

Crystalline Gallium Nitride Deposition by RF-Biased Atomic Layer Annealing

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A method has been developed for depositing polycrystalline gallium nitride (GaN) thin films at low temperature (400 °C) with potential applications in the RF and microLED industries.^[1] There is a need to deposit GaN directly on common substrates such as silicon, SiO₂, and SiN to reduce the cost associated with using SiC wafers, especially for chiplet stacking or 2.5D integration. While ALD of GaN has been reported in the literature, the most common deposition techniques are MOCVD and MBE at high temperatures >700 °C.^[1,2] The difference in high deposition temperature and low operating temperature often results in strained material with significant defect densities.^[1] Herein we demonstrate the deposition of polycrystalline gallium nitride at a reduced temperature, 400 °C, using tris(dimethylamido)gallium (TDMAGa) and anhydrous hydrazine in an atomic layer annealing (ALA) process. It is possible that by depositing a GaN templating layer by ALA at low temperature may reduce inherent strain in the material and buffer layer thickness required to form device-quality GaN using further deposition by other techniques.

In the ALA process, each precursor is pulsed in a cyclic fashion, as performed in traditional ALD, however a brief ion bombardment step follows each precursor dosing cycle. While previously reported ALA processes rely on DC bias to accelerate ions towards conductive substrates, RF bias is required for ALA on insulating substrates. Tuning the bias to modulate the ion kinetic energy allows for maximization of the crystallization effect of the ion bombardment, as depicted in **Figure 1a**.^[3] Initial depositions were performed on c-sapphire to show that RF-biased ALA produces high quality films on a bulk insulator.

Diced c-plane sapphire substrate coupons were degreased and stripped of their native oxide by immersion in a 3:1 sulfuric acid and phosphoric acid mixture heated to 90 °C for 10 minutes. Single coupons were loaded into a home built vacuum system composed of a load lock, the HV ALD/ALA chamber, and a UHV analytical chamber containing an x-ray photoelectron spectroscopy (XPS) system, shown in **Figure 1b**. Each ALA cycle consisted of a 350 ms pulse of TDMAGa, a 3 s purge, a 200 ms pulse of N₂H₄, a 5 s purge, and a 15 s ion bombardment treatment using Kr at 6 mTorr pressure. Thin film deposition of GaN by a pulsed CVD process, without the ion bombardment step, was performed to serve as a benchmark. The growth rate of the pulsed CVD process and the ALA process were approximately 1.4 Angstroms per cycle.

Chemical composition of the GaN surface deposited by the pulsed CVD and RF-biased ALA methods revealed 49-53% Ga, 43-48% N, and 3-4% O by XPS (**Figure 2**). Composition of the films deposited by ALA appeared slightly gallium rich, however were likely stoichiometric; this is a common artifact due to the large difference in binding energies of the Ga 3d and N 1s XPS peaks, at ~26 eV and ~400 eV, respectively. Carbon content was not quantified due to the presence of Ga artifacts in the C 1s XPS region.

Grazing incidence x-ray diffraction (GIXRD), x-ray reflectivity (XRR) measurements, and atomic force microscopy (AFM) were used to examine film crystallinity, density, thickness, and roughness (Fig 2). The reference film deposited using the pulsed CVD process (left) demonstrated weak crystallinity with poor diffraction signal and an average crystallite size of ~7.8 nm in a 26.9 nm thick film. This film had a density of 5.34 g/cm³ by XRR, which was ~19% less than bulk GaN at 6.15 g/cm³. The surface of the film displayed an RMS roughness of 5.8 nm.

Gallium nitride films were deposited using the RF-biased ALA process at four substrate self-bias potentials: -36 V, -50 V, -65 V, and -80V. The RF-biased ALA film at -36 V self-bias potential demonstrated a stronger AlN (002) diffraction peak compared to the reference film deposited by pulsed CVD. The film density was 5.50 g/cm³, which was ~16% less than bulk GaN. The small crystallite sizes and poor density indicate that larger ion kinetic energy was needed to effectively crystallize the film; this was achieved by increasing the

substrate self-bias potential. For -50 V and -65 V, self-bias conditions, the films displayed stronger crystallinity as indicated by the increased GaN (002) diffraction peak intensity. These films both displayed average crystallite sizes of ~8 nm. The largest average crystallite size of 11.4 nm was observed in the film deposited at -80 V self bias. An increase in film roughness was observed in the RF-biased ALA samples compared to the pulsed CVD sample. This is likely due to the increase in film crystallinity and was reflected by the 7.6 nm RMS roughness of the film deposited at a -50 V substrate self-bias. Unfortunately, this increased surface roughness resulted in insufficient signal in XRR experiments to accurately model the film thickness and density of the highly biased ALA films; however, in DC-biased ALA of aluminum nitride (AlN), near-bulk film densities have been obtained at substrate potentials similar to those used in this study. The strong crystallinity observed by the -80 V self-bias condition indicates that near-bulk density was likely achieved.^[3] Optimization of RF-biased GaN ALA on substrates of interest (Si, SiO₂, and SiN) is currently underway for investigation into the practical application of this technique.

