNRs. The  $U_{max}$  for N-ACGNR becomes positive for each doping and reaction site. On the other hand, the  $U_{max}$  for N-ZGNR has a parity dependence with regard to the nitrogen doping site in the vicinity of the zigzag edges. For the even-numbered doping sites from the edge, the values of  $U_{max}$  are larger than 0 V, while for the odd-numbered ones, the values of  $U_{max}$  become negative. The reaction selectivity for the  $4e^-$  pathway appears only in the vicinity of armchair and zigzag edges. For the models showing the reaction selectivity, the  $sp^2$  configuration of GNR is maintained, even if reaction intermediates are adsorbed on GNR. On the other hand, reaction intermediates adsorb on GNR with  $sp^3$ -like configuration for the other models. The mechanism for appearance of the selectivity will be discussed in the presentation.

- [1] K. R. Lee *et al.*, *Electrochem. Commun.* **12**, 1052 (2010)
- [2] S. F. Huang *et al.*, *Phys. Rev. B* **80**, 235410 (2009)
- [3] Y. Uchida, S. Gomi, H. Matsuyama, A. Akaishi, and J. Nakamura, *J. Appl. Phys.* **120**, 214301 (2016)
- [4] J. K. Nørskov *et al.*, *J. Phys. Chem. B* **108**, 17886 (2004)

**TF-WeP-31 The Structure, Oxidation Resistance, Mechanical and Tribological Properties of TiAlSiNO Nanocomposite Coatings for Cutting Tools**, *Wang Ryeol Kim, S Heo*, Korea Institute of Industrial Technology (KITECH), South Korea; *H Kim*, Korean Institute of Industrial Technology (KITECH), South Korea; *J Kim, I Park*, Korea Institute of Industrial Technology (KITECH), South Korea

Functional graded TiAlSiNO nanocomposite films were deposited onto WC-Co substrate by a filtered arc ion plating system using TiAl and TiSi composite targets under  $N_2/Ar$  atmosphere. XRD and XPS analyses revealed that the synthesized TiAlSiNO films were nanocomposite consisting of nanosized (Ti,Al,Si)N crystallites embedded in an amorphous  $Si_3N_4/SiO_2$  matrix. The hardness of the TiAlSiNO films exhibited the maximum hardness values of  $\sim 47$ GPa at a Si content of  $\sim 5.63$  at.% due to the microstructural change to a nanocomposite as well as the solid-solution hardening. Besides, TiAlSiNO film with Si content of around 5.63at.% also showed perfect adhesive strength value of 105.3N. These excellent mechanical properties of Ti-Al-Si-N-O films could be help to improve the performance of machining tools and cutting tools with application of the film. Also X-ray diffractometer (XRD) analysis was conducted to investigate the crystallinity and phase transformation of the films. As a result of XRD, TiAl(18at.%)SiNO films showed the great oxidation resistance of 950°C for 30 min in air. Based on glow discharge optical emission spectroscopy (GD-OES) depth profiles, TiAl(18at.%)SiNO film annealed at 950°C for 30 min shows formation of aluminum oxide layer on the film surface. On the other hand, TiAl(7.56at.%)SiNO film had a titanium oxide layer on the surface after annealing at 950°C for 30 min. In this study, TiAlSiNO coatings were applied to insert tools. Their performances were evaluated about cutting-time and cutting-length to Inconel 718 super alloys. Performance of the coated tools were evaluated and compared with different TiAlSiNO coatings onto cemented carbide substrates. Especially, the TiAlSi(5.63at%)N coated tool showed better performance and best tool life.

**TF-WeP-32 Influence of Silicon Addition on the Mechanical and Tribological Properties of Zirconium Nitride Coatings Deposited by Hybrid Deposition System**, *Sungbo Heo, W Kim, J Lee, J Kim, I Park*, Korea Institute of Industrial Technology (KITECH), South Korea

Zr-Si-N coatings with various Si contents were synthesized by a hybrid deposition system combining arc ion plating and d.c. magnetron sputtering techniques. The influence of the Si content on the microstructure, mechanical properties and tribological properties of the Zr-Si-N coatings were investigated. The results showed that as the Si content increased from 0 to 5.8 at.%, the coatings transformed from a columnar ZrN to nanocomposite structure with a nano-sized ZrN crystallites embedded in amorphous  $Si_3N_4$  matrix and further increases of Si content lead to amorphous-like coatings. XPS analysis was applied to ZrN film and Zr-Si(5.8 at.%)N film respectively. The main peaks at 179.9 and 182.3 eV with a large percentage of area correspond to the ZrN compound. There was also a small contribution from the  $ZrO_2$  oxide phase at 182.16 and 184.59 eV. For the Si 2p region, the silicon binding energy spectrum is also divided into two peaks. The major peak located at 101.8 eV corresponds to  $Si_3N_4$  compound. The maximum hardness (H) of 33 Gpa, Young's modulus  $E$  of 265 Gpa, and  $H/E^*$  value of 0.12 were obtained at Si content of 5.8 at.% in the Zr-Si-N coatings, respectively. The coating with the lowest friction

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coefficient and the best wear resistance was also obtained at Si content of 5.8 at.%, which was mainly contributed to high value of H/E\* and formation of SiO<sub>2</sub> or Si(OH)<sub>4</sub> self-lubricating layer due to the interface tribochemical reaction.

## **TF-WeP-33 Coincident Raman and XPS Analysis of 2D-Materials, Joseph Robinson, P Mack, Thermo Fisher Scientific, UK**

Advanced materials present ever-increasing challenges to the analytical scientist. Composite materials built from nanostructures or ultra-thin films, often with complex chemistries present, are now required in a broad range of applications, and achieving full characterization is rarely managed using only one analysis method. To maintain confidence in the results from the utilization of several different methods, it is advantageous to be able to perform experiments on the same platform. Ideally, this should be without having to move the sample between several instruments, removing the need for additional registration or processing to ensure that the data is being collected from the same position.

