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 ZrO₂ Films Atomic-Layer-Deposited Using Cp-Zr(NMe₃); 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 ZrO₂ 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, the development of the ALD ZrO₂ 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 ZrO₂ thin films were deposited using Cp-Zr(NMe₃)₂ as a Zr precursor, and the effects of oxidant (H₂O, O₂) and deposition temperature (200-300°C) on their electrical properties were systematically evaluated. 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 ZrO₂ thin films were compared by examining them using transmission electron microscopy, atomic force microscopy, and X-ray diffraction. Lastly, the ALD ZrO₂ films were applied to a stacked structure of ZrO₂/Al₂O₃/ZrO₂, which has been popularly used in memory devices and their electrical properties were evaluated.


8:20am TF-MoM-2 Enantioselective Catalyst on Oxide Support: Study of the Chemical Nature of Tartaric Acid on Rutile TiO₂(110) by XPS and HREELS, Gregory Caballí, E Meriggio, Sorbonne Université, France; R Lazzari, CNRS, France; C Méthivier, Sorbonne Université, 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. In this work, the authors studied this interaction using XPS and HREELS.

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 monolayer adsorbed species (COO⁻/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 TiO₂(110) (in particular the energy differences between the C1s peaks) and complementary HREELS measurements allow to conclude that TA is absorbed as monolayer on TiO₂ 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/TiO₂ 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 power density 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 microscopy (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 Coutals, 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. 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.

Combinational 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.


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 wells 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

Monday Morning, December 3, 2018
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.


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 Imχ(2) SFG vibrational spectra (χ(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 Imχ(2) SFG spectra in the hydrogen-bonded OH stretching region s 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 s uch a ferroelectric proton ordering is t hemodynamically stable and has a n extremely high critical temperature of ~ 1 75 K [1,3], which is more than twice as large as that of ferroelectric bulk ice XI ( ~ 72 K ). In addition to these results, I will discuss our recent challenges on the interface engineering for modulation of the ferroelectric proton ordering.

Thin Films
Room Naupaka Salons 4 - Session TF-MoE
Nanostructured Surfaces and Thin Films: Synthesis and Characterization II
Nitride thin films have proven to be an invaluable class of materials with a broad range of uses. Examples include transition metal (TM) nitride nanocrystals used as hard-wearing industrial and decorative coatings, and semiconducting III-V nitrides with exceptional optoelectronic properties. We used high-throughput experimental and computational tools to investigate new inorganic ternary nitrides that have previously received very little attention. Specifically, we focused on heterovalent II-VI-N analogues to well-known III-V binary 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 cm2/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 processing 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 J/cm², and pulse duration: 1 ms, off-time: 9 ms and pulse number: 20) exhibited high conductivity (per: 9.52 μΩcm, via-hole: 12.69 μΩcm) and high adhesion strength (58) with well-sintered morphology.

Monday Afternoon, December 3, 2018
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 Burkholler, 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. Sintering parameters and cathode pressure and 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 Tanouchi, The University of Tokyo, Japan; S Shin, The University of Tokyo, AIST-UTokyo OPERANO-OIL, Japan
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 nanostructures 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 SrTiO3. By using magnetic circular dichroism, we have found that the 2DEGs of SrTiO3 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/cm² to 130 J/cm² for IGZO, from 40 J/cm² to 60 J/cm² 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 Ga₂O₃ 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 for CNT dispersed Ga₂O₃ depends on Rayleigh scattering and a high light transparency will be expected for CNT dispersed VWBG oxides. In this paper, the fabrication of CNT dispersed Ga₂O₃ 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 Ga₂O₃ precursor solution was prepared as follows [1]. The 3.65 g (12.5 mmol) of ethylenediamine-N, N', N'-tetraacetic acid (EDTA) and 5.00 g (12.5 mmol) of Ga(NO₃)₂·9H₂O (n = 7–9) [calculated as Ga(NO₃)₂·8H₂O] 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⁻¹. CNT solution of ethanol solvent (CNT; 0.0583 mmol g⁻¹). 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⁻¹ at 600°C for 30 min. Thickness of the resultant CNT doped Ga₂O₃ 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 Ga₂O₃ film is 2 x 10⁴Ω·cm. The results indicate that the CNT-dispersed VWBG oxides have a potential for the application of UV transparent oxides.

