

# Progress on Gallium Nitride Semiconductor Growth by Plasma Sputtering

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## ABSTRACT

Plasma sputtering based growth of Gallium Nitride (GaN) is explored as a scalable and cost-effective method for obtaining thin crystalline III-V nitride films. Structural and optical characterization of the first series of growths on sapphire substrates indicates the growth of GaN, albeit with poor structural and optical properties.

## Introduction

The growth of III-V nitride semiconductors is traditionally achieved by epitaxial techniques such as Molecular Beam Epitaxy (MBE) or Metal-Organic Chemical Vapor Deposition (MOCVD) [1]. These growth techniques produce films and heterostructures of high crystalline quality, which is necessary for short-wavelength optoelectronic devices, and high-power high-frequency electronic devices. The device costs and cost-of-ownership from using these epitaxial growth techniques are typically high, owing to the slow growth rates and infrastructure investment, and alternate techniques to grow large area GaN layers on various substrates are being considered. One such technique is Hydride Vapor Phase Epitaxy (HVPE) [1], which has recently been used to grow GaN layers on sapphire, as well as InGaN/GaN heterostructures. In this work, preliminary results from an attempt to grow GaN using a novel technique – Biased Target Deposition (BTD) [2,3] are reported. This growth technique uses a remote plasma source and a widely variable bias on the sputter target to give unprecedented control of process particle energetics and allows the growth of crystalline films [4,5]. Sputtering has been applied to the growth of GaN [6 and citations therein], but none of these techniques proved suitable, scalable or cost effective enough for widespread deployment. BTD promises to meet these criteria with future development.

## EXPERIMENTAL

Gallium nitride (GaN) was grown on sapphire wafers and characterized by x-ray diffraction (XRD) and photoluminescence. The growth reactor consisted of a commercially-available 4Wave Laboratory Alloy Nanolayer Sputtering (LANS) biased target sputter deposition (BTD) vacuum chamber with a base pressure of  $2\text{E-}8$  Torr. A modified Kaufman & Robinson Inc. (KRI) EH-1000 end-Hall plasma source coupled with a KRI LHC thermionic hollow-cathode electron source were used to provide low energy plasma to fill the interior of the

chamber. The plasma forming gas was a mixture consisting of 30 sccm of argon (Ar) and 3 to 30 sccm of nitrogen ( $\text{N}_2$ ). The anode of the end-Hall source was biased at  $\sim 65$  volts positive with respect to ground (the walls of the vacuum chamber were grounded) and the cathode of the hollow cathode was biased 13 volts negative with respect to ground to sustain a discharge in the anode region of 8 amperes. The emission current of the cathode was set to 8.5 amperes. Under these conditions, the plasma consisted of mainly  $\text{Ar}^+$  and  $\text{N}_2^+$  ions totaling  $\sim 2$  amperes of continuous ion current flow with a kinetic energy distribution ranging from 65 electron volts (eV) to 0 eV (median energy 35-40 eV) and a slight over supply of electron flux. Pumping via a Helix Technology CT-10 cryo-pump resulted in an ambient pressure of  $5 - 7 \times 10^{-4}$  Torr, depending upon  $\text{N}_2$  flow.

The sputtering geometry was a right-angled geometry. The plasma source directly faced the growth substrate at a distance of 240 mm, with the axis between them horizontal. A gallium metal sputter target was located 114 mm gravitationally below this axis, centered between the plasma source and the substrate. The gallium target was 105 mm diameter and faced gravitationally upward to contain the gallium metal as a liquid. In this geometry, it is essential to spin the growth substrate on the source-substrate axis to obtain lateral thickness uniformity of the growth across the substrate. The spin rate was 10 rpm.

The gallium sputter target was contained in a water-cooled, copper-topped heat exchanger 112 mm diameter with an 8 mm tall ring of boron nitride ceramic glued to it. The container thus formed was filled with 99.999% pure gallium pellets. The pellets were then melted with a hot air gun and allowed to cool to form a solid mass. The sputtering process itself remelts the gallium (m.p. =  $30^\circ\text{C}$ ) even at low sputtering power of  $\sim 100$  watts and with  $15^\circ\text{C}$  cooling water flowing through the heat exchanger. The melted gallium initially had dross on the surface, probably due to native oxide on the pellets. Three cycles of sputtering the target for about  $\frac{1}{2}$  hour after it melted, then cooling, venting the vacuum chamber and lightly sanding the target with 400 grit carbide sandpaper eliminated the dross and gave a mirror-like surface.

