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 (A) 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 (A). The hardness and elastic modulus of the multilayer reached their maximum when Λ is about 8.5 nm. The hardness. H3/E*2 ratios and critical loads LC in scratch test showed an initial increase. followed by a decrease with a decreasing modulation period (Λ). The modulation period (Λ) at 8.5 nm exhibited the highest hardness, H3/E*2 ratios and critical loads.

TF-WeP-3 Effect of α -(Al_xGa_{1-x})₂O₃ Overgrowth on MSM-Type α -Ga₂O₃ Ultraviolet Photodetectors Grown by Mist CVD, Kenichiro Rikitake, T Yamaguchi, T Onuma, T Honda, Kogakuin University, Japan

Ultraviolet (UV) photodetectors using high Al content AlGaN have been studying towards applications such as flame detection, sterilization and so on [1]. However, the growth of high-quality AlGaN with increased Al content required for UV photodetector has difficulty in epitaxy. Therefore, we have been focusing on corundum-structured gallium oxide $(\alpha\text{-}Ga_2O_3)$ as an alternative material. $a\text{-}Ga_2O_3$ has a wide bandgap of 5.3 eV, and the bandgap engineering is possible in whole composition range of (Al, Ga, In)₂O₃ alloys [2, 3]. A $\beta\text{-}Ga_2O_3$ based UV photodetector has been shown to have high responsivity [4], and Al₂O₃ deposition on $\beta\text{-}Ga_2O_3$ for surface passivation has been reported [5]. In contrast, $\alpha\text{-}Ga_2O_3$ detector has so far not yet been reported.

In this study, a metal-semiconductor-metal (MSM)-type UV photodetector using α -(Al_xGa_{1-x})₂O₃ on α -Ga₂O₃ is fabricated by mist CVD.

1-µm-thick unintentionally doped α -Ga $_2$ O $_3$ 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 $_x$ Ga $_1$ - $_x$) $_2$ O $_3$ growth using Al and Ga acetylacetonate as source materials. Then, α -Ga $_2$ O $_3$ -based MSM-type photodetector was fabricated by employing Ni (50 nm)/Au (100 nm) pads as Schottky electrodes.

Figure 1 shows XRD 2θ - ω scan profile. $(0006)\alpha$ - Al_2O_3 and $(0006)\alpha$ - Ga_2O_3 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 $(0006)\alpha$ - Ga_2O_3 diffraction peak is 39.8 arcsec. The absorption coefficient a was determined by optical transmittance measurements. Then, $(\alpha h \nu)^2$ -hv 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_xGa_{1-x})₂O₃ on α -Ga₂O₃ structure will be shown at the cofference.

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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 $MoSe_2$ is formed by selenization of MoO_3 which is fabricated on a sapphire substrate by using pulsed-laser sputtering. We report dielectric function parametric model (DFPM) of optical properties of $MoSe_2$ over the energy range of 0.74 to 6.42 eV and the temperature range from 31 to 300 K that measured by SE. We could clearly observe the existence of twelve critical point (A, A^0 , B_1 , B_2 , C_a , C_b , E, F, and E_{I-IV}) structures. The parameters were extracted by fitting the spectra with the reconstruction from twelve dispersive oscillators at each measured data. The dependence of temperature is achieved from the model parameters that are fitted by polynomial and then the dielectric functions of $MoSe_2$ for continuous temperature is determined. These results are expected to be useful in design and understanding in applied device technologies based on $MoSe_2$.

TF-WeP-5 Formation of Microwire Arrays with Dot Structure on Sol-gel Derived Cu₂O Surfaces by Thermal Annealing, Katsuhiro Uesugi, K Matsumoto, W Ikesugi, Y Nakata, Y Hoshiyama, K Obara, H Fukuda, Muroran Institute of Technology, Japan

Cu₂O is recognized as the most promising p-type oxide semiconductor because of its desirable optical properties in the visible region and high Hall mobility. It has been widely studied for the applications such as gas sensors, solar energy conversion, photocatalyst, and photosynthesis. Although Cu₂O 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 Cu₂O microwire arrays with dot structures was performed on the sol-gel derived Cu₂O films by thermal annealing.