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-π 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:

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; F Lacroix, ENSCBP - Bordeaux INP, France

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. 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.

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.


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, Hirotsuka University, Japan; Y Kato, Irie Koken Co., Ltd., Japan; A Hashimoto, National Institute for Materials Science, Japan; T Kikuchi, Kazuhiro 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 μm 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 × 10⁻¹⁰ Pa, 1.7 × 10⁻¹⁰ Pa, and 6.1 × 10⁻¹⁰ Pa, respectively (Fig. 2). The pumping speeds of the bellows were estimated to be 0.028, 0.23, and 0.23 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

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 Aluminoxide 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 of nano and microstructures of complex shape.

References

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 Chipatecu-Godoy, O Ceballos-Sanchez, D Silva-Cabrera, F Corona-Davila, J Raboño-Borbolla, CINVESTAV-Unidad Queretaro, Mexico; Alberto Herrera-Gomez, CINVESTAV-Unidad Queretaro, Mexico, Mexico

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 layer interface 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.

References

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

Transition-metal (TM) nitrades exhibit an enormous range of properties and offer a smorgasbord of opportunities for materials scientists. Cubic TM nitrades have wide single-phase compound fields that can be exploited. We show results for vacancy hardening in 3d Group-IV TiN(001) and Group-V VN(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(001) remain constant due primarily to the presence of isoelectronic antides. Strong electron/phonon coupling in VN, 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 ScC_xTiN(001) layers show TiN is strongly reflecting up to the reflectance edge at hν= 2.3 eV, while ScN is transparent, and ρ(α) = x^2.11 for the alloy. ZrN is intermediate with hν= 3.04 eV. Thus, hard decorative coatings can be obtained with a wide palette of colors.

Superconducting transitions Tc for the Group-IV TM nitrades range from 10.4 K for ZrN to 9.18 K for HfN to 5.35 K for TiN. For superconductivity, superhard nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanorods. 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--W:N and V--M:O: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,M):O:N, 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 Martinez-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 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 currently being intensively investigated as alternative active layer materials for photodetectors, light-emitting diodes, laser devices, sensors and X-ray detectors, among others.
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. Schlam, 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.


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$_2$ Coating on Ferritic Stainless Steel for SOFC Interconnect Application, Shujiang Gong, 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$_2$ alloy coating has been deposited on SUS 343 ferritic stainless steel via magnetron sputtering method. Electrically conductive NiFe$_2$O$_3$ spinel coatings were thermally developed on the steels from the sputtered NiFe$_2$O$_4$ coatings in air at 800°C. Initial oxidation behaviors of NiFe$_2$O$_4$ 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$_2$O$_3$ layer followed with NiFe$_2$O$_4$ 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$_2$O$_4$ 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 investigated, 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/SiC 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 (α-Zr(0)) 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.
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 oxide solution, and the transformation from solid oxide to precipitated metallic 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 niobate 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 Ag₂O + Ag₂O/Nb₂O₅ on the surface, which is beneficial for formation of Ag₂O/MoO₃/AgNbO₃ during sliding at medium and low temperatures, thereby reducing friction.

