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The growth of high-quality and self-separation GaN thick-films by hydride vapor phase epitaxy

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ABSTRACT

About 1.2 mm thick GaN bulk crystals were obtained by combining a pulsed NH_3-flow modulation (PFM) method and a self-separation method of short-shutting NH_3 flow when using hydride vapor phase epitaxy (HVPE). High crystal quality of bulk GaN was evaluated by X-ray rocking curves (XRC) and the full width at half maximum (FWHM) values were 110, 72 and 83 arcsec for (002), (102) and (100) reflection planes, respectively. The PFM method is proved to be effective in reducing cracks and keeping the surface smooth. And the method of short-shutting NH_3 flow can lead to GaN thick layer separate from sapphire substrate when cooling from the high growth temperature. Growth and separation mechanisms were investigated. Two states were found in PFM method. With PFM method modulating between high quality state and low stress state, 300 μm thick GaN layers without cracks were obtained. Study of spontaneous separation mechanism revealed that the separation attributed to formation of voids inside the GaN layer.

1. Introduction

In recent ten years, GaN-based alloys and devices have made great improvement for applications in short wave-length optoelectronics and high-power high-frequency electronics [1,2]. Given the difficulty of obtaining high quality GaN substrates, most current nitride-based devices are hetero-epitaxially grown on lattice-mismatched substrates, such as sapphire, Si, GaAs and SiC. But conventional GaN films on these foreign substrates tend to result in high threading dislocation (TD) density (10^9 cm^{-2}) due to the large lattice mismatch and thermal mismatch between GaN films and their substrates. So the lack of GaN native substrate is the main obstacle for the further development of nitride-based devices. Many approaches, including N_2 high pressure solution (HPNS) [3], ammonothermal [4] and Na-flux methods [5], have been proposed to produce bulk GaN. However most of these methods require high pressure (~10 atm.) or high temperature (>1400 °C), and the synthesizing of GaN is at a low growth rate. With the advantage of high growth rate and easily controlled growth conditions, hydride vapor phase epitaxy (HVPE) is the most promising method to obtain freestanding GaN substrate. In order to prepare FS-GaN by HVPE, GaN films are initially grown on hetero-substrates, subsequently followed by removal of substrates. The methods employed to produce FS-GaN include pattern structure [6,7], laser lift-off (LLO) [8] and mechanical lapping [9] the drawbacks of which are complicated, time and money-wasting.

In this paper, some simple methods are used to realize a bulk GaN crystal with high crystal quality and nearly no residual strain. A pulsed NH_3-flow modulation method [10] is adopted to increase the crystal quality and reduce the crack density on the surface. A large size GaN bulk with a dislocation density (DD) in the order of 10^6 cm^{-2} is obtained by a self-separation method of forming a void layer inside the GaN layer. The self-separation method of abruptly changing growth conditions, which is easily controlled and time-saving. It is a useful method to produce FS-GaN. The effect of the abrupt changes in growth conditions and thermal mismatch as a cause for this separation mechanism is discussed. The properties of the resulting bulk GaN have also been studied and presented in this work.

2. Experimental

Fig. 1a shows a schematic diagram of the vertical type HVPE system used in this work. All GaN samples were deposited on 2–4 μm thick MOCVD-GaN templates at a low-pressure of 200 Torr with metallic gallium(Ga), hydrogen chloride(HCl) and ammonia(NH_3) as sources. The GaCl was first synthesized upstream in a separated reactor by the reaction of HCl with Ga at 920 °C. It was then transported separately from in different quartz tubes to the deposition zone. The growth temperature was 1060 °C. A hydrogen and