A metal precursor solution was prepared by the mixing of copper ($\rm II$) 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. $\text{Cu}_2\text{O}(111)$ peak was observed by the X-ray diffraction measurement of the samples. A lot of wires spread through from dot structures were observed on the surfaces. A typical structure of the wires was 1.6 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 (T_g) and crystallization (T_x). It has been reported that Au-based MGs possess negative dielectric constants and could be used as plasmonic materials. Furthermore, with a low T_g temperature of Au-based thin-film MGs (TFMGs), large dimensions of nanostructures can be thermally

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

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

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

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

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

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

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

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

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

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

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

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

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

Non-evaporable getter (NEG) coatings are widely used for accelerators because they are ideal for maintain ultrahigh vacuum (UHV), and are oil free, magnetic-field free, vibration free, economical, and energy saving. Recently, we have developed a new NEG coating for pumping H2 and CO, and named it as oxygen-free Pd/Ti coating. In oxygen-free Pd/Ti coating Ti thin film is deposited and overcoated by Pd thin film under clean UHV conditions in the range of 10⁻⁷–10⁻⁸ Pa [T. Miyazawa, M. Kurihara, S. Ohno, N. Terashima, Y. Natsui, H. Kato, T. Kikuchi, and K. Mase, J. Vac. Sci. Technol. A, in press.]. When the oxygen-free Pd/Ti thin film is exposed to the atmosphere, the Pd surface is contaminated with organic compounds to some degree, resulting in a decline of the pumping speeds. In the present paper, we report removal of the carbon contamination and improvement of the pumping speeds of the oxygen-free Pd/Ti thin film using UHV or O2 annealing. Unannealed, UHV annealed, and O2 annealed (annealed under O₂ pressure of 1.3 × 10⁻⁴ Pa) oxygen-free Pd/Ti thin films were analyzed with X-ray photoelectron spectroscopy using synchrotron radiation. The carbon coverage of the unannealed sample was estimated as 0.90 ML. On the other hand, the carbon coverages of UHV annealed and O2 annealed samples were estimated as 0.41 and 0.10 ML, respectively. The pumping speed of the oxygen-free Pd/Ti for H₂ and CO after baking under O_2 pressure of 1.3 \times 10⁻⁴ Pa was improved by a factor of 3.7 and 16.3 in comparison with UHV baking, respectively [T. Miyazawa, Y. Kano, Y. Nakayama, K. Ozawa, T. Kikuchi, and K. Mase, in preparation.].

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

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

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]. After baking at 150 °C for 12 h, the pumping speeds of the NEG pump were measured with the orifice method. Pumping speeds of 500-320, 370-260, 400-300, and 310-170 L s⁻¹ were estimated for H₂ after the first, second, third, and fourth venting-activating cycles in a pumped-quantity range of 0.01-10 Pa L . On the other hand, pumping speeds of 510-440, 590-470, and 880-690 L s⁻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 O_2 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 O_2 pressure of 1.3×10^{-4} Pa. The new NEG pumps are a suitable alternative to conventional NEG pumps or titanium sublimation pumps.

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

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

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

Acknowledgments

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TF-WeP-13 Realization of Three Optical States with High Contrast by Doping Nitrogen into Ge₂Sb₂Te₅, 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 Ge₂Sb₂Te₅, 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, *M Wen, Meijia Wang, M Wu, Jilin University, China*

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

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

The layer deposition technique Pulsed Laser Deposition (PLD) provides a feasible way to produce pure carbon films with a wide range of mechanical properties. These properties cover, depending on the deposition parameters, indentation hardness $H_{\rm IT}$ from 20 GPa to 60 GPa and indentation modulus $E_{\rm IT}$ from 300 GPa to 620 GPa what could be correlated with Raman spectra determined on these films. Thus, the ratio of the disordered and the graphitic peaks provides an efficient w ay 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 were characterized with SEM, EBSD and EDS. Through this study, it was found that the microstructure of DED processed layers dramatically differs from conventional bulk carbon steel. Especially, the nanocarbide formation and phase transformation behavior were different from those of conventional bulk materials. Therefore, this study suggests that understanding microstructure and phase transformation behavior during DED process is essential for controlling microstructures to obtain target properties of DED processed layers.

