Thin Films
Room 206 B W - Session TF-FrM
Fundamentals of Thin Films III

Moderators: Mark Losego, Georgia Institute of Technology, **Junjie Zhao**, Zhejiang University

8:45am **TF-FrM-3 Conductive Transparent Porous Al-Doped ZnO Conformal Coatings Synthesized Using Sequential Infiltration Synthesis Method***, **Vasanta Gurung**, Diana Berman,* University of North Texas

In this study we demonstrated a simple approach for the fabrication of conductive, transparent, nanoporous, and conformal aluminum-doped zinc oxide (AZO) coating using sequential infiltration synthesis (SIS) method. Block copolymer (BCP) polystyrene-block-polyvinyl pyridine (PS-b-P4VP) was employed as a polymer template for infiltrating metal-oxide precursors, leading to the synthesis of nanoporous AZO coatings. We show that both the porosity and electrical conductivity of the AZO coatings could be precisely tuned by swelling the polymer template in a suitable solvent and adjusting the number of SIS cycles. We achieved up to 80% porosity, with a low aluminum-to-zinc doping ratio of 1:17, resulting in a resistivity of approximately 7.83 Ωcm, as measured using conductive atomic force microscopy (C-AFM) and Hall effect measurements. Additionally, the AZO coating exhibited average transmittance of over 80%, confirming its high transparency. These results highlight a highly effective and reliable method for synthesizing conductive, transparent, nanoporous, and conformal AZO coatings, which exhibits a promising potential for a wide range of optoelectronic applications.

KEYWORDS:*sequential infiltration synthesis, block copolymer, aluminum-doped zinc oxide, conductivity*

9:00am **TF-FrM-4 Effect of Aminosilane Precursor and Initial Surface Silanol Density on O2 Plasma-Assisted ALD of SiO2***, **Andrew Kaye**,* Colorado School of Mines*; Bhushan Zopé,* Intermolecular, Inc.*; Xinjian Lei, Agnes Derecskei, Haripin Chandra,* EMD Electronics, USA*; Sumit Agarwal,* Colorado School of Mines

SiO_2 is a commonly used dielectric material in semiconductor manufacturing, and aminosilanes are typically used as the Si precursor during radical-assisted atomic layer deposition (ALD) of SiO_2. This work explores the role of the initial surface Si−OH density, the substrate temperature, and the structure of the aminosilane precursor on the growth per cycle (GPC) for ALD on plasma-deposited SiO_2 substrates. Specifically, we studied O_2-plasma-assisted ALD of SiO_2 using two aminosilanes, di-*sec*-butylaminosilane (DSBAS) and dimethylamino trimethylsilane (DMATMS). The surface reactions during ALD were monitored using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, and the GPC was monitored using *in situ* four-wavelength ellipsometry. On an SiO_2 surface with a high initial Si−OH group density, *in situ* ATR-FTIR spectroscopy shows that ~30% more Si−OH groups are consumed by DMATMS than DSBAS because DSBAS contains a bulkier amino leaving group than DMATMS. *In situ* ellipsometry shows that at an ALD temperature of 100 °C, the GPC using DSBAS and DMATMS are ~1.8 and ~1.2 Å, respectively. The higher GPC for DSBAS shows that the initial aminosilane coverage does not influence the GPC. We speculate that during the O_2 plasma step, O radicals can easily insert into Si−H bonds in adsorbed DSBAS. However, for adsorbed DMATMS, surface $Si-(CH_3)_3$ groups must be combusted, and then converted to Si−OH groups from species generated in the O_2 plasma.

On an SiO_2 surface with a low initial Si−OH group density, approximately the same number of Si−OH groups react with DMATMS and DSBAS. Therefore, we conclude that once the initial surface Si−OH density is sufficiently low, steric effects do not play a role in initial aminosilane adsorption on SiO_2. For both DMATMS and DSBAS, at a constant ALD temperature, the initial SiO_2 surface Si−OH group density has no effect on the GPC of SiO_2 ALD. *In situ* ellipsometry shows that on an SiO_2 surface with a low initial Si−OH group density, no nucleation delay is observed compared to a film with a high initial Si−OH group density. This implies that more Si−OH groups are produced during the first few O_2-plasma half-cycles compared to the initial density of adsorbed aminosilanes on the surface, allowing steady-state ALD to be reached within 5 ALD cycles. As ALD temperature for DSBAS increases, the GPC decreases. This is due to the thermal instability of reactive surface groups such as Si−OH and Si−H, and the areal density of these sites decreases with increasing temperature.

