

Thin Films

Room: Makai - Session TF-TuE

Thin Film Synthesis & Characterization I

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

5:40pm **TF-TuE1 Sputtering Growth of ZnO-based Semiconductors with Band Gap Tunability Over the Entire Visible Spectrum, Naho Itagaki**, Kyushu University, Japan **INVITED**

ZnO is a remarkable multi-functional material with a distinctive property set and a huge range of existing applications. Recently, some research has been directed towards development of ZnO based materials with smaller band gap (E_g), which allow light emission/absorption over a broad spectrum from the UV to the visible region. One of the most promising means to narrow the band gap is to alloy ZnO with CdO that has small direct band gap of 2.3 eV. However, there are technological challenges for the growth of high-cadmium-content CdZnO because of the crystal phase segregation between wurtzite ZnO and rocksalt CdO.

In this context, we have developed a new compound, ZnInON (ZION), which is a pseudo-binary alloy of ZnO with InN. Since both ZnO and InN have the same wurtzite crystal structure and different band gaps (ZnO: 3.4 eV; InN: 0.7 eV), the alloy may possess band-gap tunability in a wide range. Here, we first demonstrate the sputtering synthesis of ZION and the band gap tuning by changing the chemical composition ratio. The detailed analysis on the crystal structure as well as the photo-electric properties of this new material are then conducted. Finally, we discuss the advantages of ZION as light-absorbing layers of multi-quantum well (MQW) solar cells, the theoretical efficiency of which exceeds 50%.

From the analyses of wide-range reciprocal space mapping of XRD spectra, we found that ZION has the same crystal structure as wurtzite ZnO and InN. The lattice constant of ZION is in between ZnO and InN, and decreases continuously with decreasing $[Zn]/([Zn]+[In])$, which indicate that ZION is a pseudo-binary system of ZnO and InN. The transmittance spectra reveal that the optical absorption edge is shifted continuously toward longer wavelengths with decreasing $[Zn]/([In]+[Zn])$. The band gap of ZION films, being determined by Tauc's plot, changes from 3.4 eV to 1.5 eV, which covers entire visible spectrum. The analyses of transmittance spectra indicate that ZION is of direct band gap, and thus it has high absorption coefficient around 10^5 cm^{-1} . Furthermore, we found significant advantages of ZION in terms of applications in multi-quantum-well (MQW) solar cells. The lifetime of photo-generated carriers in QWs is increased by a few orders of magnitude when ZION is used as a MQW material instead of conventional GaAs-based materials, owing to the large piezoelectric field (several $\text{MV}\times\text{cm}^{-1}$) that separate electrons and holes. These results indicate that ZION is a promising material that opens new pathways for realizing new generation solar cells with very high efficiency.

6:20pm **TF-TuE3 Improvement of Thermal Stability of p-ZnO:(Al,N) Thin Films by Oxidizing Amorphous Zn₃N₂:Al Thin Films, Bingsheng Li**, Harbin Institute of Technology, China

ZnO has attracted much more attention as a potential candidate for more efficient UV-lasers due to its wide band gap of 3.374 eV and a large exciton binding energy of 60 meV. However, the problem associated with the preparation of stable p-type ZnO with high hole density hinders the ZnO-based device application as UV-emitters. Although substantial studies have been focused on this challenging issue, there are, so far, no efficient and practical doping methods to prepare stable p-ZnO with high hole density. The n-type conduction with high electron density (10^{21} cm^{-3}) have been achieved by doping ZnO with group-III elements (Al, and Ga). On the other hand, although extensive studies have been focused on the p-type doping issue of ZnO, the ZnO-based optoelectronic devices fabricated from p/n junction still suffer from p-type ZnO problem. P-type conduction has been reportedly realized with chemical doping. However, the low hole density and instability in electronic behavior become the bottleneck to improve the ZnO-based device performance.