For surface analysis, it has been common for many years to incorporate related analysis techniques onto the same instrument. For example, X-ray photoelectron spectroscopy (XPS) systems are commonly equipped with UV light sources to facilitate investigation of additional properties of materials via ultra-violet photoelectron spectroscopy (UPS). The ion source that is typically used for sample cleaning and depth profiling can also be used for low energy ion scattering (LEIS or ISS), providing more surface sensitive elemental composition information than can be delivered from XPS alone.

The latest innovation is to extend the range of offered complimentary techniques to include Raman spectroscopy. The focal points are aligned such that data can be acquired from the same point simultaneously, and that the sizes of the analysis areas are comparable in size. Chemical modifications of the material can be easily determined and quantified with XPS. Raman offers a fast way of determining the quality and conformity of the material, and direct compound identification. The greater depth of field of the Raman spectrometer also offers bulk information to complement the surface sensitive XPS data.

In this presentation we will illustrate the strengths of this combined, in-situ approach to surface analysis, illustrated with examples from the analysis of two-dimensional materials, boron nitride and molybdenum disulfide.

## **TF-WeP-34 Two-Dimensional Doping Layer for Flexible Transparent Conducting Graphene Electrodes with Low Sheet Resistance and High Stability, Y Seo, H Jang, W Jang, J Lim, Y Jang, T Gu, Dongmok Whang, Sungkyunkwan University, Republic of Korea**

Graphene, an ultra-thin flexible material with high carrier mobility and transparency, is a promising candidate for flexible transparent conducting electrodes (TCEs). However, its resistance is too high for use as a TCE material by itself. Therefore, fabricating graphene with low sheet resistance and high stability is a significant challenge for practical applications of graphene TCEs. In this study, we proposed a two-dimensional (2D) doping layer, which can stably dope graphene to develop a highly transparent graphene TCE with low sheet resistance. For this purpose, the 2D doping layer is prepared by immobilizing dopant molecules on transparent graphene oxide and simply stacking it with graphene enables efficient and stable charge transfer doping of the graphene. A TCE fabricated by alternately stacking the doping layer and graphene had a high optical transmittance of over 90% at a wavelength of 550 nm and a low sheet resistance of 50 Ω-sq<sup>-1</sup>. Furthermore, the sheet resistance showed an excellent thermal and mechanical stability with a change of only about 2% in a bending test of 20,000 cycles or at a high temperature of >200°C. This result shows that stacking graphene with stable 2D doping layer is a promising approach for graphene-based next generation TCE.

## **TF-WeP-35 Measurements of Reactive Species in Plasma-Activated Liquids Controlled by Atmospheric Pressure Plasma Operating Parameter, Hea Min Joh, T Chung, Dong-A University, Republic of Korea**

Atmospheric pressure helium plasma jet driven by a low-frequency bipolar pulsed voltage was employed for plasma-liquid interactions. Plasma treatment generated the reactive species in gas phase, and these species dissolve into the liquid phase, resulting in the appearance of reactive oxygen and nitrogen species (RONS) in liquid. To identify the correlation between the production of RONS in liquids and plasmas, we studied the effects of plasma operating parameters on the RONS in gas and liquid phase. The changes of discharge current, optical emission intensities from reactive radicals, gas temperature with the control parameters were measured and compared. The control parameters include applied voltage,

plasma with and additive oxygen flowrate. The amounts of O<sub>3</sub> and NO<sub>2</sub> in gas phase were measured by gas detector. For quantitative measurement of RONS radicals in liquid phase, several chemical methods were performed on plasma-treated HBSS (Hanks' Balanced Salt Solution). Among these RONS, the OH radicals dissolved in the liquid were monitored indirectly using the fluorescent properties of hydroxyterephthalic acid (HTA) formed by the reaction of terephthalic acid (TA) with OH radicals. The concentrations of long-living reactive species (H<sub>2</sub>O<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and O<sub>3</sub>) in liquid were detected after plasma treatment using a spectrophotometer. It was observed that the various plasma operating parameters could influence the amount of reactive species in liquid.

## **TF-WeP-36 Ultrafast and Highly-Scalable Organic-Inorganic Hybrid Perovskite Memory Devices for Emerging Memory Applications, Jang-Sik Lee, B Hwang, Pohang University of Science and Technology (POSTECH), Korea**

Organic-inorganic hybrid perovskites (OIHPs) have been used as the switching layers in resistive switching memory (RSM) devices due to distinct property of hysteresis in current-voltage (I-V) curves caused by defect migration under electric field [1-3]. For practical memory applications OIHPs are required to be prepared by vacuum deposition with good uniformity. We proposed a high-performance CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (MAPI)-based RSM device utilizing sequential vapor deposition to achieve high-density memory applications [4]. MAPI-based nanoscale RSM and cross-point array structure were fabricated to show the feasibility of OIHP-based memory with high-density data storage. Sequential vapor deposition enabled MAPI layer to be deposited inside the nanotemplates with 250 nm via-hole structures on the silicon wafers. The MAPI-based nanoscale memory showed low operating voltage, good endurance, and long data retention. Additionally, our devices showed sub-microsecond switching speed under ac bias pulses. The memory element of MAPI-based cross-point array structure showed bipolar resistive switching. This work on preparing OIHP-based nanoscale devices and the cross-point array structure will be an important step in the development of OIHPs for high-capacity information storage and for suggesting a novel approach that can be used to apply OIHPs to real memory devices on a large scale. Finally, lead-free, air-stable OIHP-based RSM with ultrafast switching and multilevel data storage capability will be introduced.

