

GROWTH OF ORIENTED THICK FILMS OF GALLIUM NITRIDE FROM THE MELT

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ABSTRACT

While significant strides have been made in the optimization of GaN-based devices on foreign substrates, a more attractive alternative would be homoepitaxy on GaN substrates. The primary motivation of this work is to explore the growth of thick films of GaN from the melt for the ultimate use as substrate material. We have previously demonstrated the synthesis of polycrystalline, wurtzitic gallium nitride and indium nitride by saturating gallium metal and indium metal with atomic nitrogen from a microwave plasma source. Plasma synthesis avoids the high equilibrium pressures required when molecular nitrogen is used as the nitrogen source. Here we report the growth of thick oriented GaN layers using the same technique by the introduction of (0001) sapphire into the melt to serve as a substrate. The mechanism of this growth is not established, but may involve transport of the metal as a liquid film onto the sapphire and subsequent reaction with atomic nitrogen. The films were characterized by x-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy. X-ray diffraction showed that the GaN films were oriented with their c-axes parallel to the sapphire c-axis. The TEM analysis confirmed the orientation and revealed a dislocation density of approximately 10^{10} cm^{-2} . The E_2 Raman active phonon modes were observed in the GaN films.

INTRODUCTION

In spite of remarkable achievement in the growth and processing of gallium nitride and related III-nitride semiconductor devices, improvement of the crystalline quality of heteroepitaxially grown GaN films is still an important issue. Extended structural defects, such as dislocations, are a problem in films grown on sapphire and SiC substrates, even with the aid of buffer layers. Vertical conduction through the substrate and buffer layers is also an issue for devices. Significant reduction in the concentration of threading dislocations has recently been achieved through the use of epitaxial lateral overgrowth (ELOG) on (0001) sapphire and SiC substrates [1,2]. However, the ideal solution to these problems would be homoepitaxy on high quality, bulk GaN substrates.

The search for a viable method for production of GaN substrates remains open. Bulk growth techniques have succeeded in growing low-dislocation ($<10^6 \text{ cm}^{-2}$) material at very high pressure ($> 15 \text{ kbar}$), but the area of the crystallites remains about 1 cm^2 [3,4]. This size

limitation has inspired several groups [5,6] to pursue hydride vapor phase epitaxy (HVPE) as a quasi-bulk approach to GaN growth yielding growth rates as high as 100 $\mu\text{m/hr}$. However, cracking is a common problem for HVPE growth of thick GaN overlayers over large areas, e.g., 2 inch (0001) sapphire wafers.

In our initial experiments, we showed that GaN and InN can be grown at sub-atmospheric pressures without the aid of a substrate from the reaction of liquid metal and activated nitrogen derived from a microwave plasma source [7-10]. While the optical quality of these crystals is quite good as determined by photoluminescence and Raman spectroscopy, the crystallite size is typically on the order of 100 μm , with some crystals as large as 1 mm.

The nitrogen saturated melts exhibit a strong tendency to wet the crucible. In some cases, the wetting was so extreme that the entire melt left the well of the crucible and formed solid nitride on the upper surfaces of the crucible [11]. This “spreading-wetting” phenomenon is a striking feature of group III metal/nitrogen melts and has been observed in Ga/N and Al/N systems by several prior investigators [12-15]. In order to promote controlled, oriented nucleation of the solid nitride from the melt, we introduce a substrate. The substrate provides a template for controlled nucleation provided the crystallization takes place at the interface between the substrate and the metal-nitrogen melt. Oriented growth will depend critically on the details of the temperature and concentration gradients as well.

In this paper, we present preliminary results on the growth of thick films of oriented GaN from the melt through the introduction of a substrate into the melt. The primary motivation of this work is to explore low pressure growth from the melt as a means to obtain thick single crystal films for use as substrates.

