Area Selective ALD
Room Grand Ballroom H-K - Session AS2-TuA2
Late Breaking Abstracts

Moderators: Silvia Armini, IMEC, Dennis Hausmann, Lam Research

4:45pm **AS2-TuA2-14 Real-time Grazing Incidence Small-angle X-ray Scattering Studies of Indium Aluminum Nitride Growth***, **Jeffrey M. Woodward**, S Rosenberg,* ASEE (residing at U.S. Naval Research Laboratory)*; S Johnson, N Nepal,* U.S. Naval Research Laboratory*; Z Robinson,* SUNY College at Brockport*; K Ludwig,* Boston University*; C Eddy,* U.S. Naval Research Laboratory

Indium aluminum nitride (InAlN) is an attractive material for power electronic applications. However, conventional methods of epitaxial growth of InAlN are challenged by a large miscibility gap and the significant differences in optimal growth conditions for the constituent aluminum nitride (AlN) and indium nitride (InN) binary compounds. Despite these challenges, the epitaxial growth of InAlN alloys throughout the entire compositional range has been demonstrated using plasma-assisted atomic layer epitaxy (ALEp)[1], a variant of atomic layer deposition in which relatively higher temperatures are utilized. In the ALEp growth of InAlN, the desired alloy compositions are achieved by forming ultra-short period superlattices of alternating InN and AlN layers, referred to as digital alloys (DA). In order to further advance these empirical efforts, significant research is needed to better understand the nucleation and growth kinetics of ALEp DA growth. To this end, we employ *in situ* grazing incidence small angle X-ray scattering (GISAXS) for the real-time study of the evolving ternary InAlN surfaces as has been done previously for binary InN[2] and AlN[3].

Here we present *in situ* GISAXS studies of ALEp growth of InN, AlN, and a range of InAlN DAs on GaN (0001) substrates, which were performed at Brookhaven National Laboratory's NSLS-II using a custom reactor. The InAlN DAs studied include $In_{0.19}Al_{0.81}N$ (3 AlN cycles and 2 InN cycles per supercycle), $In_{0.5}Al_{0.5}N$ (1 AlN cycle and 3 InN cycles per supercycle), $In_{0.64}Al_{0.36}N$ (1 AlN cycle and 5 InN cycles per supercycle) and $In_{0.83}Al_{0.17}N$ (1 AlN cycle and 14 InN cycles per supercycle). Preliminary analysis of the data suggests that while the pure InN and AlN grew in 3D and 2D modes, respectively, the InAlN growth mode did not follow a simple trend as the nominal composition was tuned from InN to AlN. Instead, select compositions (50% and 83% In) exhibited predominantly 3D growth, while others (19% and 64% In) exhibited 2D growth. *Ex situ* X-ray reflectivity data show evidence of phase separation in the 83% In DA.

[1] N. Nepal, V.R. Anderson, J.K. Hite, and C.R. Eddy, Thin Solid Films **589**, 47 (2015)

[2] J.M. Woodward, S.G. Rosenberg, A.C. Kozen, N. Nepal, S.D. Johnson, C. Wagenbach, A.H. Rowley, Z.R. Robinson, H. Joress, K.F. Ludwig Jr, C.R. Eddy Jr, J. Vac. Sci. Technol. A **37**, 030901 (2019)

[3] V.R. Anderson, N. Nepal, S.D. Johnson, Z.R. Robinson, A. Nath, A.C. Kozen, S.B. Qadri, A. DeMasi, J.K. Hite, K.F. Ludwig, and C.R. Eddy, J. Vac. Sci. Technol. A **35**, 031508 (2017)

5:00pm **AS2-TuA2-15 Expanding the Materials Library of Sequential Infiltration Synthesis: Conductive Indium and Gallium Oxides Grown in Polymers***, **Ruben Waldman**,* University of Chicago*; N Jeon, D Mandia, O Heinonen, S Darling, A Martinson,* Argonne National Laboratory

Over the past decade, researchers have developed a deeper understanding of how the chemistry of ALD can be applied to polymeric substrates. Polymers are fundamentally unlike traditional ALD substrates in that precursors diffuse through the polymer and associate with functional groups that are distributed throughout the volume of polymer, rather than on a two-dimensional surface.

