Deposition of Cubic GaN Films by Reactive Laser Ablation of Liquid Ga Target in Ammonia

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GaN is a promising semiconducting material with extensive applications in both electronic devices operating under high temperature and optoelectronic devices.[1] In particular, GaN has generated considerable interest due to the development of GaN-based blue light-emitting diodes and lasers[2] and much work has been performed to improve the quality of epitaxially grown thin films.

As well known, GaN exists in equilibrium hexagonal wurtzite structure or metastable cubic zinc blende structure.[3] For the last 10 years, most of the work has been concentrated on hexagonal GaN since it is much easier to grow high quality films. However, cubic GaN has some advantages over wurtzite GaN such as lower band gap (about 3.3 eV),[4] higher carrier mobility, and easier doping.[5] Accordingly, much interest has been shown on the growth of cubic GaN, recently.[5-9] Although many researchers have attempted to grow high-quality GaN films on Si, GaN films grown directly on Si by conventional techniques were found to be phase-mixtured, containing both cubic and hexagonal phases.[10,11] which is considered to originate from the large lattice mismatch between GaN and Si.

In this communication, we report a synthesis of cubic GaN film on Si(100) by reactive laser ablation of liquid Ga metal in NH_3. As demonstrated by the pioneering work of Xiao *et al.*,[12] ejection of droplets from the metallic target, a common problem in pulsed laser deposition, is avoided by using a liquid target. Such droplets are mostly produced by successive laser irradiation of a solid target surface, which causes melt/freeze cycles and subsequent surface roughening, and finally ejection of thermally decoupled material.[13]

The experimental setup is shown in Figure 1. Deposition of GaN was performed in an ammonia atmosphere on a 10×10 mm^2 Si(100) substrate at room temperature. The deposition chamber was flushed 3 times by flowing ultra-high purity (99.9999%) ammonia before laser irradiation.

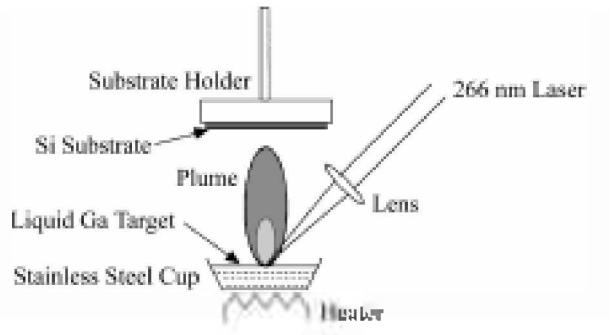

Figure 1. The experimental setup.

The 266 nm radiation from a Nd : YAG laser (Spectra-Physics GCR150-10, 10 Hz, 7 ns pulse duration) was focused onto the liquid Ga target by using a 300 mm lens at an incident angle of 45°. The Ga metal was heated in a stainless steel cup to 38 °C. The distance between the Ga target and the substrate was 5 cm.

A typical SEM image of GaN film grown by reactive laser ablation is depicted in Figure 2. The GaN film was nanocrystalline with an approximate mean diameter of 90 nm. Nanocrystalline GaN is a topic of utmost interest due to its novel properties and possible applications to new devices and technologies.[14] However, study of nanocrystalline GaN has been hampered by a lack of developed synthesis methods. Figure 3 shows an XRD spectrum of the GaN film, where the two peaks at 39.7° and 57.6° correspond to (200) and (220) Bragg peaks due to the cubic GaN nanocrystals, respectively. Considering that GaN films were either phase-mixed[10,11] or hexagonal[13] according to the previous works on GaN deposition on Si without buffer layer, it is quite striking that we have observed only cubic GaN in the film. As of now, we do not have a clear explanation about our results but we suspect that the growth of cubic GaN film is triggered by a nitrogen-deficient condition since the free energy difference between metastable cubic and stable hexagonal phases decreases with the increase of the vacancy concentration, making cubic phase more stable.[6]

Laser ablation of Ga in NH_3 was previously found to yield $Ga(NH_3)_n$ clusters in the gas phase. $Ga(NH_3)_n$ clusters are

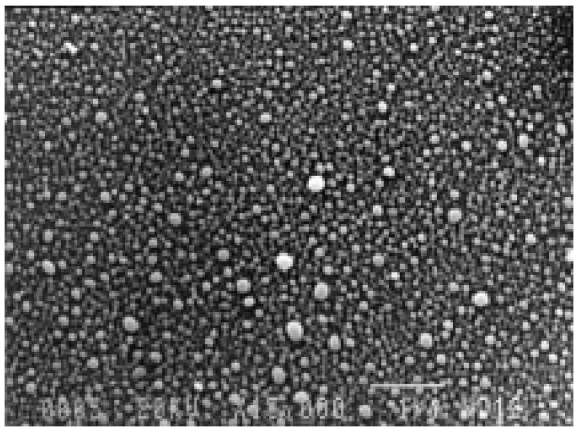

Figure 2. SEM image of the GaN film grown on Si(100) substrate at room temperature by reactive laser ablation of liquid Ga metal target in ammonia atmosphere (50 mTorr). The laser fluence was 3.8 J/cm^2. The target-to-substrate distance was 5 cm and the target temperature as 38 °C.

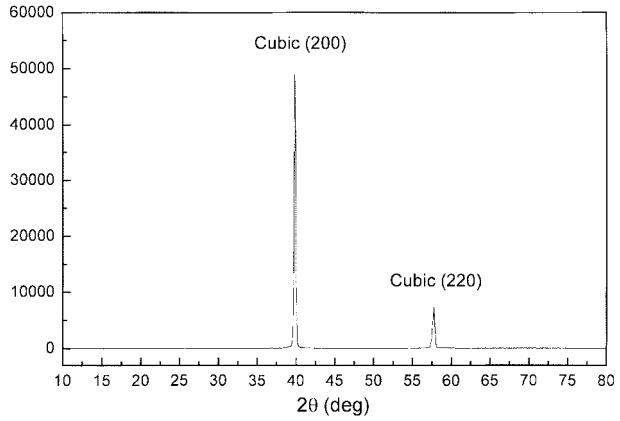

Figure 3. XRD spectrum of the GaN film. The two peaks at 39.7° and 57.6° correspond to (200) and (220) Bragg peaks due to the cubic GaN nanocrystals, respectively.

adsorbed on the Si surface through a dangling bond and formation of GaN is made possible by dissociation of N-H bonds.[15] Although it is not energetically allowed to dissociate NH_3 by single photon absorption, the possibility of fragmentation of NH_3 *via* multiphoton absorption or collisional activation in the plume is not to be ruled out. In such case, formation of GaN in the gas phase by the following reaction may also be considered:

$$NH_3 \rightarrow NH_2 + H,\ NH_2 \rightarrow NH + H \quad (1)$$

$$Ga + NH \rightarrow GaN + H \quad (2)$$

Therefore, elevation of plume temperature by increasing the laser fluence is expected to increase the density of activated nitrogen in the gas phase.

In conclusion, we have grown nanocrystalline cubic GaN films on Si(100) substrate at room temperature by reactive laser ablation of Ga metal in NH_3. Further experiments will be performed to investigate the effects of nitrogen-deficiency on the crystallinity of the GaN film by changing the laser fluence and ammonia pressure.

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