GROWTH METHOD

Previously, polycrystalline, wurtzitic gallium nitride and indium nitride were synthesized *without a substrate* by saturating gallium or indium metal with atomic nitrogen from a microwave plasma source. Details of this growth method have been published elsewhere [7], but we provide a brief overview here for completeness. In the case of GaN growth, high purity Ga metal was heated in vacuum to a temperature 900°C and exposed to a nitrogen plasma operating at 5 torr and 400W of microwave power at 2.45 GHz. The metal source was pre-treated with a hydrogen plasma immediately prior to the nitridation to remove contaminants from the surface. A polycrystalline crust of GaN formed on the surface of the Ga during cooling of the melt.

In the present work, the growth technique is a variation on this basic nitridation procedure, with the differences primarily being the geometry and inclusion of a substrate. A c-plane sapphire substrate was situated to provide the metal-nitrogen melt a template against which

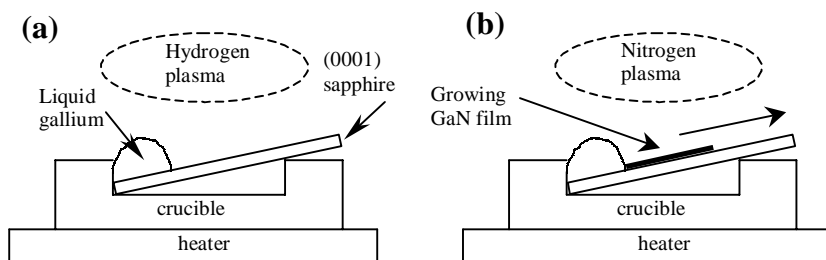


Figure 1. Schematic drawings of growth configuration. (a) The metal and substrate are first exposed to a hydrogen plasma to clean the surfaces. (b) After exposure to nitrogen plasma, a thin liquid metal film moves across the substrate and is converted to GaN.

to wet. For this paper, we present the growth of two different samples, A and B. The heater for these experiments was a RF inductively coupled graphite susceptor held at 900°C. The crucible for sample A was situated on top of a protective molybdenum plate on the susceptor and the crucible temperature was 700-

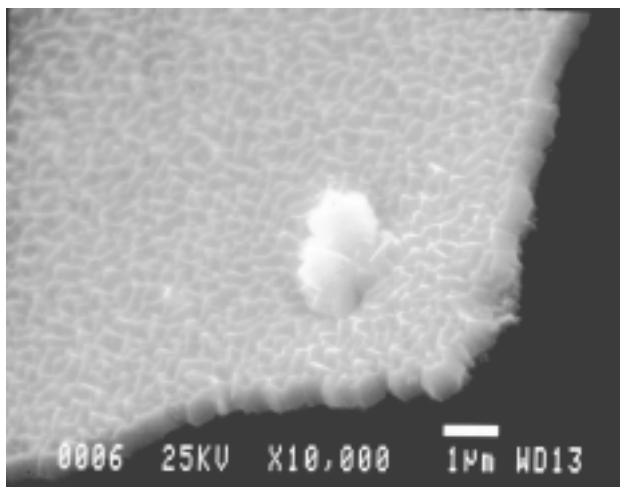


Figure 2. SEM image of a portion of a GaN layer that has peeled away from the (0001) sapphire substrate.

800°C. For sample B, the crucible was embedded in the heater so its temperature was 900°C. Prior to deposition, the sapphire was degreased in boiling organic solvents, rinsed in deionized water, and blown dry with nitrogen. The substrate and 99.99999% pure Ga source metal were heated under vacuum to a temperature of 700-900°C and exposed to the hydrogen plasma pre-treatment before replacing the hydrogen flow with nitrogen (see Figure 1). For sample A, after several minutes of plasma nitridation at the growth temperature, a dull film was visually observed to move up the substrate. Total nitridation time for sample A was 2 hours. For sample B, after several minutes of plasma nitridation at the growth

temperature, a thin, reflective metal film was visually observed to move up the substrate and to subsequently darken and form a solid. Total nitridation time for sample B was 45 minutes.