[1] C. Gu and J.-S. Lee, ACS Nano 10, 5413 (2016)

[2] B. Hwang, C. Gu, D. Lee, and J. -S. Lee, Scientific Reports 7, 43794 (2017).

[3] B. Hwang and J. -S. Lee, Scientific Reports 7, 673 (2017).

[4] B. Hwang and J. -S. Lee, Advanced Materials 29, 1701048 (2017).

## Thin Films

### Room Naupaka Salons 4 - Session TF-WeE

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

**Moderator:** Lars Hultman, Linköping University

5:40pm **TF-WeE-1 Novel Metallic-Glass Nanotube Arrays: Synthesis, Characterization and Applications**, *Jinn P. Chu*, National Taiwan University of Science and Technology, Taiwan, Republic of China

**INVITED**

Thin film metallic glass (TFMG) is a new class of metallic thin film with unique characteristics, including high strength, high ductility, smooth surface, absence of grain boundaries, low coefficient of friction, and corrosion resistance, though their bulk forms are already well-known for properties such as because of their amorphous structure. Thin films prepared by vapor-to-solid deposition are expected to be further from equilibrium than those prepared by liquid-to-solid melting or casting processes. This is expected to further improve the glass forming ability and widen the composition range for amorphization. In this talk, we successfully fabricated the first-ever metallic glass nanotubes (MGNTs) on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter [1]. The MGNT surface becomes hydrophobic and repels water. Upon heating and cooling the array, water can be repelled and attached to the surface [1]. Two examples will be presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. With a detection time of 10 min, the detection limit for streptavidin is estimated to be 25 nM. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Further, the array is prepared on a heating device on Si and, with an applied electric voltage to the heating device underneath, the MGNT surface was heated to generate an extending force from these nanochambers up to ~75°C in order for the array to be functioned as biomimetic artificial suckers for thermally adhesion response in biological systems [3]. As a result, the adhesive forces of the MGNT arrays can be as high as 11.2 N cm<sup>-2</sup>.

#### References

- [1] J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, Metallic glass nanotube arrays: preparation and surface characterizations, *Materials Today*, 21 (2018), 178-185.
- [2] W. T. Chen, S. S. Li, J. P. Chu, K. C. Feng, J. K. Chen, Fabrication of ordered metallic glass nanotube arrays for label-free biosensing with diffractive reflectance, *Biosensors and Bioelectronics*, 102 (2018), 129-135.
- [3] W. T. Chen, K. Manivannan, C. C. Yu, J. P. Chu and J. K. Chen, Fabrication of an artificial nanosucker device with a large area nanotube array of metallic glass, *Nanoscale*, 10 (2018) 1366-1375.

6:20pm **TF-WeE-3 Growth and Characterization of Atomically-thin MoS<sub>2</sub>-MoSe<sub>2</sub> Hetero-Junctions Synthesized by Vapor-Phase Chalcogenization**, *Andres De Luna Bugallo*, CINVESTAV Querétaro México, Mexico; *I Bilgin*, D Rubin, Northeastern University; *K Fujisawa*, Penn State University; *M Terrones*, Pennsylvania State University; *S Kar*, Northeastern University

Junctions between disparate electronic materials have been a focus of fundamental and applied research for over a century, and with the emergence of two dimensional (2D) semiconductors this focus has only intensified. In particular, the electronic and optical properties of 2D hetero-junctions synthesized directly from vapor-phase growth depend on the atomically-sharp interface. In this work, we present an in-depth characterization of vapor phase chalcogenization (VPC) synthesized of 2D molybdenum disulfide/molybdenum diselenide (MoS<sub>2</sub>/MoSe<sub>2</sub>) hetero-junctions exhibiting multiple morphologies. We investigated both, lateral in-plane heterojunctions and vertical out-of-plane heterojunctions with morphologies that range from being atomically-abrupt interfaces with varying degrees of doping, mixing, and alloying. High-resolution microscopy/spectroscopy performed on well-defined regions of these samples show distinguish among these regions, which also exhibit novel physical phenomena. In particular, we demonstrate strong supported-or-suspended sample dependent suppression of certain photoluminescence (PL) and Raman vibrational modes. We also describe atomically-resolved

scanning transmission electron microscopy of these hetero-junctions, revealing defects, doping, and formation of different types of Moiré superlattices. This work aims at providing a comprehensive multi-probe high-resolution characterization of TMD heterojunctions.

6:40pm **TF-WeE-4 Band-engineering of (TiO<sub>2</sub>)<sub>1-x</sub>(TaON)<sub>x</sub> Thin Films for Photochemical Applications**, *Tetsuya Hasegawa*, University of Tokyo, Japan

Titanium dioxide (TiO<sub>2</sub>) has been extensively studied for photocatalytic applications. Recently, we synthesized epitaxial thin films of anatase tantalum oxynitride (TaON), which has a smaller bandgap and larger refractive index than TiO<sub>2</sub> [1,2]. Alloying of anatase TiO<sub>2</sub> and TaON would enable band structure engineering of TiO<sub>2</sub> in a controller manner. In this study, we have grown thin films of an anatase (TiO<sub>2</sub>)<sub>1-x</sub>(TaON)<sub>x</sub> (TTON) solid solution and investigated their optical properties and band alignment. Epitaxial thin films of TTON (0.1 ≤ x ≤ 0.9) were deposited on (LaAlO<sub>3</sub>)<sub>0.3</sub>(SrAl<sub>0.5</sub>Ta<sub>0.5</sub>O<sub>3</sub>)<sub>0.7</sub> substrates by nitrogen plasma-assisted pulsed laser deposition technique. X-ray diffraction confirmed epitaxial growth of phase-pure anatase TTON, of which lattice constants changed with x in agreement with Vegard's law. Optical properties and band alignment were examined spectroscopic ellipsometry and X-ray photoelectron spectroscopy, respectively. The bandgap of TTON systematically decreased with increasing x, mainly due to upward shift in the valence band maximum through evolution of shallow N 2p band. Meanwhile, the position of the conduction band minimum was insensitive to x. The band alignment of anatase TTON was found to be suitable for photocatalytic water splitting with visible light. The refractive index of anatase TTON monotonically increased with x, possibly originating from the higher covalency of metal-N bonds than that of metal-O bonds.