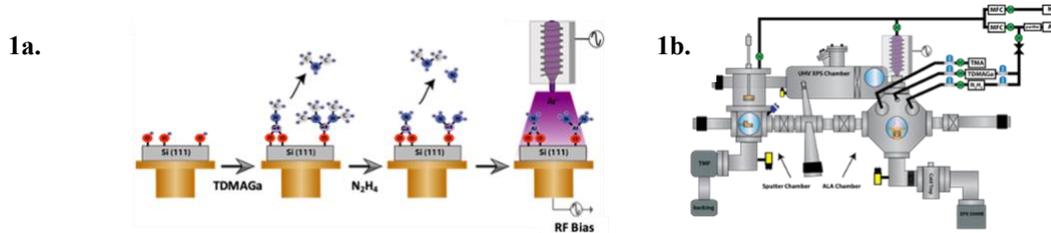


Figure 1. ALA process and equipment: **a)** ALA process combines a traditional ALD precursor dosing cycle with a low-energy ion bombardment step at the end of each cycle. This crystallizes the material. **b)** Combination HV deposition chamber, front right, and UHV analytical chamber, back center. Note the chamber allows for XPS analysis without vacuum break by transfer through the load lock chamber.

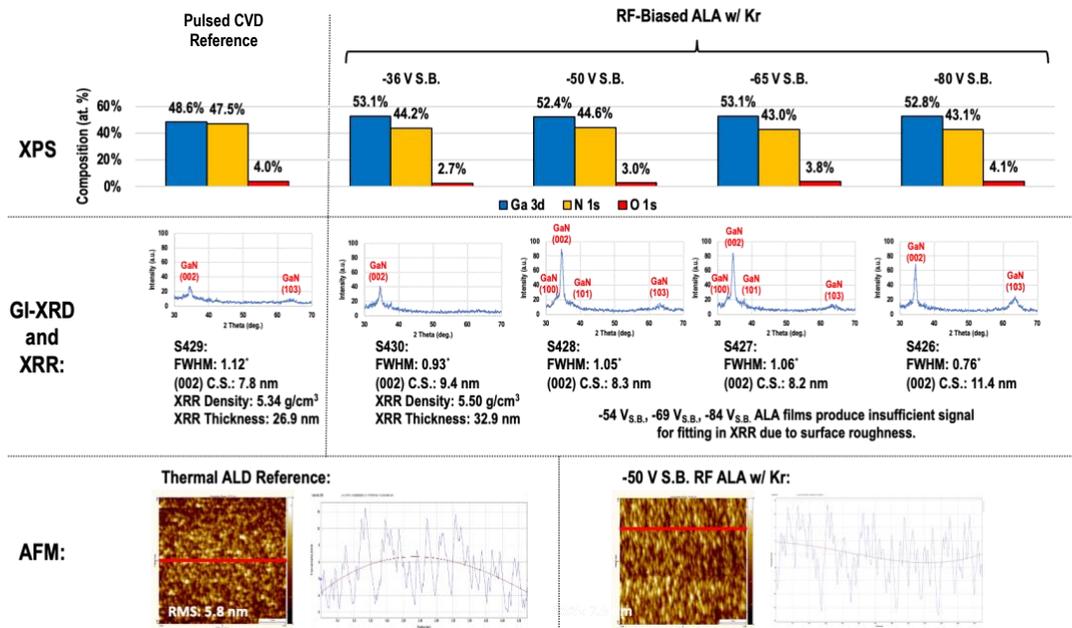


Figure 2. X-ray photoelectron spectroscopy composition, grazing incidence x-ray diffraction, x-ray reflectivity, and atomic force microscopy studies of the films deposited by the reference pulsed CVD process and by RF-biased ALA at four self-bias potentials. Note the increased crystallinity due to ALA and increasing magnitude of self-bias potential. Films are roughened by ALA process relative to the pulsed CVD process, likely due to increasing average crystallite size.

[1] Wang, W. *et al.* *Sci. Rep.* **6** (2016)
 [2] Fong, W.K *et al.* *J. Cryst. Growth* **223**, 3 (2001)
 [3] Ueda, S.T. *et al.* *Appl. Surf. Sci.* **554**, 15 (2021)