9:15am **TF-FrM-5 Low-Temperature Growth of Epitaxial III-Nitride Films via Hollow Cathode Plasma Atomic Layer Deposition***, **Steven Allaby**, Habeeb Mousa, Fatih Bayansal, Abiodun Aderibigbe, Mustafa Yavuz, Steven Suib, Helena Silva, Necmi Biyikli,* University of Connecticut

The III-nitride compound semiconductor family plays a critical role in optoelectronic devices and transistor channel materials, particularly for high-power and high-frequency applications. In this study, AlN, GaN, and InN thin films were deposited on c-plane sapphire and n-Si(111) substrates via hollow cathode plasma atomic layer deposition (HCP-ALD). Trimethylaluminum (TMA) was used as the aluminum precursor; triethylgallium (TEG) for gallium; and trimethylindium (TMI) for indium. N2 and H2 plasma were included for AlN and GaN, while N2 was included for InN. For each III-nitride film, the effect of adding argon to the plasma gas composition was investigated. All film depositions took place under 100W rf-power and at a substrate temperature of 200°C.

The resulting films were characterized using ellipsometry, x-ray diffraction (XRD), ultraviolet-visible spectroscopy (UV-Vis), and scanning transmission electron microscopy (STEM) imaging. In situ ellipsometry showed linear growth in AlN; accelerated growth in GaN; and delayed growth in InN. The growth per cycle (GPC) values were obtained as 1.21, 0.45, and 1.10 Å for AlN, GaN, and InN, respectively. Spectroscopic ellipsometry showed an increase in refractive index when Ar was included for AlN and InN, while refractive index decreased when Ar was included for GaN. XRD patterns showed highly crystalline films oriented along the (002) plane. Ar inclusion resulted in an increase in the (002) peak for GaN and InN films, while it reduced the (002) peak for AlN. From UV-Vis and Tauc analysis, the optical bandgaps were obtained as 5.80, 3.22, and 1.96 eV for AlN, GaN, and InN, respectively. High-angle annular dark-field (HAADF) STEM images showed monocrystalline films for AlN and GaN, forming smooth interfaces with sapphire. InN appeared polycrystalline with distinct grain boundaries.

Future work involves characterizing the electrical properties of III-nitride films, performing Hall effect measurements to obtain conductivity type, carrier concentration, and mobility. X-ray photoelectron spectroscopy will be performed to determine the amount of carbon and oxygen impurities in the films. After optimizing InN and GaN, InGaN will be alloyed under similar conditions to enable bandgap engineering.

This work contributes to the development of stable and reliable n-type nitride semiconductors for back-end-of-line (BEOL) transistor channel materials.

9:30am **TF-FrM-6 Understanding Oxygen Evolution Reaction and Charge Transfer Behavior at the Electrode-Electrolyte Interface Using Pulsed Laser-Deposited Ruthenium Oxide Thin Films***, **Mengxin Liu**,* North Carolina A&T State University

Ruthenium oxide (RuO_2), regarded as one of the benchmarks for oxygen evolution reaction electrocatalyst materials during water splitting, has been grown in epitaxial thin film form using a pulsed laser deposition method. The precision in the RuO_2 thin films structure, surface orientation, and oxygen stoichiometry have been investigated using high-resolution structural characterization techniques that include x-ray diffraction, x-ray reflectometry, Raman Spectroscopy, and x-ray photoelectron spectroscopy. Following the structural characterization, the films were subjected to four-probe resistivity and Hall measurements via the Van der Pauw method and electrochemical measurements via a three-electrode system. The control in the RuO_2 thin film surface orientation was realized using high-quality single crystal rutile Titanium oxide (TiO_2) substrates with (100), (101), and (110) orientations. Due to different atomic arrangements of Ru and O atoms and interatomic orbital positions in these planes, these films profoundly differ in electrical resistivity, charge carrier density, and dominance in the nature of charge carriers, hence, in the net electrochemical properties. The electrochemical measurements and analysis carried out on the RuO_2 thin film with (101) orientation displays the highest electrochemical current density and the lowest onset potential among the RuO_2 films with other orientations. The next part of our study has focused on understanding the role of oxygen defects in RuO_2 thin films in their electrochemical properties. For this purpose, RuO_2 thin films were on TiO_2 substrates with (110) orientation at substrate temperatures of 500, 600, and 700 °C. After the deposition was over, all the films were cooled to room temperature from the deposition temperature in two hours under the high vacuum conditions of $2\text{-}3\times10^{-6}$ Torr. The x-ray photoelectron spectroscopy results carried out on these films have shown that the binding energy center of the corresponding Ru3d doublet peaks for the 700 °C sample is 0.5 eV lower than for the 500 and 600 °C samples. These results indicate the formation of oxygen vacancies with the variation of Ru oxidation states near the top surface of the thin film. According to the electrochemical measurement, the 700 °C sample displays the lowest overpotential (500 mV) at the current density of 10 mA/cm^2 and also the lowest Tafel slope (101.6 mV/dec) than others. Additionally, the electrochemical double larger capacitance of the deposited thin films, measured by different methods, indicates that the 700 °C has the highest value of 61.20 μF, compared with the 26.87 and 28.35 μF for 500 and 600 ° samples, respectively.