#### References

- [1] A. Suzuki, Y. Hirose, D. Oka, S. Nakao, T. Fukumura, S. Ishii, K. Saso, H. Matsuzaki, and T. Hasegawa, *Chem. Mater.* **26**, 976 (2014)
- [2] A. Suzuki, Y. Hirose, D. Oka, S. Nakao, T. Fukumura and T. Hasegawa, *Jpn. J. Appl. Phys.* **54** 080303 (2015).

7:00pm **TF-WeE-5 Exploring Mechanical and Liquid-phase Exfoliation of HOPG through Low-energy Ion Beam Analysis**, *Paolo Branchini*, INFN RomaTre, Italy; *S De Rosa*, National Institute of Nuclear Physics Roma Tre, Italy; *L Tortora*, INFN RomaTre, Italy; *R Yivliain*, *G Bussetti*, Politecnico di Milano, Italy

Among two-dimensional semiconductors, graphene is universally recognized as an emerging material having potentials for a wide range of applications including organic electronics and photonics. Graphene flakes can be produced following different preparation protocols,<sup>[1]</sup> such as: dry and liquid-phase exfoliation, growth on SiC and metal substrates, CVD, molecular beam epitaxy, atomic layer epitaxy, chemical synthesis etc.. Within the European Graphene flagship program, different analytical techniques [SEM/FIB, TEM, EDS, SPM, XPS, XRD, Raman] are routinely adopted to provide the structural and chemical characterization and to validate the production process.

Here, we propose ToF-SIMS combined with multivariate analysis as validation tool for monitoring the graphene production. In particular, we focused the research on most diffused production methods: (i) the mechanical exfoliation by adhesive tape and (ii) the dispersion of graphene flakes inside an electrochemical bath after the intercalation of ions inside a graphite (HOPG) sample.

The (i) preparation protocol foresees the deposition of graphene onto a silicon wafer, which is then cleaned with acetone, ethanol, and deionized water and dried on a hot plate maintained at 300°C for 1min. The (ii) procedure requires an acid media (e.g. sulphuric or perchloric solutions), purified by bubbling Ar gas inside a separator funnel for several hours. A three-electrode cell is then exploited for inducing ion intercalation in graphite, used as a working electrode, which expands the crystal helping the weakening of the layer-layer interaction.

The high sensitivity of ToF-SIMS technique (few ppm) reveals graphene contamination due to the presence of residual glue coming from the scotch-tape. Furthermore, PCA and K-means cluster analysis were successfully applied to ToF-SIMS high resolution images, showing three different contributions from silicon substrate, residual glue, and graphite/graphene layers. At the same way, results from the graphite mother-crystal, used in the electrochemical approach, also show residual compounds related to the production process such as SO<sub>2</sub>, SO<sub>3</sub>, ClO<sup>-</sup>, ClO<sub>2</sub>, ClO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>. Dual beam depth profiling experiments showed that these compounds are present not only onto the HOPG surface but also between

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graphite terraces and inside the nanoprotusions produced during the intercalation process. These preliminary results contribute to shed light on the chemistry of the intercalation process.

## References

G. Bussetti, R. Yivlialin, D. Allia, A. Li Bassi, C. Castiglioni, M. Tommasini, C. Spartaco Casari, M. Passoni, P. Biagioni, F. Ciccacci, and L. Duo, *J. Phys. Chem. C* 2016, 120, 6088–6093

7:40pm **TF-WeE-7 Altering Cu-Ni Alloy Composition to Control 2D h-BN Growth**, **Boris Feigelson**, Naval Research Laboratory; *K Sridhara, J Hite, J Wollmershauser*, US Naval Research Laboratory

Atomically thin two dimensional hexagonal boron nitride (2D h-BN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance. Growth of single and multi-layer (2-10 layers) h-BN films of high crystalline quality in controlled manner is still a challenge.

In this work, h-BN films were grown by atmospheric-pressure CVD on metal substrates (Cu, Ni and Cu-Ni alloys). A vertical custom-made CVD reactor was used to grow h-BN films. The design of the vertical reactor allows the simultaneous growth of a few samples of h-BN on different substrates in the same run. Ni-Cu and Cu-Ni alloys were prepared by electroplating Cu on to Ni and Ni on Cu foils, respectively, followed by thermal annealing and polishing [1] to create alloy substrates with increasing Cu or Ni concentrations (at 10 wt.% increments from 10-50 wt.% Cu in Ni and 10-50 wt.% Ni in Cu).

As it was shown in our previous work [2], Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) can be used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the  $A_{2u}(\text{LO})$  vibrational mode were found for thin 2D h-BN films in contact with Cu and Ni. The lower-energy  $A_{2u}(\text{LO})1$  sub-band around  $819 \text{ cm}^{-1}$  is related to 2D h-BN coupled with Cu substrate, while the higher energy  $A_{2u}(\text{LO})2$  sub-band around  $824 \text{ cm}^{-1}$  is related to decoupled (essentially free standing) h-BN.

The IR-active out-of-plane vibrational mode was exploited to identify and characterize 1-5 layer h-BN on metal substrates, while micro Raman spectroscopy was used to characterize thicker h-BN films. Scanning electron microscope and x-ray photoelectron spectroscopy were used to probe the h-BN crystal size and stoichiometry.

Results on how morphology and thickness of 2D h-BN films depend on Cu-Ni alloy composition will be presented.

