

## Thin Films

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

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

**Moderator:** Francisco Aguirre-Tostado, CIMAV-Monterrey

#### 5:40pm TF-MoE1 Synthesis and Characterization of Novel Nitride Semiconductor Thin Films, *S.R. Bauers, A. Holder, S. Lany, Andriy Zakutayev*, National Renewable Energy Laboratory

Nitride thin films have proven to be an invaluable class of materials with a broad range of uses. Examples include transition metal (TM) nitride rocksalts used as hard-wearing industrial and decorative coatings, and semiconducting III-N wurtzites with exceptional optoelectronic properties. We used high-throughput experimental and computational tools to investigate new inorganic ternary nitrides that have previously received very little attention. Specifically, we focused on heterovalent II-IV-N analogues to well-known III-N 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  $1 \text{ cm}^2/\text{Vs}$  – quite high as for nanocrystalline thin films. The calculated indirect bandgaps are in the visible - near IR range (0.9-2.4 eV), and the calculated static dielectric constants are large (30-80).

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

#### 6:00pm TF-MoE2 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.J. Joo, H.-S. Kim*, Hanyang University, Seoul, Korea

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

$9.52 \mu\Omega/\text{cm}$ , via-hole:  $12.69 \mu\Omega/\text{cm}$ ) and high adhesion strength (5B) with well-sintered morphology.

#### 6:20pm TF-MoE3 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.V. Taylor*, Rowan University; *E.M. Burkholder*, Johnson Matthey Inc.; *J.D. Hettinger*, Rowan University; *S. Amini*, Johnson Matthey Inc.

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

#### 6:40pm TF-MoE4 Surface and Interface Imaging by Ultrahigh Resolution Laser-based Photoemission Electron Microscopy, *Toshiyuki Taniuchi*, The University of Tokyo, Japan; *S. Shin*, The University of Tokyo, AIST-UTokyo OPERANDO-OIL, Japan

INVITED

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

#### 7:40pm TF-MoE7 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.-S. Kim*, Hanyang University, Seoul, Korea

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

indispensably required. Using light annealing system such as deep-UV, laser and flash light irradiation, the process temperature applied to the annealing of IGZO could be significantly reduced. However, the manufacturing process of the IGZO-based TFT still involves deposition process under vacuum condition because metal-based electrode (source, drain) on the IGZO layer is fabricated by a deposition process.

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

8:00pm **TF-MoE8 Carbon-nanotube Dispersed Ga<sub>2</sub>O<sub>3</sub>Films for UV Transparent Electrodes Fabricated by Molecular Precursor Method, Tohru Honda, Y. Takahashi, R. Yoshida, C. Mochizuki, H. Nagai, T. Onuma, T. Yamaguchi, M. Sato, Kogakuin University, Japan**

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

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

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

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

## Author Index

**Bold page numbers indicate presenter**

— A —

Amini, S.: TF-MoE3, **1**

— B —

Bauers, S.R.: TF-MoE1, **1**

Burkholder, E.M.: TF-MoE3, **1**

— C —

Chu, J.H.: TF-MoE2, **1**

— H —

Hettinger, J.D.: TF-MoE3, **1**

Holder, A.: TF-MoE1, **1**

Honda, T.: TF-MoE8, **2**

— J —

Joo, S.J.: TF-MoE2, **1**

— K —

Kim, H.-S.: TF-MoE2, **1**; TF-MoE7, **1**

— L —

Lany, S.: TF-MoE1, **1**

— M —

Mochizuki, C.: TF-MoE8, **2**

Moon, C.-J.: TF-MoE7, **1**

— N —

Nagai, H.: TF-MoE8, **2**

— O —

Onuma, T.: TF-MoE8, **2**

— S —

Sato, M.: TF-MoE8, **2**

Shin, S.: TF-MoE4, **1**

— T —

Takahashi, Y.: TF-MoE8, **2**

Taniuchi, T.: TF-MoE4, **1**

Taylor, G.V.: TF-MoE3, **1**

Tint, S.D.: TF-MoE3, **1**

— Y —

Yamaguchi, T.: TF-MoE8, **2**

Yoshida, R.: TF-MoE8, **2**

— Z —

Zakutayev, A.: TF-MoE1, **1**