For improving the thermal stability of p-ZnO, we introduce Al to capture the N by forming Al-N chemical bonds. The bond dissociation energy, ΔH_{298} , of Al-N is $297 \text{ kJ}\cdot\text{mol}^{-1}$, is much larger than the Zn-N ($\Delta H_{298} = 160 \text{ kJ}\cdot\text{mol}^{-1}$). Theoretical calculations suggested the possible approach to the p-type doping in ZnO with III-V Ga-N co-doping or cluster-doping, which can increase the solubility and stability of N in ZnO. Here, we use Al to stabilize the N-doping, because the corresponding bonds with N and O are stronger for Al than for Ga. For stabilizing N in p-type ZnO, the key issue is

to reduce the compensation of single Al doping due to the formation of only Al-O bands. Another crucial point is to make sure the Al captures more than one N-atoms to form AlN_2 , AlN_3 , and AlN_4 in ZnO. To realize that, we prepared $\text{Zn}_3\text{N}_2:\text{Al}$ and convert it to ZnO by an oxidation procedure. For $\text{Zn}_3\text{N}_2:\text{Al}$, p-ZnO appears around 600 °C and do not convert back to n-type with further increase of annealing temperature. However, for Zn_3N_2 , we did not obtain p-type ZnO. A reasonable explanation is that the Al will stabilize the N during the reaction to form ZnO from Zn_3N_2 . Comparing with previous reports, the thermal stability is improved. However, the hole density is still low and needs further improvements. More details about the structural, optical, and electronic properties of the samples will be given in the presentation.

We will optimize the concentration of Al dopant in $\text{Zn}_3\text{N}_2:\text{Al}$. The dependence of the hole density in ZnO, oxidized from $\text{Zn}_3\text{N}_2:\text{Al}$, on the Al concentration in $\text{Zn}_3\text{N}_2:\text{Al}$ will be studied.

6:40pm **TF-TuE4 Well-Ordered Monolayers of Alkali-doped Coronene and Picene, Yoichi Yamada, M. Yano, M. Endo, E. Shimizu, Y. Hasegawa, M. Sasaki**, University of Tsukuba, Japan

Although the electronic modifications of the organic thin films by means of the chemical doping have been widely investigated, the structural properties of the doped organic materials have been poorly understood. This is generally due to an inhomogeneity of the doped materials, hindering the detailed understanding of the structure. However, structural information is inevitable for understanding the mechanism of the doping. For the basic investigation on the doping of the organic materials, we utilize well-defined monolayers of organic materials. We model the doping by depositing the dopant onto the monolayer. When the substrate is inert enough, self-organization of the dopants and host materials will be facilitated and well-ordered doped monolayer will be obtained. We focus mainly on so-called "metal-intercalated aromatic superconductors" discovered in 2010 in K-doped picene [1]. Since its discovery, electronic properties of these materials have been investigated by means of the photoemission spectroscopy. However, contradicting results, deviating from a metallic to an insulating ground state, have been obtained. It is speculated that there exists notable variation of the structures in the thin films used in the photoemission studies. The theoretical reports have also reached contradicting results and have suggested that the electronic states are quite sensitive to the molecular arrangements. Therefore it is demanded to realize the well-ordered samples of these materials. Here we demonstrated the fabrication of the well-defined monolayer of the metal-intercalated aromatic superconductors, such as K-doped picene and coronene. These systems enable us the systematic investigations of the relation between structure and electronic properties. It is found that the alkali-doping causes a rearrangement of the host monolayers, based on the scanning tunneling microscopy and the X-ray absorption spectroscopy. Upon the reconstruction, electronic states of the host molecules also change drastically, suggesting the charge transfer from alkali metals to the molecule, revealed by means of the photoelectron spectroscopy. These observations confirm that the well-ordered monolayer, as realized in this study, can properly model the doping process [2,3].

[1] R. Mitsuhashi, et al., Nature 464, 76 (2010)

[2] M. Yano, et al., J. Chem. Phys. 141, 034708 (2014)

[3] Y. Hasegawa, et al., J. Phys. Chem. C (in press)

7:00pm **TF-TuE5 Electrochromic Thin Film Synthesis, Understanding and Performance Enhancement, Yi Ren, S.Y. Chiam, J. Liu**, Institute of Materials Research and Engineering, Singapore