[1] K. Sridhara, B. N. Feigelson, J. A. Wollmershauser, J. K. Hite, A. Nath, S. C. Hernández, M. S. Fuhrer and D. K. Gaskill (2017). *Crystal Growth & Design* 17(4): 1669-1678.

[2] B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, *Nanoscale* 7, 3694 (2015)

8:00pm **TF-WeE-8 Internal Photoemission Spectroscopy Measurements of Energy Barriers between Metallic Glass Thin Films and ALD Dielectrics**, *M Jenkins, John Conley, Jr.*, Oregon State University

Metal/insulator/metal (MIM) structures are used as high speed diodes for rectenna based harvesting and sensing of IR radiation, capacitors, resistive memory, and hot-electron transistors. To better control electric fields and improve performance of these devices, there is growing interest in integrating metallic glassy (amorphous) thin films as smooth electrodes with uniform work function. Precise knowledge of metal/insulator barrier heights,  $\phi_{\text{Bn}}$ , is critical for predicting, understanding, and optimizing MIM device charge transport and operation. In the simplest model, charge transfer across the interface is neglected, and  $\phi_{\text{Bn}}$  should vary with the vacuum work function of the metal,  $\Phi_{\text{M,vac}}$ , so that  $\phi_{\text{Bn}} = \Phi_{\text{M,vac}} - \chi_i$  where  $\chi_i$  is the insulator electron affinity. In induced gap state theory, charge transfer at intrinsic interface traps which create an interfacial dipole that drives the metal Fermi level,  $E_{\text{FM}}$ , towards the charge neutral level of the insulator,  $E_{\text{CNL,i}}$ , the energy at which the dominant character of the interface states switches from donor-like to acceptor-like. A metal on an insulator will behave as if it has an effective work function,  $\Phi_{\text{M-eff}}$ , different from  $\Phi_{\text{M,vac}}$ , so that  $\Phi_{\text{M-eff}} = E_{\text{CNL,i}} + S(\Phi_{\text{M,vac}} - E_{\text{CNL,i}})$ .  $S$  is the slope that describes how much  $\Phi_{\text{M-eff}}$  on a given dielectric will change in response to  $\Phi_{\text{M,vac}}$ . Empirically,  $S = 1/(1 + 0.1(\epsilon_{\text{HF}} - 1)^2)$ . As the high frequency dielectric constant,  $\epsilon_{\text{HF}}$ , increases,  $S$  decreases and the insulator more effectively "pins"  $E_{\text{FM}}$  at  $E_{\text{CNL,i}}$ . Finally, actual  $\phi_{\text{Bn}}$ 's depend on deposition method and can deviate substantially

due to extrinsic interface traps. Thus it is necessary to directly measure  $\phi_{\text{Bn}}$  for a given metal-insulator combination.

In this work, we use IPE spectroscopy to measure  $\phi_{\text{Bn}}$  of the thin film glassy metals ZrCuAlNi, TaWSi, and TaNiSi in MIM stacks with various insulators deposited via ALD.<sup>2,3</sup> To date, there have been few reports of IPE measurements of MIM structures and only one an amorphous metal.<sup>4</sup> Results are referenced to TaN, Al, and Au barriers on the same devices.

Ta-based metal  $\phi_{\text{Bn}}$ 's change with  $\Phi_{\text{M}}$  for  $\text{Al}_2\text{O}_3$ , but  $\text{HfO}_2$   $\phi_{\text{Bn}}$  are relatively constant, likely due to pinning. The asymmetry in the I-V response is qualitatively consistent with the IPE determined  $\phi_{\text{Bn}}$ . TaWSi and TaNiSi electrodes showed consistently higher  $\phi_{\text{Bn}}$ 's than ZCAN electrodes and comparable performance to TaN. With low roughness and thermal stability approaching  $900^\circ\text{C}$ , TaWSi is a promising electrode for MIM diodes.

<sup>1</sup> Yeo et al. *J. Appl. Phys.* 92, 7266 (2002).

<sup>2</sup> N. Alimardani et al. *J. Vac. Sci. Technol. A* 30, 01A113 (2012).

<sup>3</sup> McGlone et al. *MRS Commun.* 7 (2017).

4. M.A. Jenkins et al. *Physica Status Solidi (RRL)* 12, 1700437 (2018).

8:20pm **TF-WeE-9 New Insights into the Kinetics of Chemical Vapor Deposition of Two-dimensional hBN Layers on Pd(111)**, **Pedro Arias**, University of California, Los Angeles; *A Abdulslam*, Colorado School of Mines; *A Ebnonnasir*, University of California, Los Angeles; *C Ciobanu*, Colorado School of Mines; *S Kodambaka*, University of California, Los Angeles

Using in situ variable-temperature scanning tunneling microscopy (VT-STM) and density functional theory (DFT), we investigated the surface structure and growth kinetics of two-dimensional hexagonal boron nitride (hBN) monolayer on Pd(111). STM images of polydomain hBN monolayers, grown via dissociative chemisorption of borazine on Pd(111)/ $\text{Al}_2\text{O}_3(0001)$  thin films, reveal moiré patterns with periodicities between 0.6 nm and 2.8 nm corresponding to four different orientations on Pd(111). We observe tunneling-parameter dependent apparent surface corrugation  $\Delta z$  in the STM images of the hBN domains. Furthermore, for the largest moiré pattern periodicities, we observe a bifurcation behavior in which some domains are nearly flat, and others develop significant hill-and-valley geometric corrugations. We suggest that hBN/Pd can have either mainly geometric or mainly electronic corrugation, depending on the domain orientation.<sup>1</sup> This behavior is unlike any other monolayer hBN-on-metal system.