TF-WeP-23 Development of Low-Emissivity Optical Filters Using Double Cannon Sputtering, Ramon 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 de 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 this work is the construction of a Low-E filter made up of stack layers: $glass/Si_3N_4/Al/Al_2O_3/Si_3N_4$, with a high transmittance in the visible region > 80% and high reflectance in the infrared region. This filter has the novelty of employing aluminum (Al) instead of silver (Ag) as a reflector of IR to obtain a cheaper, efficient and durable Low-E filter. The Al is protected with silicon nitride (Si_3N_4) for hardness, high density, and high refraction index (Signore, et al, 2012), furthermore, alumina (Al_2O_3) 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).

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

TF-WeP-25 Investigation of 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 Research Center; Y Tseng, S Chang, National Chiao Tung University, Republic of China Two-dimensional materials have attracted tremendous attention die 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 NbS₂ ratio in the semiconducting MoS₂ film. Using in-situ x-ray absorption spectroscopy (XAS) and ambient-pressure xphotoelectron spectroscopy (ARXPS) techniques at national synchrotron radiation research center (NSRRC), we found that CO₂ acted as 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 kurtosis value was obtained at this IB intensity. Therefore, we are convinced that the PEG films irradiated at this low IB intensity show potential as alternative alignment layer in LC applications.

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

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

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

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

Au nanowires were fabricated using conventional electron-beam lithography and lift-off process. They were patterned on resist-coated 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.

Al-assisted FCE system is composed of four engines; learning, evaluation, inference and FCE engines. First, the feature values of conductance quantization obtained from previous experiments were stored in an initial database in learning engine. Then, FCE parameters were evaluated using cost function in evaluation engine. After the evaluation, FCE parameters were optimized by genetic algorithm (GA)-based selection methods in inference engine. Finally, FCE procedure using optimized experimental parameters was applied to Au nanowires in FCE engine. As a result, Au atomic junctions were fabricated by Al-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 Al-assisted FCE implemented on FPGA.

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

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

First, 2x1-6x6 series-parallel-connected Au nanogaps with the initial gap separation of 40-70 nm were fabricated with electron-beam lithography and lift-off processes. After the activation, the total resistance of the seriesparallel-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-parallelconnected 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-parallelconnected 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 seriesparallel-connected nanogaps can be applicable to the shortest path problems.

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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 (2e¹) pathway, O_2 molecule is reduced to H_2O_2 , and for the direct four-electron (4e¹) pathway, the final product is H_2O . H_2O_2 for the 2e¹ pathway might corrode a carbon based electrocatalyst itself, leading to low durability. We also examined the selectivity with respect to these two pathways.

The calculation models are the N-ACGNRs and the N-ZZGNRs, in which a C atom is substituted by a N atom for each doping site from edge to in-plane. The reaction sites are set to C atoms adjacent to the N atom. We calculated the values of U_{max} for each doping site and reaction site for the N-ACGNRs and the N-ZZGNRs. The Umax for N-ACGNR becomes positive for each doping and reaction site. On the other hand, the Umax for N-ZGNR has a parity dependence with regard to the nitrogen doping site in the vicinity of the zigzag edges. For the even-numbered doping sites from the edge, the values of U_{max} are larger than 0 V, while for the odd-numbered ones, the values of U_{max} become negative. The reaction selectivity for the $4e^{-}$ pathway appears only in the vicinity of armchair and zigzag edges. For the models showing the reaction selectivity, the sp2 configuration of GNR is maintained, even if reaction intermediates are adsorbed on GNR. On the other hand, reaction intermediates adsorb on GNR with sp3-like configuration for the other models. The mechanism for appearance of the selectivity will be discussed in the presentation.