**TF-TuP-5 High rate Reactive Sputter-deposition of WO₃ Films by using Two Different Deposition Methods, Yoji Yasuda, Y Hoshi, Tokyo Polytechnic University, Japan**

Tungsten oxide (WO₃) is well known as a functional material with excellent gasochromic, electrochromic, and photocatalytic properties. Nanostructured WO₃ films prepared by glancing angle sputter deposition and high-rate gas flow sputtering were prepared by Horpratham et al. and Oka et al., respectively. We have already reported that high-rate deposition of WO₃ films at a deposition rate (R₉) of more than 600 nm/min can be achieved by pulsed dc planar magnetron sputtering (PMS). However, poor gasochromatic 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 WO₃ 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. R₉ of more than 120 nm/min was easily realized with an increase in the sputtering voltage above 700 V. A typical WO₃ film obtained by PMS exhibited information on homogeneous 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-6 Initial Growth of Pentacene Thin Film on Si(001) Substrate, Takayuki Suzuki, K Yagyu, H Tochihara, Fukuoka University, Japan**

Initial growth process of the pentacene molecules on the clean Si(001)-2×1 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 crystallized, but disorder, where the molecules adsorb flatly. It does not have any ordered domain structure. The first pentacene layer that is crystallized 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 ‘α’, the ‘β’ and the ‘γ’ domains. Among them, the ‘β’ 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 μm. 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 ‘β’ 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**


**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, and Fukuoka University, Japan**

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 [CPz₂(NMe₃)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, Heungsop Song, D Shin, J Jeong, H Park, D Ko, Yonsei University, Korea, Republic of Korea**

Titanium dioxide (TiO₂) 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. TiO₂ 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 TiO₂ processes show a low growth-per-cycle (GPC) of less than 1 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 H₂O film [1]. In this presentation, we report the growth behavior of TiO₂ film with the DFM-applied and the conventional ALD growing method, using tetakis-dimethylamido-titanium [Ti(NMe₃)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, TiO₂ 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 SiO₂ that has been most widely used in the semiconductor industry.

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 increased 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 β peak which is a-15 structure and the increase of α 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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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$_2$ gas ratio on TiN and TiAlN Thin Films Synthesized via RF Magnetron Sputtering. Jason Audrey Lerciero, 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$_2$ 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 a TiAl target. Argon:nitrogen (Ar:N$_2$) partial pressure ratios were varied at 0.1, 0.2, and 0.3 to grow the TiN and TiAlN films. Scanning electron microscope (SEM) images of TiN showed rough, ‘pyramid-like’ grains. Higher N$_2$ content resulted in more compact grains. The TiAlN films formed were denser ‘cauliflower-like’ grains. Cross-sectional SEM images showed both films having columnar structure with increasing grain diameter as N$_2$ content is increased. Energy dispersive x-ray spectroscopy mapping of TiN showed over-stoichiometric Ti/N, TiAlN maps showed almost 1:1 Ti:Al ratio, but an abundance of N, confirming the formation of TiAlN. X-ray diffraction (XRD) results of TiN showed presence of (111), (200), and (311) TiN crystallographic planes. Decreasing N$_2$ content in the system resulted in the increase in intensity of (111) and (220) planes while increase in N$_2$ resulted in broadening of (111) plane. TiAlN XRD results showed formation of (111), (200), and (202) peaks. Increasing N$_2$ enhances the (200) peak. The 80:20 Ar:N$_2$ 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 Kudo, 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$_2$) particle and hydrocarbon were confirmed as wear debris. It was also observed that the SiO$_2$ 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 Si-C (Si + H$_2$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$_2$ particle, whereas the C atoms tend to remain on the SiC surface. The distribution of C, Si, H, and O atoms except H$_2$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

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 bio-functional 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], lubricant-resistant thin-film metallic glass [3] and non-stick syringe needles[4]. TiB thin films grown from compound TiB$_2$ targets by magnetron sputter deposition are typically highly over-stoichiometric due to differences in Ti and B preferential ejections angles and gas-phase scavenging 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$_2$ 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.