Using the VT-STM, we investigated the chemical vapor deposition (CVD) kinetics of hBN monolayers on Pd(111). In each experiment, STM images are acquired while exposing Pd(111) to borazine ( $10^{-7} - 10^{-6}$  Torr) at temperatures 573 K and 673 K and for times up to 2500 s. The STM images reveal the nucleation and growth of two-dimensional islands on the Pd surfaces. From the images, we measure the areal coverage, island sizes, and island density as a function of time, temperature, and borazine flux. Our STM images reveal an unusual nucleation and growth mode: at lower deposition rate and higher temperature, islands form on terraces; increasing the deposition rate and/or lowering the temperature result in preferential nucleation and growth at the step edges. Interestingly, the attachment of the deposited species is observed on both up and down steps. We attribute this phenomenon to the structure and the highly anisotropic bonding of borazine on Pd(111). Our results provide new insights into the growth dynamics of two-dimensional layered materials.

<sup>1</sup>P. Arias, A. Abdulslam, A. Ebnonnasir, C. V. Ciobanu and S. Kodambaka, *2D Materials* 5 (4), 045001 (2018).

8:40pm **TF-WeE-10 Very High Refractive Index Transition Metal Dichalcogenide Photonic Conformal Coatings by Conversion of ALD Metal Oxides**, **Shaul Aloni**, *A Schwartzberg, C Chen, C Kastl*, Lawrence Berkeley National Laboratory

Materials for nanophotonic devices ideally combine ease of deposition, very high refractive index, and facile pattern formation through lithographic templating and/or etching. In this work, we present a scalable method for producing high refractive index WS<sub>2</sub> layers by chemical conversion of WO<sub>3</sub> synthesized via atomic layer deposition (ALD). These conformal nanocrystalline thin films demonstrate a surprisingly high index of refraction ( $n > 3.9$ ), and structural fidelity compatible with lithographically defined features down to  $\sim 10$  nm. Although this process yields highly polycrystalline films, the optical constants are in agreement with those reported for single crystal bulk WS<sub>2</sub>. Subsequently, we demonstrate three photonic structures - first, a two-dimensional hole array made possible by patterning and etching an ALD WO<sub>3</sub> thin film before

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conversion, second, an analogue of the 2D hole array first patterned into fused silica before conformal coating and conversion, and third, a three-dimensional inverse opal photonic crystal made by conformal coating of a self-assembled polystyrene bead template. These results can be trivially extended to other transition metal dichalcogenides, thus opening new opportunities for photonic devices based on high refractive index materials.



## Thin Films

### Room Naupaka Salons 4 - Session TF-ThM

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

8:00am **TF-ThM-1 Interface and Surface Control of MoS<sub>2</sub>-based Nanoelectronic Devices with Organic Treatment**, *Takhee Lee*, Seoul National University, Republic of Korea

Transition metal dichalcogenide (TMD) two-dimensional (2D) atomic layered materials have recently drawn considerable attention as promising semiconductors for future ultrathin layered nanoelectronic device applications. Unlike graphene, TMD materials have a semiconductor band gap, for example, molybdenum disulfide (MoS<sub>2</sub>) that has been widely studied is known to have a direct band gap of ~1.9 eV as a single MoS<sub>2</sub> layer and an indirect band gap of ~1.2 eV as a bulk MoS<sub>2</sub> crystal.

In this talk, I will present our group research works on MoS<sub>2</sub>-based nanoelectronic devices. In particular, I explain the following topics on the electrical properties of MoS<sub>2</sub> FETs; the effect by the environments such as oxygen and water [1], gate bias stress-dependent device instability [2], interface control by high energetic proton beam irradiation [3], surface treatment by molecules for sulfur vacancy passivation of MoS<sub>2</sub> [4], and hybrid devices of organic materials and MoS<sub>2</sub> [5].

#### References

- [1] W. Park et al., *Nanotechnology*, 24, 095202 (2013)
- [2] K. Cho et al., *ACS Nano*, 7, 7751 (2013).
- [3] T.-Y. Kim et al., *ACS Nano*, 8, 2774 (2014).
- [4] K. Cho et al., *ACS Nano*, 9, 8044 (2015); K. Cho et al. *Adv. Mater.* 30, 1705540 (2018).
- [5] J.-K. Kim et al., *Scientific Reports*, 6, 36775 (2016); J. Pak et al., *Nanoscale*, 7, 18780 (2015).

8:40am **TF-ThM-3 Epitaxial GdFe<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3</sub> Multiferroic Thin Films Grown Device Using Operando X-ray Technique**, *Shu-Jui Chang*, *M Chung*, National Chiao Tung University, Republic of China; *Y Liu*, *H Lee*, National Synchrotron Radiation Research Center; *Y Tseng*, National Chiao Tung University, Republic of China

Complex oxides have been extensively investigated due to complicated structural and electronic orbitals. The physical properties of these oxides may vary with growth mechanism. Among all the growing methods, radio frequency (RF) sputtering possesses advantages of good stoichiometry, great reproducibility and less pricy. This work demonstrates the fabrication of epitaxial GdFe<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3</sub> thin film (abbreviated as GFNO) by RF sputtering, analysis of fundamental physical properties and the application in the research in ferromagnetic and multiferroic layer heterostructure interface with in-situ spectroscopy technique. The epitaxial nature properties of thin film were examined by synchrotron radiation high resolution X-ray scattering at NSRRC. In addition to structure, the analysis on ferroelectricity (polarization and leakage), magnetism, electronic configuration and valence state have been also conducted with the result of room-temperature ferroelectricity and ferrimagnetism of GFNO thin film. Using in-situ XAS, XMCD and MOKE analysis have been conducted to investigate the effect of the electric field on the Co and GFNO interface. The native cobalt oxide in the interface has been found to transfer into metallic state due to the enhancement in the intensity of XAS absorption peak. Meanwhile, the intensity of XMCD also increases, indicating that the spin moment has also increases. In MOKE analysis, the coercivity of cobalt declines with rising applied electric field which comes from the increase in metallic state cobalt. This work was financially supported by the "Center for the Semiconductor Technology Research" from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. Also supported in part by the Ministry of Science and Technology, Taiwan, under Grant MOST-107-3017-F-009-002.

