ALD Fundamentals
Room Grand Ballroom E-G - Session AF2-TuM

Precursors and Processes II

Moderators: Dr. Paul Poodt, Holst Centre / TNO, Dr. Paul J. Ragogna, University of Western Ontario, Canada

11:00am **AF2-TuM-13 Influence of Plasma Species on the Growth Kinetics, Morphology, and Crystalline Properties of Epitaxial InN Films Grown by Plasma-Enhanced Atomic Layer Deposition***, **Jeffrey Woodward**, D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Huntington Ingalls Industries*; S. Walton, J. Hite, M. Mastro,* U.S. Naval Research Laboratory

The controlled co-delivery of reactive and energetic plasma species during plasma-enhanced atomic layer deposition (PEALD) enables the growth of epitaxial layers at significantly reduced temperatures which are prohibitive to other methods. However, this capability is challenged by the complexity which arises from the reliance on plasma-surface interactions, and it is thus necessary to understand the influence of the plasma properties on the growth kinetics and resultant film properties. Among the III-nitride binary compounds, indium nitride (InN) is particularly well-suited for the investigation of the roles of reactive and energetic plasma species, as high-quality crystalline films can be achieved using trimethylindium (TMI) and a relatively simple N_2/Ar plasma rather than N_2/Ar/H_2 or NH_3/Ar plasmas which generate greater varieties of species. This was explored in recent studies of InN PEALD on gallium nitride (GaN) using *in situ* synchrotron x-ray scattering, which revealed that the growth mode is correlated with the relative density of atomic N, while coarsening behavior is influenced by ion flux.[1]

In this work, epitaxial InN films are grown by PEALD on GaN (0001) at approximately 320 °C using TMI and N_2/Ar plasma within various regimes of plasma species generation in order to investigate the influence on the resultant film structural properties. Optical emission spectroscopy and Langmuir probe measurements are used to correlate the production of atomic N and ions with the N_2 and Ar gas flows into the inductively coupled plasma source. The InN films are characterized by atomic force microscopy (AFM), x-ray reflectivity (XRR), high-resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), and synchrotron grazing incidence wide-angle x-ray scattering (GIWAXS). The films are found to exhibit wurtzite phase and sixfold rotational symmetry with a clear epitaxial relationship to the GaN. Low fluxes of atomic N are found to promote larger domains, increased crystalline order, and smoother morphology compared to films grown with high atomic N fluxes. For the high atomic N flux condition, increasing ion flux is found to promote a very rough morphology containing large cluster-like features and decreased in-plane crystalline order, but increased out-of-plane crystalline order and a reduction in mosaic twist.

[1] J. M. Woodward *et al.*, J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:15am **AF2-TuM-14 Towards Self-Limiting III-Nitride Epitaxy via Hollow-Cathode Nitrogen Plasmas***, N. Ibrahimli, S. Ilhom, A. Mohammad, J. Grasso, B. Willis,* University of Connecticut*; A. Okyay,* Stanford University*; **Necmi Biyikli**,* University of Connecticut

Research efforts on low-temperature synthesis of crystalline GaN thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, stainless-steel based hollow-cathode plasma (HCP) sources revealed highly (002) oriented polycrystalline GaN films on Si(100) substrates. Upon further modification of the hollow-cathode plasma source and reactor chamber design, in this study, monocrystalline GaN films on sapphire substrates was achieved at temperatures as low as 240 ℃. In this presentation we share our experimental findings on the epitaxial growth efforts of the entire wide bandgap III-nitride binary compounds including GaN, AlN, InN, and BN using self-limiting HCP-ALD.

The films were deposited using metal-alkyl precursors (triethylgallium, trimethylaluminum, trimethylindium, and triethylboron) and various nitrogen plasmas (N_2/H_2, N_2-only, N_2/Ar, and N_2/H_2/Ar) as metal precursor and nitrogen co-reactant, respectively. Growth experiments have been performed within 200 – 250 °C temperature and 100 – 200 W rf-power range. *In-situ* Ar-plasma annealing cycles were also employed to enhance the surface crystallization process. *In-situ* ellipsometry and optical emission spectroscopy (OES) were employed to monitor the surface ligand-exchange reactions, plasma surface interactions, and reaction byproducts in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness, growth-per-cycle (GPC), and optical properties of the films. When compared to reference films grown on Si(100) substrates, GPC values obtained for III-nitride films on sapphire substrates showed a notable increase.

For GaN samples, grazing-incidence XRD (GIXRD) measurements revealed single-phase hexagonal polycrystalline films on Si(100) substrates while GaN/sapphire samples exhibited no crystal peaks at all. Rocking curve XRD scans displayed a strong single (002) peak, confirming the monocrystalline character of the GaN films on sapphire substrates. We attribute this improvement in crystal quality to the synergistic impact of customized HCP-ALD reactor, large-diameter hollow-cathode plasma source, and optimized growth conditions (plasma gas mixture, rf-power, chamber pressure). Among the binary III-nitride compounds, InN and BN films showed highest and lowest GPC values, respectively. With further improvement in film properties, we aim to achieve device quality electrical properties that can be used for back-end-of-the-line (BEOL) transistor channel layers.