3 Yu et al, APL MATERIALS 4, 116101 (2016)
4 JP Chu et al, Scientific Reports 6:31847

7:40pm TF-TuE-7 Influence of Defect Structures in MoS$_2$ Tribofilm Generated from MoDTC at DLC/DLC Interface on Friction Behavior: A Molecular Dynamics Simulation, Masahiro Saito, N Miyazaki, Y Ootani, N Ozawa, M Kudo, 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$_2$ 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$_2$ largely depends on sliding condition. However, understanding of the dependency is not sufficient because of the difficulty 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$_2$ tribo-film has some influence on friction. Thus, in order to investigate influence of defect structures in MoS$_2$- 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$_2$ layers are sandwiched between two diamond-like carbon (DLC) substrates because DLC is a coating material used in engine cylinders. Here, we investigated
the influence of the defects by comparing the friction behavior of the MoS$_2$ layers with and without defect structures. As the defect structures, we considered grain boundary structures in the MoS$_2$ 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 model without defect showed that the contact surface of DLC and MoS$_2$ was the sliding interface. The simulation with grain boundaries showed that the contact surface of MoS$_2$ and MoS$_2$ was the sliding interface since C-S bonds were formed between DLC and MoS$_2$ around grain boundaries. In addition, the MoS$_2$ layers with grain boundaries showed higher friction force because the grain boundaries in neighboring MoS$_2$ layers interact each other. The simulation model with distorted layer structure showed that the MoS$_2$ edge adhered to DLC since C-S and Mo-C bonds were formed between DLC and MoS$_2$. The shear stress acting on the unstable MoS$_2$ edge accelerated the chemical bond formation. In summary, we found that interactions between MoS$_2$ grain boundaries and formation of chemical bonds between MoS$_2$ and DLC sliding surface around defect are significant frictional resistance.


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$^3$/sp$^3$ ratio of hybridized carbon and hydrogen atoms that are present in the DLC matrix. High sp$^3$ 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$_2$H$_2$) was used as the carbon source with argon (Ar) as background gas. Doping was also done by introducing nitrogen (N$_2$) 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 $10^4$ A/cm$^2$. The dissociation of Ar/C$_2$H$_2$ and Ar/C$_2$H$_2$/N$_2$ plasma were obtained using a residual gas analyzer. The mass spectra of the Ar/C$_2$H$_4$, ion beam showed the presence of mostly hydrocarbon radicals such as C$_2$H$_4^+$, C$_2$H$_3^+$, C$_2$H$_2^+$ as well as heavier C$_n$H$_m$+ radicals and monatomic carbon (C$^+$). For Ar/C$_2$H$_2$/N$_2$ 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$^3$ 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$^3$ and sp$^2$ 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$_2$H$_2$ content. Hardness testing via nanoindentation showed 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(P1) 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 $\mu$Ω·cm).

Acknowledgments
This work was supported by a National Research Foundation of Korea (NRF), funded by the Ministry of Education (2015R1A1A09058418, 2012R1A6A1029029, and 2013M2A2A9043280). This work was also supported by the Industrial Strategic technology development program (10076562, Development of fiber reinforced thermoplastic nano-composite via fiber bundle spreading for high quality resin impregnation process and its application to the underbody shield component for protecting battery pack of an electric-vehicle) funded by the Ministry of Trade, industry & Energy (MI, Korea).
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

Wednesday Morning, December 5, 2018

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

INVIITED

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 SiO2), 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.

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 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
The research is supported by “Australian Government Research Training Program Scholarship”. This work was performed in part at the South Australian node of the Australian National Fabrication Facility under the National Collaborative Research Infrastructure Strategy.

References

9:00am TF-WeM-4 In situ Studies of Surface Morphological Evolution During Indium Nitride Growth by Atomic Layer Epitaxy, Charles Eddy Jr., N Neupane, S Rosenberg, U.S. Naval Research Laboratory; V Anderson, Sotera Defense Solutions; J Woodward, U.S. Naval Research Laboratory; C Wagenbach, Boston University; A Kazen, U.S. Naval Research Laboratory; Z Robinson, College at Brockport - SUNY; I 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 nitrations 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.