9:00am **TF-ThM-4 Effect of the Ultrasonic Treatment on the Si-SiO<sub>2</sub> System Defects Structure**, *Daniel Kropman*, Tallinn University, Estonia; *V Seeman*, Tartu University, Estonia; *A Medvids*, Riga Technical University, Latvia; *P Onufrievs*, Riga Technicacal University, Latvia

The effect of ultrasonic treatment (UST) on the defect structure of the Si-SiO<sub>2</sub> system by means of electron spin resonance(ESR),selective etching, MOS capacitance technique and secondary ions mass-spectroscopy is

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presented. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and may be caused by vibration energy dissipation, which are a function of defect centres type. In the ESR spectra of Si samples a signal with g=1.9996 (Pa centres) connected with vacancy complexes is observed. After UST appears another signal with g=2.0055 (broken bonds of Si atoms). The influence of the US frequency and sample orientation on the ESR signal intensity varies for different centres. The frequency and orientation dependence of the ESR signal with g=1.9996 and the lack of this dependence for the centres with g=2.0055 show that vibration energy dissipation depends on the type of defect centers. Defect density at the interface grows with an increase of US wave intensity or changes nonmonotonously depending on the oxide thickness and crystallographic orientation. In the samples with thick oxide/0,6 mkm there is a maximum in the dependence of the charge carriers lifetime on the US wave amplitude and in the samples with thin oxides /0,3 mkm/ there is a minimum. This shows that the structural defects form electrically active centres and their density can be varied by US. The density of point defects and absorbed impurities at the Si-SiO<sub>2</sub> interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation condition. US is widely used not only for materials treatment but in medicine as well (cancer treatment).

#### References:

- [1]D.Kropman,V.Poll,L.Tambek,T.Karner,U.Abru.Ultrasonics 36(1998)10211025 [2]D.Kropman,S.Dolgov.Physica satatus Solidi © v.9,issue 10-11,p.2173-2176

9:40am **TF-ThM-6 Charge Induced Disorder Controls the Thermal Conductivity of Entropy Stabilized Oxides**, *Jeffrey Braun*, *C Rost*, University of Virginia; *M Lim*, North Carolina State University; *A Giri*, *D Olson*, University of Virginia; *G Kotsonis*, Pennsylvania State University; *G Stan*, National Institute of Standards and Technology; *D Brenner*, North Carolina State University; *J Maria*, Pennsylvania State University; *P Hopkins*, University of Virginia

Manipulating a crystalline material's configurational entropy through the introduction of unique atomic species can produce novel materials with desirable mechanical and electrical properties. From a thermal transport perspective, large differences between elemental properties such as mass and interatomic force can reduce the rate at which phonons carry heat and thus reduce the thermal conductivity. Recent advances in materials synthesis have enabled the fabrication of entropy-stabilized ceramics, opening the door for understanding the implications of extreme disorder on thermal transport. Measuring the structural, mechanical, and thermal properties of single-crystal entropy stabilized oxides, we show that local ionic charge disorder can effectively reduce thermal conductivity without compromising mechanical stiffness. These materials demonstrate similar thermal conductivities to their amorphous counterparts, in agreement with the theoretical minimum limit, resulting in this class of material possessing the highest ratio of elastic modulus to thermal conductivity of any isotropic crystal.

10:20am **TF-ThM-8 Thermal Boundary Conductance Across Heteroepitaxial ZnO/GaN Interfaces: Experimental Assessment of the Phonon Gas Model**, *John Gaskins*, University of Virginia; *G Kotsonis*, Pennsylvania State University; *A Giri*, University of Virginia; *S Ju*, University of Tokyo, Japan; *A Rohskopf*, Massachusetts Institute of Technology; *Y Wang*, *T Bai*, University of California, Los Angeles; *E Sachet*, *C Shelton*, North Carolina State University; *Z Liu*, University of Notre Dame; *Z Cheng*, Georgia Institute of Technology; *B Foley*, Pennsylvania State University; *S Graham*, Georgia Institute of Technology; *T Luo*, University of Notre Dame; *A Henry*, Massachusetts Institute of Technology; *M Goorsky*, University of California, Los Angeles; *J Shiomi*, University of Tokyo, Japan; *J Maria*, Pennsylvania State University; *P Hopkins*, University of Virginia

We present experimental measurements of the thermal boundary conductance (TBC) from 77 – 500 K across isolated heteroepitaxially grown ZnO films on GaN substrates. This data provides an assessment of the underlying assumptions driving phonon gas based models, such as the diffuse mismatch model (DMM), and atomistic Green's function (AGF) formalisms used to predict TBC. Our measurements, when compared to previous experimental data, suggest that TBC can be influenced by long wavelength, zone center modes in a material on one side of the interface as opposed to the "vibrational mismatch" concept assumed in the DMM; this disagreement is pronounced at high temperatures. At room temperature, we measure the ZnO/GaN TBC as 490[+150, -110] MW m<sup>-2</sup>

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$K^{-1}$ . The disagreement among the DMM and A GF, and the experimental data at these elevated temperatures, suggests a non-negligible contribution from other types of modes that are not accounted for in the fundamental assumptions of these harmonic based formalisms, which may rely on anharmonicity. Given the high quality of these ZnO/GaN interfaces, these results provide an invaluable, critical, and quantitative assessment of the accuracy of assumptions in the current state of the art computational approaches used to predict phonon TBC across interfaces.