RESULTS AND DISCUSSION

Sample A was smooth, mirror-like, and transparent. X-ray Diffraction (XRD) showed that the primary reflections were from the (0002) and (0004) planes of wurtzitic GaN, indicating a preferred orientation with the c-axis perpendicular to the surface. A Scanning Electron Microscope (SEM) image of a portion of the film that peeled away from the substrate is shown in Figure 2. In order to characterize the structural quality of the film, Transmission Electron Microscope (TEM) analysis was performed. The TEM image of sample A in Figure 3 shows that the film has a columnar structure with a high density of stacking faults and a 0.5 – 0.7 deg. texturing. The overall film thickness is about 1 µm. The selected area diffraction pattern (SADP) taken along the $[11\bar{2}0]_{\text{GaN}}$ zone axis shown in Figure 4 indicates that the basic

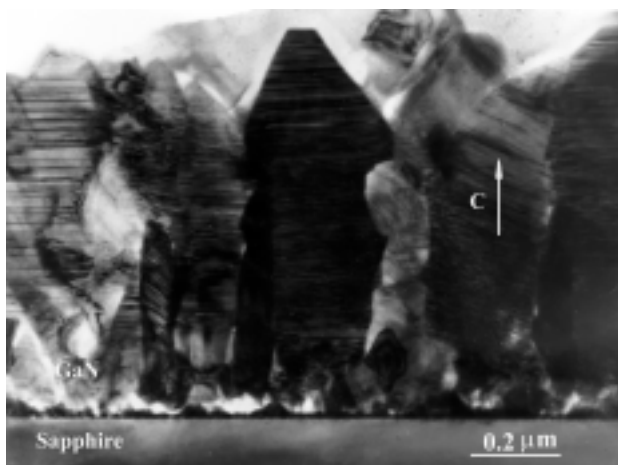


Figure 3. TEM image of GaN film sample A. The arrow marks the direction of the c-axis of the sapphire substrate.

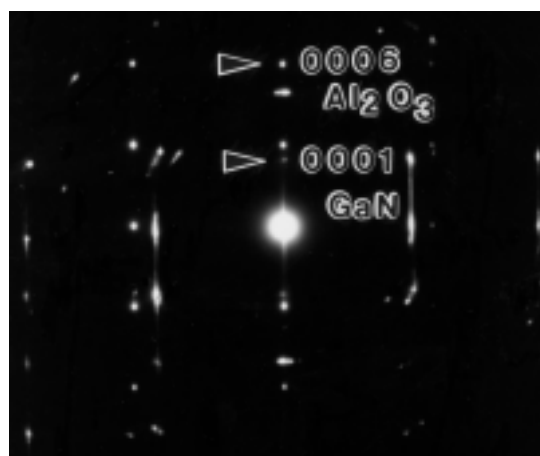


Figure 4. Selected area diffraction pattern of GaN film sample A taken along the $[11\bar{2}0]$ zone axis.