11:00am TF-WeM-10 Effect of Atomic Layer Deposition Grown VO2 Film Morphology and Crystallinity on Opto-Electronic Phase Transition, Jason Avila, ASE postdoc fellow; M Currie, B Downey, V Wheeler, Naval Research Laboratory

VO₂ 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 VO₂ 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 VO₂, therefore post deposition annealing is required to achieve crystallinity. In this study, we examine the impact of annealing conditions on the crystallinity, composition, morphology, and metal-to-insulator transition of as-grown amorphous ALD VO₂ films on sapphire. By controlling annealing conditions such as temperature, time, and O₂ pressure, this study demonstrates a control over film morphologies and phase transition properties of the VO₂ film. One such example is decreasing the VO₂ 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 VO₂ 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 fabrication 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

We believe that our findings on this growth mode will offer new opportunities for designing materials with unprecedented properties.
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 Prof. Nanishi and Araki of Ritsumeikan University for their help with the experiments.


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 thin 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.
Wednesday Afternoon Poster Sessions, December 5, 2018

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 (Λ) 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 (Λ) were analyzed by TEM, SEM, XRD, Scratch test, Rockwell hardmeter and nanoindenter. It was found that the grain size of TiAlSiN/CrN multilayer increased with a decreasing modulation period (Λ). The hardness and elastic modulus of the multilayer reached their maximum when Λ is about 8.5 nm. The hardness, H/E*2 ratio, and hardness to elastic load ratio LC in scratch test showed a critical increase, followed by a decrease with a decreasing modulation period (Λ). The modulation period (Λ) at 8.5 nm exhibited the highest hardness, H/E*2 ratios and critical loads.

TF-WeP-3 Effect of α-(Al,Ga)3O5 Overgrowth on MSM-Type α-Ga2O3 Ultraviolet Photodetectors Grown by MIST CVD, Kenichiro Rikitake, T Yamaguchi, T Onuma, T Honda, Kokagun 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 (α-Ga2O3) as an alternative material. α-Ga2O3 has a wide bandgap of 5.3 eV, and the bandgap engineering is possible in whole composition range of [Al, Ga, In]O2:αO2 alloys [2, 3]. A β-Ga2O3-based UV photodetector has been shown to have high responsivity [4], and Al2O3 deposition on β-Ga2O3 for surface passivation has been reported [5]. In contrast, α-Ga2O3 detector has so far not yet been reported.

In this study, a metal-semiconductor-metal (MSM)-type UV photodetector using α-(Al,Ga)3O5 on α-Ga2O3 is fabricated by mist CVD. 1-μm-thick unintentionally doped α-Ga2O3 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,Ga)2O5 grown using Al and Ga acetylacetonate as source materials. Then, α-Ga2O3-based MSM-type photodetector was fabricated by employing Ni (50 nm)/Au (100 nm) pads as Schottky electrodes.

Figure 1 shows XRD 2θ-scans. Profile of 0006α-Al2O3 and 0006α-Ga2O3 diffraction peaks were observed. 2θ-ω 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 0006α-Ga2O3 diffraction peak is 39.8 arcsec. The absorption coefficient a was determined by optical transmittance measurements. Then, (a)hv-Ihv 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 α-Ga2O3 film. Surface effect on MSM-type UV photodetectors using α-(Al,Ga)3O5 on α-Ga2O3 structure was shown at the conference.


TF-WeP-4 Continuous Dielectric Function of Monolayer MoSe2 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 (MoSe2) 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. MoSe2 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 MoSe2 at low and room temperatures by using spectroscopic ellipsometry (SE). However, in order to apply properly for device applications, the dielectric function of monolayer MoSe2 had better be well known for continuous temperature.

In this work, monolayer MoSe2 is formed by selenization of MoO2 which is fabricated on a sapphire substrate by using pulsed-laser sputtering. We report dielectric function parametric model (DFPM) of optical properties of MoSe2 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', B, B', C, C', E, F, and E1ω) structures. The parameters were extracted by fitting the spectra with a 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 MoSe2 for continuous temperature is determined. These results are expected to be useful in design and understanding in applied device technologies based on MoSe2.