9:45am **TF-FrM-7 Growth of Ag Nanomorphologies by High-Temperature Glancing Angle Deposition — from Initial Growth Stage to Whisker/Plate Formation***, **Motofumi Suzuki**,* Kyoto University, Japan*; Khushi Aggarwal,* Indian Institute of Technology Delhi, India*; Ayako Miki, Taisei Morita, Kota Saeki, Taichi Banno, Kyoko Namura,* Kyoto University, Japan

It is known that high-temperature glancing angle deposition (HT-GLAD), where vapor is deposited at an angle greater than 80° from the substrate normal onto a substrate heated to a temperature exceeding one-third of the melting point of the evaporated material, can induce whisker growth in metals such as Al, Cu, Ag, Au, Mn, Fe, Co, Ni, Ti, and Zn. These whiskers can have diameters ranging from several tens to several hundreds of nanometers and lengths of several micrometers or more [1]. Among these metals, the morphologies of Al [2] and Fe [3] have been studied in detail concerning substrate temperature and deposition amount. However, the mechanisms of nucleation and the development of complex morphologies remain unclear.

In this presentation, we will report on the results of investigating the HT-GLAD of Ag at higher substrate temperatures than previously reported.

The Si substrate was introduced into the vacuum chamber, evacuated to the 10^{-5} Pa range, and then heated to a temperature between 500 °C and 625 °C. A tungsten (W) basket, serving as the evaporation source, was positioned at an angle of 83° from the substrate normal. Approximately 1 g of Ag grains were loaded into the W basket, and evaporation commenced after the substrate temperature had stabilized. The deposition amount was monitored using a quartz crystal thickness monitor, and was converted to a average thickness of 10-60 nm.

At a substrate temperature of 500 °C, no significant structures were observed at a deposition amount of 10 nm. However, when the deposition amount exceeded 20 nm, numerous particles and whiskers with diameters of less than 100 nm grew on the surface. Additionally, platelets, which had not been observed in conventional HT-GLAD, were found to grow with their wide surfaces facing the incident direction of the Ag vapor.

In the presentation, we will discuss the effects of substrate temperature and materials on the growth mechanism of Ag nanomorphology.

[1] M. Suzuki et al.: Jpn. J. Appl. Phys. 52 (2013) 110116.

[2] M. Suzuki et al.: J. Vac. Sci. Technol. A 25 (2007) 1098.

[3] M. Suzuki et al.: Proc. SPIE 7041 (2008) 70410H.

10:00am **TF-FrM-8 Controlled Growth of Tellurium Network Structures for Multi-Spectral Photodetector Applications***, **Ahmed Adel A. Abdelazeez**, Wanseok Oh, Yizhou Wang, Tom Schmedake, Yong Zhang, Haitao Zhang,* University of North Carolina at Charlotte