Electrochromic (EC) thin films are important for enabling technologies such as smart windows and non-volatile displays. To date, various organic EC films have been shown to possess high coloration efficiency and many color variety, while inorganic films have demonstrated excellent optical modulation and cycling stability. In addition, flexible EC devices that are retrofittable to existing windows can also be achieved by utilizing organic or porous inorganic films, and this poses new challenges in device integration and performance enhancement. In this presentation, I will first talk about various synthesis methods used by us for EC thin film deposition. Solution-based methods which target for low-cost and large-scale fabrication will be emphasized. Besides chemical bath deposition and electroplating, an innovative dip coating method with better thickness control will be introduced. Materials covered range from inorganic metal oxides (such as nickel, tungsten, molybdenum and tantalum oxide) to organic polymer electrolytes. We found that different synthesis methods result in films with different structure, phase and defect density. These differences in turn significantly affect the electrochromic performance of the material. Therefore, in the second part of the presentation, I will focus

on characterizing and correlating the physical and electrochromic properties of the synthesized films. As an example, layered nickel oxide/hydroxide will be discussed in details. With different synthesis methods and post treatments, we are able to investigate the electrochromic performance of films with different structures (compact, porous and nanostructured), phases (α and β phase), defect density (amount of Ni^{3+} sites) and intercalated species (water and anions). By changing electrolyte, we can also study the role of different ions in causing the color change, in particular, H^+ , OH^- and Li^+ . Recently, we have successfully identified the causes of the activation and degradation phenomenon observed in oxide material. We have also proved the importance of having existing reaction sites such as defects for improved electrochromic reaction involving Li^+ . The above knowledge can be extended to other layered material such as tungsten and molybdenum oxides. Last but not least, our ongoing work also focuses on synthesizing and characterizing thin films that can be functioned as solid electrolyte in electrochromic device. Besides the organic polymer electrolyte, we also look at emerging inorganic metal oxide electrolyte such as tantalum oxide. Their synthesis and ion conducting properties play significant role in device integration and performance.

7:40pm **TF-TuE7 Thin Film Synthesis via Nanogrinding**, *Chris Papadopoulos*, University of Victoria, Canada

Thin films composed of nanoscale particles possess unique and varied electrical, optical and mechanical properties, which can be used to create advanced functional materials and nanostructured composites for devices. Such thin films find applications in electronics, optics, photovoltaics, energy storage, biomedicine, etc.

Here we describe a general approach to nanoparticle thin film synthesis based on *colloidal* or *nanogrinding*. Nanogrinding can produce large amounts of nanoscale particles in an appropriate solvent without the use of complex chemical or physical processing. The nanogrinding method typically employs planetary ball milling to grind a starting bulk powder into a nanoscale colloidal suspension suitable for thin film coating. Ball milling uses the rotary motion of a grinding jar containing the sample, grinding beads and a liquid medium, which is arranged eccentrically on a so-called sun wheel. The efficient energy transfer during planetary ball motion leads to nanogrinding being a fast and inexpensive process for the creation of nanostructured thin films. In addition, nanogrinding is very flexible allowing the formation of semiconducting, metallic or insulating particles and films. These unique advantages combine to create a general solution-based processing approach for thin film surface coatings and devices (including non-planar geometries).

Results of nanogrinding trials using high-purity bulk materials (Si, silicides, oxides) and characterization of the nanoparticles and films via electron microscopy, scanning probe methods, Raman spectroscopy and elemental analysis are presented. Zirconia grinding vessels and either zirconia or silicon nitride beads are used in a planetary ball mill to grind readily available high-purity powders initially consisting of ~10-50 micron particles dispersed in solvent. Grinding speeds and times are varied between 200-1000 rpm and 10-500 minutes, respectively. After milling, the resulting colloidal dispersions are optionally filtered and deposited on a substrate for further analysis. As grinding time is increased, the resulting particles and films display good uniformity with sizes below 100 nm. Atomic force microscopy of the particles showed that diameters down to ~2-4 nm could be achieved. Elemental analysis indicates that contamination from the grinding tools is minimal.

Nanogrinding is an efficient route to directly creating nanoparticles suitable for thin film deposition of various materials from solution. By adjusting the grinding parameters, the size and dispersion of the particles can be controlled and their properties optimized for applications, including thin film electronic and optical devices.

