

A Comparative Study of Low-Temperature III-V Nitrides ALD in Thermal and Radical-Enhanced Modes

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In the field of III-V nitrides, nowadays research is strongly focused on electron devices employing epitaxially grown gallium nitride (GaN) and aluminum gallium nitride (AlGaN) layers, as certain properties of these materials are superior to silicon. Still, the production of GaN/AlGaN in monocrystalline form leads to a high cost. Developing the polycrystalline films with cheaper production techniques may pave the way to more widespread adoption of these nitrides in microelectronics and lighting. Atomic layer deposition (ALD) allows in this light for less stringent (compared to epitaxial techniques) growth requirements, enabling reduced process temperatures and direct growth on a large variety of substrates, e.g., on Si and SiO₂. ALD combines accurate thickness control with a high degree of uniformity and conformality. Despite of the growing number of publications w.r.t. various applications of the ALD poly-nitrides, the question if they exhibit competitive advantages for being implemented in electron devices remains open.

It is generally accepted that due to a sufficient chemical activity of ammonia (NH₃) with surface methyl groups (-CH₃) after a trimethylaluminum (TMA) pulse, ALD of AlN readily occurs in purely thermal mode at low temperatures (< 370 °C). This is opposite to thermal deposition of GaN films from trimethylgallium (TMG) and NH₃ precursors. It is reported that due to a low chemical activity of NH₃ with the film surface after a TMG pulse, low-temperature deposition hardly occurs in purely thermal regime. The majority of reports on low-temperature deposition of GaN have therefore used additional means of activation (e.g., plasma) to dissociate NH₃, thereby enhancing the reactivity with TMG-exposed surface by means of forming NH_x radicals.

This work reports on the deposition of GaN films at a temperature of 400 °C, in a purely thermal chemical mode using TMG and NH₃, and compares that with plasma-enhanced GaN ALD. The demonstrated plasma-free process can be beneficial for industrial-scale batch-type reactors where uniform radical delivery is hard to achieve.

The proposed approach utilizes the strong adduct-formation chemistry of the Lewis-acid TMG and the Lewis-base NH₃ [1, 2] on the growth surface. Beyond a specific temperature, the TMG:NH₃ surface adduct is expected to dissociate into Ga-NH₂-Ga linkage, forming the first monolayer of GaN in a self-limiting fashion. Alternating pulses of TMG and NH₃ with in-between purges therefore result in film growth from a sequence of such self-limiting surface reactions. The growth per cycle (GPC) has shown an increase with NH₃ partial pressure [3], in accordance with the adduct reaction kinetics. This pressure-dependence of the growth has been in-situ monitored by spectroscopic ellipsometry (SE), revealing a maximum GPC value of 0.045 nm/cycle. The grazing incidence X-ray diffraction (GIXRD) scans confirmed polycrystalline wurtzitic structure of the GaN. The compositional depth profile obtained by X-ray photoelectron spectroscopy (XPS) revealed the formation of a stoichiometric GaN. The efficient removal of methyl groups (i.e., carbon) from the films has been confirmed by the low carbon content (1 at. %). Increasing the temperature from 400 °C to 550 °C activated the thermal decomposition of TMG, suppressing the adduct formation kinetics, breaking the mechanism of carbon removal from the films and thereby increasing the carbon content up to 10 at. %.

The research efforts were further directed towards ALD of boron nitride (BN) films from BBr₃ and NH₃ precursors, exploring the role of adduct-formation chemistry in that process as well. The performed comparison between radical-enhanced and pure-thermal deposition of BN and GaN layers will be shown in the presentation, clarifying the film formation mechanisms. The purely thermal radical-free deposition of poly-GaN films will be highlighted, focussing on the growth mechanism, ALD window, and film properties.

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