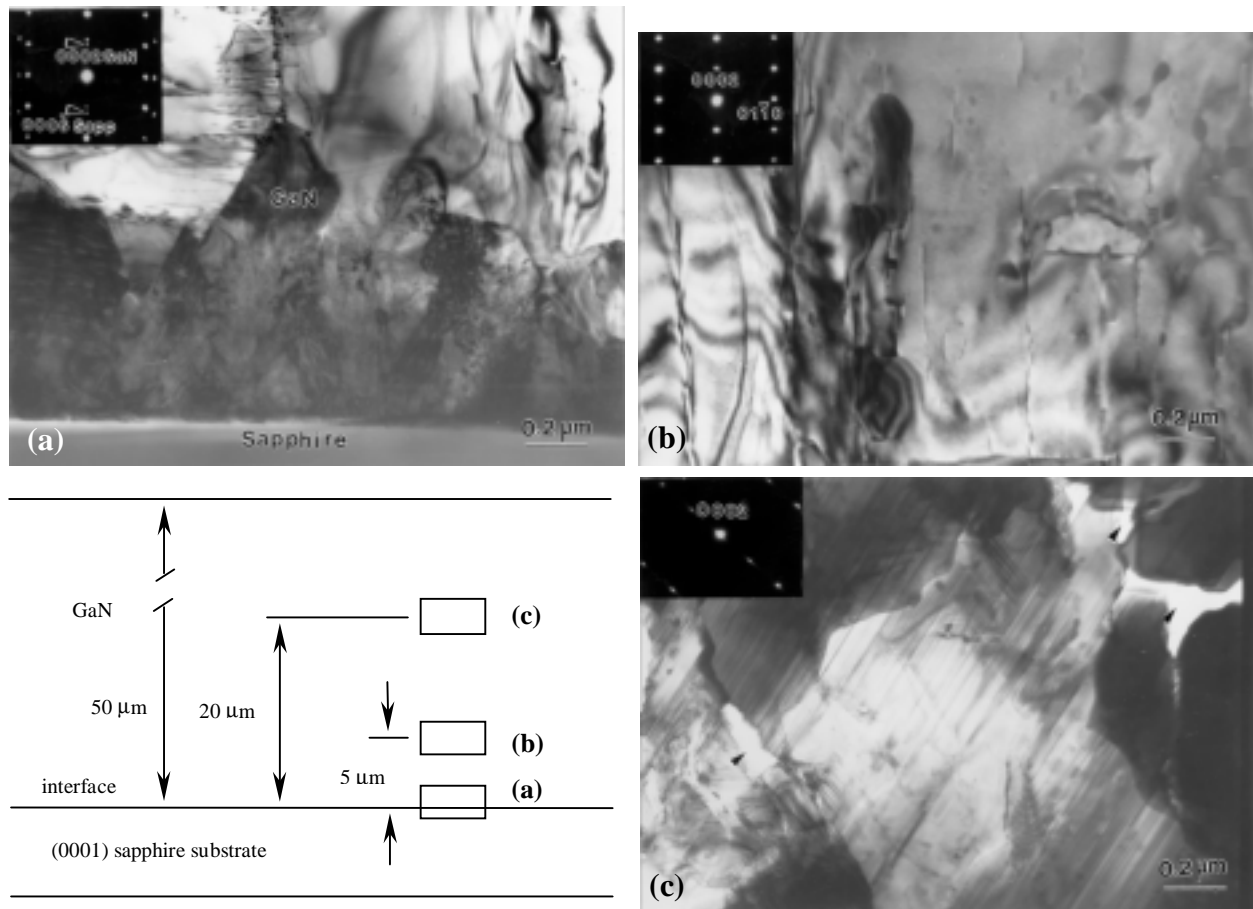


Figure 5. Cross-sectional TEM images of a 50 μm thick area of GaN film on (0001) sapphire substrate sample B near the (a) interface, (b) about 5 μm from the interface, and (c) about 20 μm from the interface. The inserts are selective area diffraction patterns taken along the $[11\bar{2}0]$ zone axis.

orientational relationship is $(0001)_{\text{GaN}}// (0001)_{\text{Sapp}}$ and $[11\bar{2}0]_{\text{GaN}}// [1\bar{1}00]_{\text{Sapp}}$. No Raman spectra could be obtained from this film.