Sputtering of the gallium metal was accomplished by bi-polar pulsed DC bias of the target heat exchanger. The negative

pulses were 11 microseconds ( $\mu\text{s}$ ) long and -850 volts with respect to ground while the positive pulses were 3  $\mu\text{s}$  long and +10 volts. Average currents drawn by the two pulse trains were 165 mA for the negative, of which 33 mA was capacitive, and 100 mA for the positive.

The substrate holder had a removable titanium carrier plate, 140 mm diameter, to hold and center the 2-inch (50.8 mm) sapphire wafer. The wafers were 0.432 mm thick, epi polished on one side and C-plane oriented. Various methods were used to clamp the wafer to the Ti plate, since it was gravitationally vertical during growth. As mentioned, the Ti plate was spun at 10 rpm on the plasma source-substrate axis. Behind the Ti plate was a 1500 watt infrared emissive heater from Heraeus Noblelight which was not spun. A bare-junction thermocouple of 0.010" (0.25 mm) dia. wire was attached to the heater.

The usual growth process consisted of mounting a sapphire wafer on the Ti carrier plate and masking a small portion (1 mm dia. spot) with graphite colloid in isopropyl alcohol, so that it later be dissolved away and growth thickness measured with a Tencor P12 profilometer, load-locking the sapphire wafer into place, starting wafer spin and heating the substrate holder to the desired temperature behind a closed shutter. The plasma source was started and allowed to stabilize for 10 min. The shutter was opened for two minutes to pre-clean the sapphire surface with gentle ion bombardment, as specified above. After that, the shutter was closed and the gallium target was sputtered, to melt it and condition it. When ready to do growth, the shutter was opened. Growth was stopped by closing the shutter. In some cases, a bare-junction thermocouple of 0.005" (0.12 mm) dia. wire was fastened to the edge of the wafer using a screw and washer, so substrate spin could not be used for those runs. An attempt was made to correlate the wafer temperature so measured with the temperature of the heater.

High resolution x-ray diffraction (HRXRD) was used to characterize the epitaxial film quality/crystallinity. The HRXRD measurements were taken with a Panalytical X'pert Pro MRD system. The characterization was done with X-rays of 30 keV. Photoluminescence (PL) spectra emitted by the GaN sample were measured when the sample was pumped by a 3 ps pulsed coherent radiation at the wavelength of 208 nm. The pump beam was the output of quadrupling the frequency of the laser pulses at a central wavelength of 832 nm using two  $\text{BaB}_2\text{O}_4$  crystals[7]. The average power of the pump beam focused on the samples surface was set to 1.0 mW. The collected PL signal was sent through a double monochromator and then detected by a photomultiplier tube. A lock-in amplifier was used to reduce the measurement noise.

## RESULTS

A first growth of GaN was done with the sapphire substrate at room temperature and using 30 sccm  $\text{N}_2$  flow through the plasma source. The resultant 260 nm thick film was transparent with a slightly grey color. The XRD confirmed that the film showed no long-range order.

The attempt to correlate a direct wafer temperature measurement with the temperature of the heater failed, within the time allotted, for two reasons. The direct measurement gave temperature readings that drifted during a run and varied from run to run for the same heater power. Also, the Ti wafer carrier plate warped, after heating, in a cylindrical fashion by about 2-3 mm total bending over its 140 mm diameter.

Crystalline GaN growth was attempted at nitrogen flow rates of 3, 7, 10, 12, 15 and 30 sccm with two different heater power settings. The resultant growths for 3 sccm were black and powdery, for 7 sccm were transparent brown and dense, for 10 sccm were transparent grey and dense and for 12, 15 and 30 sccm were transparent light grey and dense. For the grey, dense films, the growth rate was  $\sim 600$  nm/hour. Figure 1 shows the X-ray diffraction scan of the GaN sample grown with 15 sccm of  $\text{N}_2$  and at 896 watts of heater power. The large peak at  $20.709^\circ$  confirms the crystallinity of the sapphire substrate, and a small GaN (002) peak is observed. Figure 2 shows the photoluminescence response of the GaN sample grown with 7 sccm of  $\text{N}_2$  and at 896 watts of heater power. A small emission at 365 nm is consistent with the GaN bandgap.