## 10:40am TF-ThM-9 Studies on Hot-wall Deposited Cadmium Sulphide (CdS) Thin Films for Buffer Layers in Thin Film Solar Cell, *Balaji Gururajan*,

*B Rangasamy, P Sankaran, P Nagarajan, S Kaliappan, K Dhonan*, PSG College of Technology, India; *V Asokan*, Chalmers University of Technology, Sweden; *M Natarajan*, Coimbatore Institute of Technology, India; *D Velauthapillai*, Western Norway University of Applied Sciences, Norway

Cadmium Sulphide (CdS) thin films were deposited onto well-cleaned soda lime glass substrates using hot wall deposition technique at room temperature. The structure of the as-deposited CdS thin films was found to be hexagonal and oriented along  $\langle 0\ 0\ 2 \rangle$  direction. The CdS films were then annealed to 300 °C and crystallinity of the films was found to improve with the presence of additional diffraction peaks along  $\langle 0\ 0\ 2 \rangle$ ,  $\langle 1\ 0\ 1 \rangle$ ,  $\langle 1\ 0\ 2 \rangle$ ,  $\langle 1\ 1\ 2 \rangle$  directions. Raman Spectroscopy of the annealed films confirmed the hexagonal structure with a shift observed at 312  $\text{cm}^{-1}$ . Selected area electron diffraction (SAED) pattern acquired from transmission electron microscopy analysis substantiated the hexagonal phase formation. X-ray photoelectron spectroscopy (XPS) confirmed the stoichiometric nature of CdS thin films with Cd:S atomic ratio of 1. Field emission scanning electron microscopy (FESEM) images revealed smooth morphology of the CdS films with distinctive grains. Atomic force microscopy (AFM) results indicated a surface roughness of 4.47 nm. Transmission spectra of the films were studied and the transparency was found to be above 80%. The optical band gap was found to be around 2.4 eV in accordance with the reported values. The results obtained clearly show that device quality CdS buffer layers can be effectively deposited using Hot-wall deposition.

## 11:00am TF-ThM-10 Intrinsic Photoluminescent Properties of Crystalline and Amorphous $\text{Cd}_2\text{V}_2\text{O}_7$ , *Erika Cervantes Juárez*, *R Lozada Morales*, *A Meza Rocha*, *R Licona Ibarra*, BUAP, Mexico

$\text{Cd}_2\text{V}_2\text{O}_7$  compounds in crystalline and amorphous phases were fabricated by the melt-quenching process. Characterizations such as X-ray diffraction, Raman spectroscopy and photoluminescence were performed. X-ray diffraction patterns of the crystalline sample showed peaks associated with a pure  $\text{Cd}_2\text{V}_2\text{O}_7$  monoclinic structure, in agreement with the Raman vibrational spectrum. In the case of the amorphous sample, X-ray diffraction patterns only exhibited a broad band, typical of a glassy structure, whereas its Raman spectrum displayed two broad vibrational modes centered at 350 and 850  $\text{cm}^{-1}$ , attributed to stretching vibrations of  $\text{VO}_3$  groups. In spite of the structural differences, both samples presented similar photoluminescence features, consisting of a wide band in the 375–525 nm range with two peaks at 411 and 432 nm, associated respectively with the  ${}^3\text{T}_2 \rightarrow {}^1\text{A}_1$  and  ${}^3\text{T}_1 \rightarrow {}^1\text{A}_1$  electronic transitions in the  $\text{VO}_4$  tetrahedron, under 340 nm excitation. Thus, blue light emission with CIE1931 chromaticity coordinates  $x \sim 0.200$  and  $y \sim 0.145$ , and color purity of 62–63%, is achieved from the crystalline and amorphous  $\text{Cd}_2\text{V}_2\text{O}_7$  compounds. The emission decay time profiles were well fitted to a bi-exponential function from which the calculated average lifetime values resulted to be  $112 \pm 13$  and  $99 \pm 4$  ns for the crystalline and amorphous  $\text{Cd}_2\text{V}_2\text{O}_7$  samples, respectively. Theoretical calculations based on the density of electronic states revealed that the photoluminescence arises through charge transference processes from  $3d$  orbitals of four-fold coordinated vanadiums to  $2p$  orbitals of three-fold coordinated oxygens in the  $\text{VO}_4$  tetrahedron, being the basic unit of  $\text{Cd}_2\text{V}_2\text{O}_7$  in crystalline and amorphous phases.

## 11:20am TF-ThM-11 The Effect of Tin Impurities on CdTe Thin Films Solar Cell, *J Ríos-González*, CINVESTAV-Unidad Mérida, Mexico; *R Mis-Fernández*, *I Rimmaudo*, *E Camacho-Espinosa*, *Juan Luis Peña*, CINVESTAV-Unidad Mérida, Mexico, México

The doping of CdTe has been investigated with different materials such as Sb, As, Mg, Se, Bi. Sn-doped CdTe is a promising intermediate band photovoltaic material, therefore the optoelectronic and structural properties have been investigated in this work. Tin was co-sublimated with CdTe films by close-spaced sublimation (CSS) process in Ar environment to avoid Sn oxidation. CdTe:Sn was deposited on a superstrate structure, glass/ITO/ZnO/CdS, and Cu/Mo bi-layer was used as back contact. The amount of tin doping was kept constant. Well shaped and uniform grains

were found by Field Emission Scanning Electron Microscopy (FE-SEM) analysis (about  $\sim 3\ \mu\text{m}$ ). Also it was observed a morphological changes between as-deposited CdTe and Sn-doping CdTe. Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS) showed presence of tin in the CdTe films. X-rays Diffraction (XRD) revealed peaks corresponding to the SnTe compound, as well as CdTe peaks strongly orientated along the (220) and (311) directions. The CdTe:Sn and as-deposited films showed a band gap of 1.49 eV. The measured efficiency of CdTe:Sn solar cell was 5.4%.

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