8:00pm **TF-TuE8 Effect of Annealing on Current Conduction Mechanism in High-k Dielectric Thin Films Deposited on Silicon Substrates**, *Anil Khairnar, P.A. Deshmukh, V.S. Patil, K.S. Agrawal, A.M. Mahajan*, North Maharashtra University Jalgaon, Maharashtra, India-425001, India

Abstract:

The ever increasing demand for functionality and speed for semiconductor applications requires enhanced performance, which is achieved by the continuous miniaturization of CMOS dimensions. However, as we further reduce the device dimension, transistor with conventional structure and material is attaining its fundamental scaling limit. Beyond the 22 nm node fundamental as well as practical constraints will limit the maximum performance achievable by these scaled transistors. The integration of high-k gate dielectric provides a promising solution to continue improving the device performance, as their higher k-value allows a physically thicker layer while aiming the same capacitance and Equivalent Oxide Thickness (EOT). This study primarily focused on studying the electrical properties of high-k

MOS capacitors with metal gate electrodes. In this work, we have deposited HfO_2 and Al_2O_3 thin film deposited on silicon substrate by RF sputtering technique and Plasma enhanced atomic layer deposition system (PEALD) respectively. The deposition of HfO_2 is confirmed by FTIR measurement. Current density vs voltage characteristics have been studied by I-V measurement further comparative study of current conduction mechanisms is done. In MOS structure due to the charge trapping and interface characteristics of dielectric films causes leakage current in dielectrics. The density of leakage current has been investigated and analyzed, by current-voltage and conduction mechanisms. Among the various conduction mechanisms HfO_2 and Al_2O_3 film on Si follows the Fowler Nordheim (FN) tunneling. The Poole Frenkel (PF) emission, Schottky emission (SE) and Trap assist tunneling (TAT) also studied. The barrier height (ϕ_b) is calculated of experimental work through Fowler Nordheim tunneling mechanism.

Keywords - HfO_2 , Al_2O_3 , high-k, leakage current density, FN tunneling.

8:20pm **TF-TuE9 Effects of Very High Frequency O_2 Plasma Reactant on High-k Film Properties Deposited by Atomic Layer Deposition**, *Gilsang Yoo, I.K. Oh, C.W. Lee*, Yonsei University, Republic of Korea, *T.H. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea, Republic of Korea, *H.B.R. Lee*, Incheon National University, Republic of Korea, *H.J. Kim*, Yonsei University, Republic of Korea

High permittivity (high-k) dielectrics have been explored for an alternative gate insulator to conventional SiO_2 in the metal oxide semiconductor field effect transistor (MOSFET) technology. Among various high-k deposition techniques, atomic layer deposition (ALD) appears to be one of the suitable methods due to its excellent process controllability for extremely thin high-k films. Plasma-enhanced atomic layer deposition (PE-ALD) using plasma reactant has been spotlighted because of its several benefits over conventional thermal ALD using gas reactant, such as lower process temperature and improved film properties by the reactive radicals of reactants. However, use of plasma reactants negatively influences electrical properties of high-k films in MOSFET since ion bombardment of energetic radicals generates defects in films. Instead of radio frequency (RF) plasma which is usually used for plasma assisted processes, very high frequency (VHF) plasma for chemical vapor deposition (CVD) process was reported. The negative effects of plasma on film properties were reduced in VHF plasma process due to its lower ion kinetic energy and higher plasma density than RF plasma. Therefore, VHF plasma is expected to be a better plasma reactant for PE-ALD than RF plasma in the context of high growth rate and low ion damage. However, there has been no report on PE-ALD using VHF plasma reactant.

For this study, Al_2O_3 PE-ALD were developed using Trimethylaluminum (TMA) precursor and O_2 plasma reactant on Si substrate. O_2 plasma reactant was generated using two different frequencies, 13.56 MHz and 60 MHz for RF and VHF, respectively. The processes exhibited ALD mode with good self-saturation behavior and linear growth as a function of growth cycles. To investigate the characteristics of plasma density and electron temperature, a Langmuir probe was installed in the chamber. The thickness and density of the films was analyzed by spectroscopic ellipsometry and X-ray reflectivity (XRR), respectively. By using VHF plasma, better film properties were observed compared to RF plasma. The growth rate of VHF plasma (2.7 Å/cycle) was higher than that of RF plasma (2.3 Å/cycle). In addition, the VHF PE-ALD film was denser than RF PE-ALD film (3.26 for VHF and 3.11 g/cm^3 for RF plasma), since ion and radical density generated by VHF is higher than those by RF. The VHF PE-ALD provides improved film qualities, such as low leakage current and low interface trap density, compared to RF PE-ALD grown film. The VHF plasma reactant for PE-ALD has potentials for various applications which require very thin and dense films in nanoscale regime.

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