In one implementation of ALD in polymers called sequential infiltration synthesis (SIS), very long static exposures of precursors are used to enable diffusion into the polymer bulk. The published SIS materials library is quite limited compared to the broad ALD materials library. Aluminum oxide (Al_2O_3), as synthesized via SIS with trimethylaluminum (TMAl) and water, is by far the most studied system and has been utilized in applications ranging from lithography to oil sorption. Prior attempts to expand this library build upon on a primary SIS cycle of Al_2O_3 to act as a scaffold for subsequent synthesis of other materials. However, the insulating Al_2O_3 is detrimental to the properties of optoelectronically interesting materials. A detailed understanding of the physical and chemical processes of solvation, diffusion, and complexation between ALD precursors and polymer functionalities is required to engineer hybrid polymer-metal oxide devices and to develop a broader library of SIS materials.

Through a combined experimental and first principles computational study we have developed primary SIS processes for two previously unreported materials – indium oxide (In_2O_3) and gallium oxide (Ga_2O_3) – using congeners to TMAl (TMIn, TMGa) and water. Through Fourier transform infrared spectroscopy and density functional theory, we elucidate the binding configuration and affinity of TMAl, TMIn, and TMGa for the carbonyl functional groups in polymethylmethacrylate (PMMA). We find that the three form isostructural adducts, though TMAl binds three times more strongly, and observe that the kinetics of adduct formation/dissociation for TMAl are more than ten times slower than for TMIn or TMGa.

With detailed knowledge of the TMIn reaction kinetics we designed an SIS recipe with exposure and purge durations tuned to the time-scales of vapor diffusion in and out of the polymer film. This led to the templated synthesis of In_2O_3/PMMA hybrid films which are readily converted upon annealing to crystalline, conductive In_2O_3 films. Notably, we observe substantial SIS growth rates of In_2O_3 at 80 °C, well below what is possible with these precursors in ALD. This suggests that complexation with polymers can catalyze reactions, opening routes for further exploration of low temperature deposition processes.

5:15pm **AS2-TuA2-16 Highly Efficient and Stable Organic – Inorganic Halide Perovskite Solar Cells with ALD-grown Charge Transport Layers***, **Hyunjung Shin**,* Sungkyunkwan University, Republic of Korea

$CH_3NH_3PbI_3$ with perovskite crystal structure has attracted considerable interest for high power conversion efficiency. Metal oxide grown *via* ALD provides pinhole-free uniform and dense films which are suited to function as passivation layer since ALD is deposited by self-limiting sequential chemical reaction. ALD chemistry for TiO_2, SnO_2, and ZnO are well known and the process requires relatively low deposition temperature as much as ~ 100 °C, which is applicable to deposit onto halide perovskite materials. In this presentation, we report highly efficient perovskite solar cells having a long-term stability that adapts uniform and dense inorganic charge transport layer (TiO_2, SnO_2, Al:ZnO, and NiO) grown by atomic layer deposition (ALD) at relatively low temperature. Ultra-thin un-doped NiO films were prepared by ALD with a highly precise control over the thickness. Thin enough (5 ~ 7.5 nm in thickness) NiO films with the thickness of few times of Debye length (1 ~ 2 nm for NiO) show enough conductivities achieved by overlapping space charge regions, which finally exhibited a highest PCE of 17.40 % with a negligible current-voltage hysteresis. Furthermore, highly dense inorganic electron transport layer (ETL) has been deposited onto perovskite using ALD process at relatively low temperature (100 ^{o}C). The devices shows excellent water-resistant properties and long-term stability at 85 °C under illumination compared to devices without ETL grown by ALD. **References** [1] H. Shin, et. al. "Perovskite Solar Cells with Inorganic Electron and Hole Transporting Layers Exhibiting Long – Term (≈ 500 h) Stability at 85 ° C under Continuous 1 Sun Illumination in Ambient Air", Adv. Mater., (2018) [2] H. Shin, et. al., "Atomic Layer Deposition of SnO Electron-Transporting Layer for Planar Perovskite Solar Cells with a Power Conversion Efficiency of 18.3 %" , Chem Comm (2019) [3] **Shin, H.** et. al. "Atomic Layer Deposition for Efficient and Stable Perovskite Solar Cells" *ChemComm* (2019)

Author Index

Bold page numbers indicate presenter