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

Functional graded TiAlSiNO nanocomposite films were deposited onto WC-Co substrate by a filtered arc ion plating system using TiAl and TiSi composite targets under N₂/Ar atmosphere. XRD and XPS analyses revealed that the synthesized TiAlSiNO films were nanocomposite consisting of nanosized (Ti,Al,Si)N crystallites embedded in an amorphous Si₃N₄/SiO₂ matrix. The hardness of the TiAlSiNO 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, TiAlSiNO film with Si content of around 5.63at.% also showed perfect adhesive strength value of 105.3N. These excellent mechanical properties of Ti-Al-Si-N-O films could be help to improve the performance of machining tools and cutting tools with application of the film. Also X-ray diffactometer (XRD) analysis was conducted to investigate the crystallinity and phase transformation of the films. As a result of XRD, TiAl(18at.%)SiNO films showed the great oxidation resistance of 950°C for 30 min in air. Based on glow discharge optical emission spectroscopy (GD-OES) depth profiles, TiAl(18at.%)SiNO film annealed at 950°C for 30 min shows formation of aluminum oxide layer on the film surface. On the other hand, TiAl(7.56at.%)SiNO film had a titanium oxide layer on the surface after annealing at 950°C for 30 min. In this study, TiAlSiNO coatings were applied to insert tools. Their performances were evaluated about cuttingtime and cutting-length to Inconel 718 super alloys. Performance of the coated tools were evaluated and compared with different TiAlSiNO coatings onto cemented carbide substrates. Especially. TiAlSi(5.63at%)N coated tool showed better performance and best tool life.

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

Zr-Si-N coatings with various Si contents were synthesized by a hybrid deposition system combining arc ion plating and d.c. magnetron sputtering techniques. The influence of the Si content on the microstructure, mechanical properties and tribological properties of the Zr-Si-N coatings were investigated. The results showed that as the Si content increased from 0 to 5.8 at.%, the coatings transformed from a columnar ZrN to nanocomposite structure with a nano-sized ZrN crystallites embedded in amorphous Si₃N₄ matrix and further increases of Si content lead to amorphous-like coatings. XPS analysis was applied to ZrN film and Zr-Si(5.8 at.%)-N film respectively. The main peaks at 179.9 and 182.3 eV with a large percentage of area correspond to the ZrN compound. There was also a small contribution from the ZrO2 oxide phase at 182.16 and 184.59 eV. For the Si 2p region, the silicon binding energy spectrum is also divided into two peaks. The major peak located at 101.8 eV corresponds to Si₃N₄ compound. The maximum hardness (H) of 33 Gpa, Young's modulus € of 265 Gpa, and H/E* value of 0.12 were obtained at Si content of 5.8 at.% in the Zr-Si-N coatings, respectively. The coating with the lowest friction

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coefficient and the best wear resistance was also obtained at Si content of 5.8 at.%, which was mainly contributed to high value of H/E* and formation of SiO_2 or $Si(OH)_4$ self-lubricating layer due to the interface tribochemical reaction.

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

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

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

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

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

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

Graphene, an ultra-thin flexible material with high carrier mobility and transparency, is a promising candidate for flexible transparent conducting electrodes (TCEs). However, its resistance is too high for use as a TCE material by itself. Therefore, fabricating graphene with low sheet resistance and high stability is a significant challenge for practical applications of graphene TCEs. In this study, we proposed a twodimensional (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 an excellent thermal and mechanical stability with a change of only about 2% in a bending test of 20,000 cycles or at a high temperature of >200°C. This result shows that stacking graphene with stable 2D doping layer is a promising approach for graphene-based next generation TCE.

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

Atmospheric pressure helium plasma jetdriven by a low-frequency bipolar pulsed voltage wasemployed 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 withand additive oxygen flowrate. The amounts of O_3 and NO_2 in gas phase were measured by gas detector. For quantitative measurement of RONS radicals in liquidphase, several chemical methods were performed on plasma-treated HBSS (Hanks' Balanced Salt Solution). Among these RONS, the OH radicals dissolved in the liquid were monitored indirectly using the fluorescent properties of hydroxyterephthalic acid (HTA) formed by the reaction of terephthalic acid (TA) with OH radicals. The concentrations of long-living reactive species (H_2O_2 , NO_2 -, NO_3 -, and O_3) 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 highdensity memory applications [4]. MAPI-based nanoscale RSM and crosspoint 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 crosspoint 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 highcapacity 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.

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