TF-WeP-5 Formation of Microwire Arrays with Dot Structure on Sol-gel Derived CuO Surfaces by Thermal Annealing, Katsuhiko Uesugi, K Matsumoto, W Ikouji, Y Nakata, Y Hoshiyama, K Obara, H Fukuda, Muroran Institute of Technology, Japan

CuO 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 photovoltaics. Although CuO 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 CuO microwire arrays with dot structures was performed on the sol-gel derived CuO 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. CuO(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 μm in width and 200-340 μm 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 (Tg) and crystallization (Tc). It has been reported that Au-based MGs possess negative dielectric constants and could be used as plasmonic materials. Furthermore, with a low Tc temperature of Au-based thin-film MGs (TFMGs), large dimensions of nanostructures can be thermally...
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 (MGN) 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, MGN 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 MGN array for plasmonic applications.

References

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, a fabricated REBCO thin film superconducting wire was 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 Mithivier, LRS - CNRS Sorbonne Université, France; H Cruguel, INSPE - 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 electrospay 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 disoriented from the crystallographic axes,
- While arginine assemblies 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.

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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 H₂ and CO (Fig. 1) [1]. Before 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⁻¹ were estimated for H₂ after the first, second, third, and fourth venting-activating cycles in a pumped-quantity range of 0.01–0.03 Pa L. On the other hand, pumping speeds of 510–440, 390–470, and 880–690 L s⁻¹ 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 O₂ pressure of 1.3 × 10⁻⁴ Pa, pumping speeds of 680–240 L s⁻¹ and 900–470 L s⁻¹ were estimated for H₂ 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 O₂ pressure of 1.3 × 10⁻⁴ Pa. The new NEG pumps are a suitable alternative to conventional NEG pumps or titanium sublimation pumps.

Reference


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 Electode, Chung-hyun Ryu, J Chu, A Supriya, H Kim, Hanyang University, Seoul, Korea

In this study, flash light sintering method of Cu nanoparticle (NP) 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

This work was supported by a National Research Foundation of Korea (NRF), funded by the Ministry of Education (2015R1D1A1A09058418, 2012R1A6A1029029, and 2013M2A2A9043280). This work was also supported by the Industrial Strategic technology development program (10076562, Development of fiber reinforced thermoplastic nano-composite via fiber bundle spreading for high quality resin impregnation process and its application to the underbody shield component for protecting battery pack of an electric-vehicle) funded by the Ministry of Trade, industry & Energy (MI, Korea).

TF-WeP-13 Realization of Three Optical States with High Contrast by Doping Nitrogen into GeSbTe₃, 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 (ΔR) caused by phase transitions. However, only ΔR 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 ΔR 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 ΔR. Here, combined with experiments, theoretical calculations and Tauc-Lorentz model, we reveal the microscopic mechanism and propose a method to increase the ΔR among the three phases. The results show that ΔR 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 GeSbTe₃, the ΔR between metastable and stable phase is significantly increased from 7% to 22%, exceeding the commercial requirement; meanwhile, the ΔR between amorphous and metastable phase is also increased from 20% to 37%, meaning that the tertiary optical state of large ΔR is obtained. This study not only reveals the origin of ΔR, 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, Mejia Wong, 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 transformation. Herein, nanocrystalline@amorphous core-shell nanostructure has been successfully assembled in the sputtered TA-19 alloy film only by regulating bias voltages (Vₛ), and then Vₛ 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 Vₛ, while single-phase nanocrystalline occurs at Vₛ = ~40 V and amorphous dominated structure appears at Vₛ = ~200 V. The hardness value of 11.2 GPa achieves at Vₛ = ~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 Vₛ = ~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 Vₛ 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 Holdan, 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 Hᵣ from 20 GPa to 60 GPa and indentation modulus Eᵣ from 300 GPa to 620 GPa what could be correlated with these determined on these films. Thus, the ratio of the ordered and the graphic 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
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 was 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 built 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 Rodriguez 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 Autonoma de Mexico, México**