Recently, tellurium (Te) has gained significant interest for its unique helical atomic chain structure bonded by van der Waals (vdW) forces. It exhibits thickness-dependent electronic properties similarly to two-dimensional (2D) materials, along with strong spin–orbital coupling from its chiral structure and enhanced environmental stability. As a p-type semiconductor, Te has a narrow band gap (1.2 to 0.3 eV), large responsivity, high detectivity, high on/off ratios, and high carrier mobility, making it a promising material for short-wavelength infrared (SWIR) photodetection. Although a convenient physical vapor deposition (PVD) has been widely applied as a tailored growth technique for the Te growth, the critical parameters controlling the synthesis of 2D and 1D Te structures remain unclear. Herein, this research focuses on understanding the growth mechanism of Te nano- and microstructures. Key parameters, such as pressure, temperature, and growth time, have been systematically explored to study their effects on growth evolution. Various Te structures, including microspheres, microrods, microplates, nanowires, etc., have been synthesized at different growth zones. This study makes it possible to realize controlled growth of different Te structures and a research focus is centered on a unique Te network structure of microrods (Te-Net). This innovative structure is the first of its kind to be reported, as previous reports have mostly been focused on individual micro- or nanostructure. The network structure enables low-cost device fabrication without sophisticated lithography.

The Te-Net based photodetectors demonstrate excellent responsivity (R) and detectivity (D*) under different illumination conditions, with typical values as high as R = 0.43 A/W and D* =3.98 × 10^7 Jones at 405 nm. At 532 nm and 808 nm, the device exhibits responsivity of 8.6 × 10^{-3} A/W and 7.3 × 10^{-3} A/W, and detectivity of 9.6 × 10^5 Jones and 7.4 × 10^5 Jones, respectively. We are investigating the photoresponse mechanisms including direct carrier photogeneration and local heating for further performance improvement. One important phenomenon we discovered is that the devices are extremely sensitive to the dark environment with the room lights off. No significant visible/near-infrared light was detected from the dark environment using a commercial spectrometer and no existing theory explains this phenomenon. Therefore, future research will focus on investigating the source of the light signals and the mechanism of this extreme sensitivity. We are looking into the device performance under illumination of other light sources, especially those in the SWIR to mid-wavelength infrared ranges

10:30am **TF-FrM-10 A Comparative Study of Effects of Ultraviolet Irradiation and Laser Curing on Hydrogenated Amorphous Carbon Thin Films***, **Md. Mahfujur Rahman**, Rajib Chowdhury, Seonhee Jang,* University of Louisiana

Hydrogenated amorphous carbon (a-C:H) materials can be utilized in a variety of applications, mainly as protective, wear-resistant, or anti-reflective coatings for optical windows. The a-C:H materials show distinct material properties, such as high density, hardness, chemical inertness, and electrical resistivity. The fabricated a-C:H materials are often subjected to a post-processing to enhance optical and physical properties such as refractive index, extinction coefficient, optical bandgap, and surface roughness. For the post-processing of the a-C:H materials, ultraviolet (UV) irradiation and laser curing are considered. In this study, the a-C:H films deposited by plasma-enhanced chemical vapor deposition (PECVD) method underwent the UV irradiation or laser curing, and the effects of these post-processing treatments on the a-C:H thin films were investigated and compared. First, the a-C:H films were deposited on Si (100) substrates by PECVD using cyclohexane (C_6H_{12}) precursor at room temperature with a plasma power of 80 W. The pristine films exhibited characteristics of being optically transparent, hydrophobic, and topologically smooth.

For UV irradiation, the a-C:H thin films were exposed to a 255 nm light source in air. The UV irradiances were 2.2 and 16.5 mW/cm^2, respectively, and irradiation times were 1 and 4 hours. For laser curing, the a-C:H films were exposed to Nd:YAG laser source. The Nd:YAG laser had a wavelength of 1064 nm, a pulse duration of 4 ns, and a pulse rate of 3.75 Hz. The laser fluences were 100 and 400 mJ/cm^2, respectively. The a-C:H films were characterized using Fourier-transform infrared spectroscopy (FTIR), ellipsometry, contact angle geometry, and atomic force microscopy (AFM) to identify chemical bonding structure, optical properties, wettability, and surface morphology, respectively.

UV irradiation reduced the film thickness due to surface ablation. Despite the changes in thickness, the films were optically transparent with a smooth surface topology. Additionally, while the optical bandgap decreased, the wettability of the films increased substantially. Hydrogen depletion and oxygen incorporation were confirmed by characterizing the films with FTIR. On the contrary, the post-processing laser cured films did not show a significant change in thickness but exhibited an even smoother surface compared to pristine films. FTIR analysis showed an improved sp^3 bonding network and a reduced graphitic sp^2 content. In conclusion, this comparative study highlights the significance of selecting an appropriate curing method based on specific application requirements.