Parts of sample B had a rough, gray surface and some areas were shiny, yellow, and transparent. Figure 5(a) shows a TEM image of the region near the substrate. The region extending from the interface to about 0.6 μm from the interface shows a typical tooth-like grain structure with a mean width of 0.2 μm . The c -axes of all grains are within 10° of the normal to the interface indicating a textured structure. Above this region, the quality of the GaN grains suddenly improved. The orientational relationship indicated in the inserted SADP is $(0001)_{\text{GaN}}// (0001)_{\text{Sapp}}$ and $[11\bar{2}0]_{\text{GaN}}// [1\bar{1}00]_{\text{Sapp}}$. A TEM image of a region about 5 μm away from the sapphire interface is shown in fig. 5(b). This area is composed of single crystal GaN with the c -axis perpendicular to the interface (see below). A contrast micrograph (not shown here) shows that most of the defects are threading edge-dislocations and basal screw-dislocations with the Burgers vector $\mathbf{b} = 1/3[11\bar{2}0]_{\text{GaN}}$. Dislocation densities are of the order of $10^{10}/\text{cm}^2$. The inset is a SADP taken along the $[11\bar{2}0]$ zone axis. This image is typical of the film up to about 15-20 μm from the interface. Figure 5(c) shows a micrograph 20 μm away from the interface between the GaN film and the sapphire substrate. Here, the material is polycrystalline and the orientational relationship with the sapphire is lost. In addition, there is a high density of stacking faults and several holes are observed. Due to the high density of stacking faults, the SADP

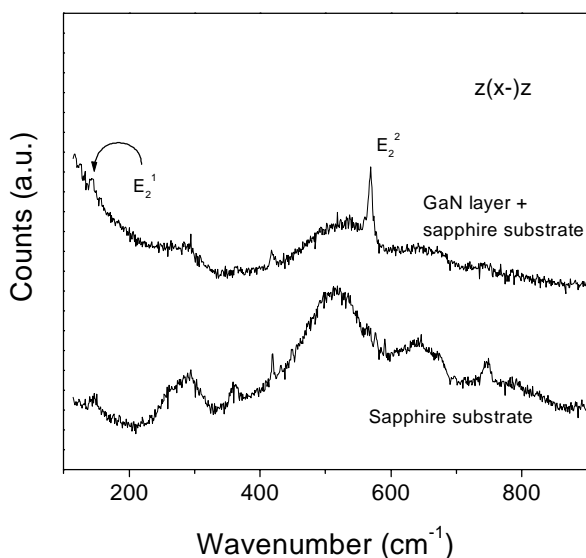


Figure 6. Raman spectrum of GaN film on c-plane sapphire substrate sample B and the spectrum from the substrate before deposition.

clearly shows streaks along the c-axis direction. The average thickness of the film is approximately 100 μm .

Raman spectra were taken in the $z(x-)z$ configuration from a shiny yellow area of the film. From this scattering geometry, the allowable symmetry modes are E_2 and $A_1(\text{LO})$. The E_2 high and low modes are easily observable in Figure 6.

For sample A, grown at the lower temperature, the growth rate was 0.5 $\mu\text{m/hr}$. Sample B, grown at 900 $^\circ\text{C}$, had a growth rate of over 100 $\mu\text{m/hr}$, which is similar to that achievable by HVPE. While the defect density of these films is high, these preliminary results are promising considering the growth was carried out on sapphire without an intentional buffer layer.

While the growth mechanism is still unclear, several points can be made. The GaN can be formed either from the vapor or by crystallization from the melt, and, likely, both mechanisms play a role. The vapor pressure of the liquid Ga and the nitrogen activity are high enough to support the growth rates observed. We propose that the initial textured growth at the interface may be vapor growth of GaN, and the rapid change to single crystal material marks the point at which wetting and growth from the melt begins. The upper portion of the film is polycrystalline. This loss of single crystallinity can occur for a number of reasons; for example, onset of interface instability.

CONCLUSIONS

Thick films of GaN are grown on (0001) sapphire by conversion of a layer of gallium metal by a nitrogen plasma. The films are highly oriented with $(0001)_{\text{GaN}}// (0001)_{\text{Sapp}}$ and $[11\bar{2}0]_{\text{GaN}}// [1\bar{1}00]_{\text{Sapp}}$. For a sample grown at an overall rate of 100 $\mu\text{m/hr}$, dislocation densities are 10^{10} cm^{-2} for the single crystal region of the film and strong Raman active optical phonon modes are observed. These preliminary results indicate that direct conversion of nitrogen saturated gallium melts to the solid nitride may be an alternative for growth of thick GaN films for use as substrates.

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