The implementation of Low emissivity (Low-E) filters in windows for buildings reduces the 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 this 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 the work is the construction of a Low-E filter made up of stack layers: glass/SiN/Al/AlOx/SiNx, 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 (SiNx) for hardness, high density, and high refraction index (Signore, et al, 2012), furthermore, alumina (Al2O3) 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:

**TF-WeP-25 Investigation of CO2 Sensing Efficiency and Mechanism Based on P-type MoS2. Kuan-Sheng Li, C Yang, National Chiao Tung University, Republic of China; C Wang, National Synchrotron Radiation 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 CO2 sensing efficiency and sensing mechanism based on P-type MoS2, 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 Nb:Si ratio in the semiconducting MoS2 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 CO2 acted as an electron acceptor. However, the resistance of P-type MoS2 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-roughness value was maintained at this IB intensity. Therefore, we are convinced that the PEG films irradiated at this low IB intensity show potential as alternative alignment layer film 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 with 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 Hirato, 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 SiO2/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 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,
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


TF-WeP-29 Electromigration-Induced Structural Modification of Series-Parallel-Connected Au Nanopads, Koji Minami, S Tan, 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 thorough 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


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\textsuperscript{-}) pathway, O\textsubscript{2} molecule is reduced to H\textsubscript{2}O\textsubscript{2}, and for the direct four-electron (4e\textsuperscript{-}) pathway, the final product is H\textsubscript{2}O\textsubscript{2}, for the 2e\textsuperscript{-} 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-ZZGNRs and the N-ZGGNRs, 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 Umax for N-ACGNR becomes positive for each doping and reaction site. On the other hand, the U_{max} for N-ZGZN has a parity dependence with regard to the nitrogen doping site in the vicinity of the nanogap 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\textsuperscript{-} pathway appears only in the vicinity of armchair and zigzag edges. For the models showing the reaction selectivity, the sp\textsuperscript{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\textsuperscript{3}like configuration for the other models. The mechanism for appearance of the selectivity will be discussed in the presentation.

References


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

Functional graded TiaSINO nanocomposite films were deposited onto WC-Co substrate by a filtered arc ion plating system using TiAl and TiSi composite targets under N\textsubscript{2}/Ar atmosphere. XRD and XPS analyses revealed that the synthesized TiaSINO films were nanocomposite consisting of nanosized (TiAl)\textsubscript{x}Si\textsubscript{y}N crystallites embedded in an amorphous Si\textsubscript{x}N\textsubscript{y}/SiO\textsubscript{2} matrix. The hardness of the TiaSINO films exhibited the maximum hardness values of ~47GPa at a Si content of ~5.63 at.\% due to the microstructural change to a nanocomposite as well as the solid-solution hardening. Besides, TiaSINO 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 helpful 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 crystalinity and phase transformation of the films. As a result of XRD, Tia(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, Tia(18at.\%)SINO film annealed at 950°C for 30 min shows formation of aluminum oxide layer on the film surface. On the other hand, Tia(7.56at.\%)SINO film had a titanium oxide layer on the surface after annealing at 950°C for 30 min. In this study, TiaSINO 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 TiaSINO coatings onto cemented carbide substrates. Especially the Tia(5.63at.\%)Ni 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\textsubscript{1-x}N\textsubscript{x} matrix and further increases of Si content lead to amorphous-like coatings. XPS analysis was applied to ZrN film and Zr–Si–N(5.8 at.\%)N film respectively. The main peaks located at 101.8 eV corresponds to Si\textsubscript{1-x}N\textsubscript{x} compound. The maximum hardness (H) of 33 GPa, Young’s modulus 4 of 265 GPa, and H/E\textsuperscript{2} 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...
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 SiO2 or Si(OH)n self-lubricating layer due to the interface tribo-
chemical 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⁻¹. Furthermore, the sheet resistance showed 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 jetdriven by a low-frequency bipolar pulsed voltage wasemplloyed 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 nitrogenspecies (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, pulse with additive oxygen flowrate. The amount of O2 and NO2 in gas phase wemeasured by gas detector. For quantitative measurement of RONS radicals in liquidphase, several chemical methodswere performed on plasma-treated HBBS (Hanks’ Balanced Salt Solution). Among these RONS, the OH radicals dissolved in the liquidwere 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(NO3, O2-, NO2-, and O3) in liquid were detected after plasma treatment using 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 CH3NH3PbI3 (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.