10:45am **TF-FrM-11 Synthesis, Characterization, and Classification of Polymer-Like Hydrogenated Amorphous Carbon***, **Seonhee Jang**, Rajib Chowdhury, Thomas Poché,* University of Louisiana at Lafayette

Hydrogenated amorphous carbon (a-C:H) films exhibit a wide range of properties that depend on the hydrogen (H) content and the hybridization of their carbon (C) atoms as sp^3, sp^2, or sp bonded. The a-C:H films with high sp^3 content offer high hardness, chemical inertness, and electrical resistivity. These properties enable the a-C:H films to apply for hardmask, diffusion barrier, sensors, protective coatings, and biocompatible films. Graphite-like a-C:H films with high sp^2 content show increased conductivity and a reduced optical bandgap. This study focuses on polymer-like a-C:H films with a varying H content of 40–50%, leading to a low-density, soft matrix with reduced cross-linking. Additionally, their friction coefficient is also influenced by H, promoting a lubricating transfer layer. This study explores their structural characteristics, emphasizing their potential applications and differences from other a-C:H subclasses.

The a-C:H thin films were deposited by plasma-enhanced chemical vapor deposition (PECVD) of a cyclohexane (C_6H_{12}) precursor. The effects of deposition parameters such as reactor pressure and plasma power on the characteristics of the polymer-like a-C:H films were investigated. For the first set of the a-C:H films, the deposition plasma power of 80W supplied from the RF power generator was fixed, and the deposition pressure varied from 19.73 to 38.00 Pa. For the second set of the a-C:H films, the pressure was maintained between 19.73 and 20.93 Pa, and the deposition plasma powers were 20, 40, 60, and 80 W. The optical, and chemical properties of the a-C:H materials were analyzed using various characterization tools such as spectroscopic ellipsometry, atomic force microscopy, Fourier transform infrared (FTIR) spectroscopy

Through these analyses, the a-C:H materials were determined to be optically transparent, topologically smooth, and hydrophobic in nature. The refractive index and FTIR spectra of the films were consistent with those of polymer-like a-C:H. The a-C:H films had optical bandgaps ranging from 3.09 to 3.69 eV, classifying them as wide-bandgap semiconductors. The materials deposited at higher plasma powers and lower pressures were found to have an increased refractive index, which is known to correlate with density. The relative H content of the a-C:H films displayed an inverse relationship with the refractive index, suggesting that H within the films inhibits cross-linking and reduces the density. These results indicate that the formation of more energetic plasma at higher plasma powers and lower pressures results in a-C:H films with a reduced H content and increased density.

11:00am **TF-FrM-12 Pulsed Laser Deposition of Bulk-Like NiO Thin Films***, **Simranjeet Kaur**,* Indian Institute of Technology Delhi, India

Nickel oxide (NiO) is a wide-bandgap transparent insulator with a band gap ranging from 3.6 eV to 4.0 eV. It is an antiferromagnetic material with the Néel temperature of 523 K, which is much larger than the room temperature. It exhibits NaCl-type face-centered cubic crystal structure with the lattice parameter of 0.417 nm. The antiferromagnetic order of NiO is associated with the antiferromagnetic alignment of the ferromagnetic (111) planes along the [111] direction. A rhombohedral distortion develops in the structure below Neel’s temperature. Here, we report the growth of (111)- and (001)-oriented NiO thin films on (0001)-Sapphire and (001)-MgO substrates using pulsed laser deposition (PLD), respectively. The DC magnetic susceptibility of the films (~120 nm) confirms that the films are antiferromagnetic at room temperature. We further proved this by showing two-magnon Raman scattering response from the films down to at least 30 nm in thickness at room temperature. We studied the optical properties of the samples using UV-vis, ellipsometry, and photoluminescence spectroscopy. In particular, we obtained the band gap of x eV, which is well within the range expected for bulk NiO. For photoluminescence measurements, we excited NiO(111)/Al_2O_3(0001) film at the wavelength of x nm, and obtained the two bands at 385nm and 405nm, respectively. The signature of exciton-magnon coupling is obtained, as the linewidth of the peak at 405nm increases with decreasing temperature, which indicates the presence of exciton-magnon coupling. Overall, our study demonstrated the pulsed laser deposition of (001)- and (111)-oriented NiO films that have bulk-like magnetic and optical properties.

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