11:30am **AF2-TuM-15 Thermal Atomic Layer Deposition of Gallium Nitride at 150 - 300°C using Tris(dimethylamido)gallium Precursor and Hydrazine***, **Adam Bertuch**,* Veeco Instruments*; J. Casamento, J. Maria,* Pennsylvania State University

Gallium nitride (GaN) and its alloys with aluminum nitride (AlN) have established themselves as leaders in electronic and photonic devices for high frequency, high voltage, and harsh environment applications.[1] This is due to their ultra-wide bandgaps, heterojunction polarization induced free carriers with high mobility in the absence of chemical doping, large thermal conductivity, and high temperature stability.The promising physical properties of this material system are generally realized by plasma assisted techniques such as molecular beam epitaxy (MBE) or high temperature metal organic chemical vapor deposition (MOCVD) processes. Accordingly, there are significant opportunities for new device functionalities and heterogeneous integration in batch processing if crystalline GaN with low impurity (e.g., oxygen and carbon) concentrations can be realized in a low temperature, plasma free process.

In this work, GaN thin films were deposited using Tris(dimethylamido)gallium (CAS 57731-40-5) and hydrazine (N_2H_4) at temperatures from 150°C to 300°C using thermal Atomic Layer Deposition (ALD). At these temperatures the process is self-limiting, exhibiting ALD behavior and a uniform growth per cycle (GPC) throughout the process chamber. For compositional analysis, the GaN films were capped *in-situ* using ALD deposited AlN with Trimethylaluminum (TMA) and Hydrazine. The ALD deposition rate for the GaN film is large, ranging from 1.2 to 1.4 Å/cycle, while the AlN growth rate is determined to be 0.30 to 0.75 Å/cycle, as a function of increasing temperature.

Compositional analysis by Auger emission spectroscopy (AES) revealed oxygen and carbon concentrations less than 5 atomic % at 300°C deposition for both the GaN and AlN film stack; among the best reported values for deposition temperatures less than 400°C.[2] Initial findings with scanning electron microscopy (SEM) show smooth continuous surface morphologies for the deposition on silicon substrates. Composition, crystallinity via X-Ray Diffraction (XRD), and RMS roughness via X-Ray Reflectivity (XRR) will be analyzed as a function of growth temperature. These results present a promising step towards the development of low temperature, plasma-free GaN based thin films.

References

[1]*High-Frequency GaN Electronic Devices,* edited by P. Fay, D. Jena, and P. Maki (Springer, 2019).

[2] S. Banerjee et al. J. Phys. Chem. C **123**, 23214 (2019).

11:45am **AF2-TuM-16 Crystalline Gallium Nitride Deposition on SiO_2/Si by RF-Biased Atomic Layer Annealing***, **Ping-che Lee**, A. Mcleod,* Univ. of Cal., San Diego*; S. Ueda,* Materials Science and Engineering Program, Univ. of Cal., San Diego*; J. Spiegelman,* Rasirc*; R. Kanjolia, M. Moinpou,* EMD Electronics*; A. Kummel,* Department of Chemistry and Biochemistry, Univ. of Cal., San Diego

High-quality GaN deposition on Si substrates attracts attention due to its high heat capacity, and thermal conductivity [1]. However, a major problem of current GaN on Si techniques is that thermal shrinkage causing microcracks during >700 ℃ MOCVD process. Here, polycrystalline GaN with 40 nm thickness on Si substrates at 275 ℃ was deposited by using an atomic layer annealing (ALA) process. Inert gas plasma was directed by an RF substrate biasing to bombard the growth surface of the ALD-grown GaN. Surface defects were healed through either atom displacement or a collision cascade[2, 3]. This GaN film was transferred to a sputter chamber and employed as a template for AlN for heat spreaders. The record high thermal conductivity AlN sputtered film (1 um thick) obtained in this work benefited from this ALA GaN layer, which improved the crystallinity and decreased the phonon-defect scattering at the interface. Other film deposition techniques could also be integrated into this novel ALA GaN layer to design a promising heat spreader.

The GI-XRD measurements (Fig. 1(a)) were preformed to investigate the film crystallinity. In the non-substrate-biased ALA, a diffraction peak at 34.5 ˚ showed that even gentle ion bombardment at the end of each cycle mobilized the surface adatoms. All of the RF-biased conditions demonstrated narrower FWHM values (0.65 ˚, 0.58 ˚, and 0.51 ˚, respectively), meaning that ions with comparatively higher momentum more effectively crystallized the films; this was further confirmed by an increase in film density observed by XRR in Table. 1.

Sputtered AlN was deposited on ALA GaN film to increase the total film thickness for thermal conductivity measurements. Grain boundary analysis (Fig. 1(b)) indicated that both the template GaN layer and sputter AlN layer had an identical bamboo grain structure. Moreover, the nanobeam electron diffraction in (Fig. 1(c) and(d)) showed that the (0002) axis of bottom GaN coincided with the top sputter AlN, which further confirmed that polycrystalline GaN layer pinned the growth direction of sputtered AlN. The larger thermal conductivity measured by time-domain thermoreflectance (TDTR) confirmed the effectiveness of this low-temperature buffer layer to achieve a record high thermal conductivity AlN (120 W/m*K) with a thickness of 1 um (Fig. 2). This local domain epitaxy relationship at the interface played a crucial role in ensuring that phonon delivering heat along (0002) axis would be relative uninterrupted by phonon-defect scattering.

[1] J. Leitner et al., Thermo. Acta, 401, 2003, 169-173,

[2] W.H. Lee et al., Appl. Surf. Sci. 525, 2020, 146615

[3] S.T Ueda et al., J. Mater. Chem. C, 10, 2022, 5707

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