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, Linkoping 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 (MGN) on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGN show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter [1]. The MGN 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 MGN 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 MGN 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 MGN arrays can be as high as 11.2 N cm⁻².

References


6:20pm TF-WeE-3 Growth and Characterization of Atomically-thin MoS₂-MoSe₂-Hetero-Junctions Synthesized by Vapor-Phase Chalcogenization, Andres De Luna Bugallo, CINVESTAV Queretaro Mexico, 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 heterojunctions 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 2D molybdenum disulfide/molybdenum diselenide (MoS₂/MoSe₂) hetero-

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

References


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}(LO) vibrational mode were found for thin 2D h-BN films in contact with Cu and Ni. The lower-energy A_{2u}(LO1) sub-band around 819 cm^{-1} is related to 2D h-BN coupled with Cu substrate, while the higher energy A_{2u}(LO2) sub-band around 824 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.


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 memory, and hot carrier devices. Metal/insulator/metal (MIM) structures are used as high speed diodes for memory, and hot carrier devices. Metal/insulator/metal (MIM) structures are used as high speed diodes for memory, and hot carrier devices. Metal/insulator/metal (MIM) structures are used as high speed diodes for memory, and hot carrier devices.

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


8:40pm TF-WeE-10 Very High Refractive Index Transition Metal Dichalcogenide Photonic Conformal Coatings by Conversion of ALD Metal Oxides, Shauf 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 WS2 layers by chemical vapor deposition of WS2 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 ~10 nm. Although this process yields highly polycrystalline films, the optical constants are in agreement with those reported for single crystal bulk WS2. Subsequently, we demonstrate three photonic structures - first, a two-dimensional hole array made possible by patterning and etching an ALD WS2 thin film before...
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 MoS2-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 disulide (MoS2) that has been widely studied is known to have a direct band gap of ~1.9 eV as a single MoS2 layer and an indirect band gap of ~1.2 eV as a bulk MoS2 crystal.

In this talk, I will present our group research works on MoS2-based nanoelectronic devices. In particular, I explain the following topics on the electrical properties of MoS2 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 MoS2 [4], and hybrid devices of organic materials and MoS2 [5].

References

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.

References:

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; S Ju, University of Tokyo, Japan; A Rohtskopf, 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 Shiom, 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 2nO/GaN TBC as 490±150, −110 MW m⁻².
K. 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, Balaaji Gururaj, B Rangasamy, P Sankaran, P Nagarajan, S Kaliappan, K Dhonan, PSG College of Technology, India; V Asokan, Chalmers University of Technology, Sweden; M Natrajan, Coimbatore Institute of Technology, India; D Velasco-Gonzalez, 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 <0 0 2> 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 <0 0 2>, <1 0 1>, <1 0 2>, <1 1 2> directions. Raman Spectroscopy of the annealed films confirmed the hexagonal structure with a shift observed at 312 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 CdV₂O₇, Erika Cervantes Juárez, R Lozada Morales, A Meza Rocha, R Licona Ibarra, BUAP, Mexico

CdV₂O₇ 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 CdV₂O₇ 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 spectroscopy and photoluminescence were performed. X-ray ray Photoelectron Spectroscopy (XPS) showed the presence of tin in the CdTe films. Xrays Diffraction (XRD) revealed peaks corresponding to the SnTe compound, as well as CdTe peaks strongly oriented 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%.

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 Rímmudo, E Camacho-Espinosa, Juan Luis Peña, CINVESTAV-Unidad Mérida, Mexico, México

The doping of CdTe has been investigated with different materials such as Sn, 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 ~ 3 µm). 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 oriented 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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