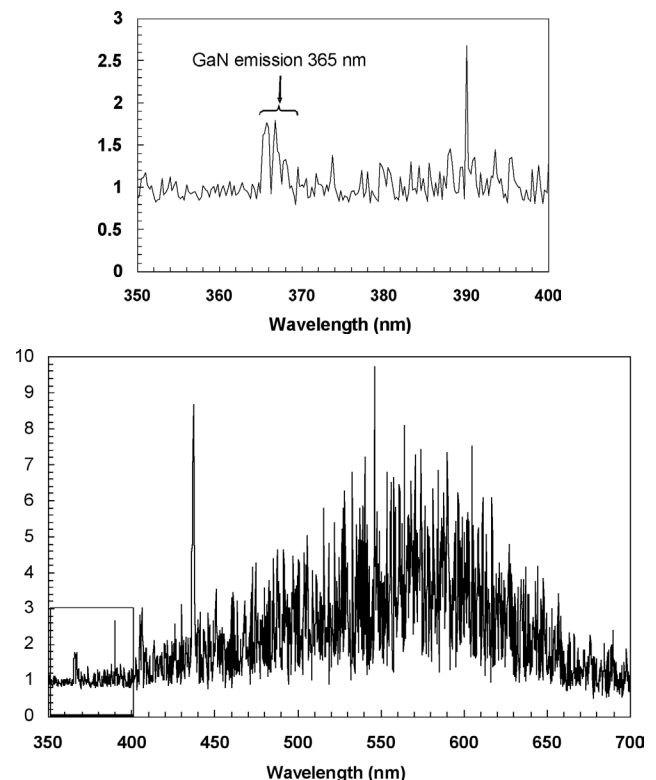


Figure 1: X-ray diffraction scan for GaN sample grown with 15 sccm  $\text{N}_2$ .

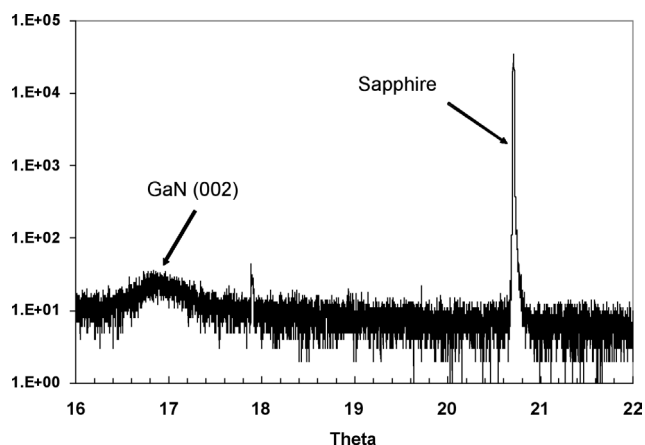


Figure 2: Photoluminescence response to 208 nm pump radiation of the GaN sample grown with 7 sccm of  $N_2$ .

## DISCUSSION

The first growth of GaN at room temperature having no long range order in the XRD is entirely expected, and is consistent with much experience that sputtering normally produces “amorphous” dielectric films at low substrate temperature.

The failed attempt to correlate a direct wafer temperature measurement with the temperature of the heater probably has several combined causes. The washer used to clamp the thermocouple junction to the wafer may have partially electrically short-circuited the junction. Thermal shifting of the washer probably exacerbated the situation. The warped substrate holder meant that the wafer could not lay flat on the holder, and there probably were temperature variations across the wafer.

GaN growth with  $N_2$  flows  $> 10$  sccm are probably providing fully nitrided GaN, as evidenced by the color changes up to that flow and the lack of color changes above it. The process, at the settings used, is energetic enough (in the sense of ion assist by  $N_2^+$  and bombardment by fast N atoms) that the degree of nitridation will be largely independent of substrate temperature, though some small effect would be expected.

Both the XRD and PL results are consistent with poor crystalline quality of the GaN. The many emitting states observed in the bandgap (wavelengths longer than 365 nm) by PL are tentatively attributed to defects. Attributing them to metallic or high-Z impurities is extremely unlikely given past studies on other materials systems and the inherent cleanliness of the BTD technique itself. It is possible that oxygen and hydrogen from residual gases in the LANS could get incorporated in the growing GaN, thus explaining some of the crystalline disorder and emitting states. But it is considered much more likely that the lack of control of wafer temperature, probably giving too low a temperature, combined with the energetic sputtering wafer environment explains the results.

Future work will focus on getting the wafer temperature under control first, then starting to vary the energetics of the process to achieve acceptable GaN crystallinity. A reflection high-energy electron diffraction (RHEED) instrument will be added to the LANS to assist in this work. Lastly, if contaminants from residual gases turn out to be a problem, growth rates and vacuum pumping can be increased dramatically, thereby increasing the ratio of Ga and N arrival relative to the impurity arrival at the growing GaN. The LANS is a small, economical research system, not optimized for semiconductor growth, but newer systems could be so optimized.

## CONCLUSIONS

GaN has been grown by sputtering from a liquid gallium sputter target in an  $Ar^+/N_2^+$  plasma environment. In these preliminary results, crystalline quality was poor. Future work to improve this will proceed along the lines discussed.

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