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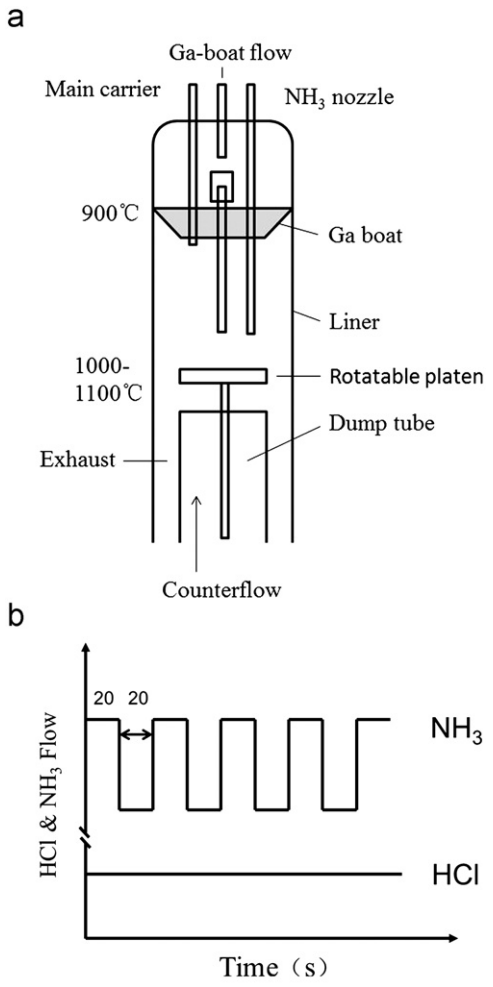

Fig. 1. (a) Schematic diagram of the vertical type HVPE system and (b) schematic illustration of pulsed flow modulation method, in which 20 s long pulses of the NH_3 flow was modulated between high and low flow rates periodically.

nitrogen gas mixture was used as a carrier. The pulsed flow modulation method (shown in Fig. 1b) was used in the growth, of which the period was about 40 s. The NH_3 flow rate was modulated between 0.7 and 1.5 slm and transported alternately into HVPE reactor, while HCl flow rate was kept as constant of 40–60 sccm. The growth rate is about 70–120 μm/h. In order to achieve self-separation GaN thick-films, NH_3 was shut and HCl was abruptly reduced to 10 sccm for a short time during the growth, then all conditions were got back to the normal.

After growth, the surface and cross-sectional morphologies were investigated by differential interference contrast microscopy (DICM) and atomic force microscopy (AFM). The DICM measurements were performed by Nikon Eclipse LV150 system. High-resolution X-ray diffraction (HR-XRD) measurements were carried out using a Bruker D8 Discovery system, delivering a pure $CuK_{\alpha 1}$ line (λ= 0.1540598 nm). Photoluminescence(PL) was carried out at room temperature to determine the crystal quality of GaN layers and optical properties as well. For PL experiment, a HeCd (λ=325 nm) laser was used as the excitation source.

3. Results and discussion

3.1. Properties of two states in PFM method

In our prior works, growth conditions such as the growth temperature and HCl flow rate, were found to have some influence on the quality of GaN layer. In this work, NH_3 flow rate was found to affect the growth rate, the surface topography and strain state of GaN. We found that the growth rate was raised from 70 to 120 μm/h when ammonia changed from 0.7 to 1.0 slm, while growth rate would keep about 120 μm/h when further increasing NH_3 flow rate to 1.5 slm.

In order to investigate the influence of different NH_3 flow rate on the quality of GaN film, two kinds of samples, of which thickness are about 30 μm, were prepared using one step growth with the same growth conditions except NH_3 flow rate. Sample 1 was grown under high NH_3 flow rate of 1.5 slm (state I), and sample 2 was grown under low NH_3 flow rate of 0.7 slm (state II). Fig. 2 is the surface images of GaN epilayer measured by DICM and AFM. For sample 1, very rough surface was observed with RMS surface roughness up to 118 nm (5 × 5 μm), shown in Fig. 2a. But no crack was seen on the surface. However, for sample 2, cracks were obviously observed in Fig. 2b with mirror and smooth surface. The AFM surface roughness of RMS value was reduced to 0.21 nm over the same scanned area.

Symmetric and asymmetric x-ray rocking curves (XRC) were measured on the GaN layer in order to determine the crystal quality. When the GaN is grown under low NH_3 flow rate conditions, the FWHM values of symmetric (00.2) and asymmetric (10.2) reflections are 194 and 260 arcsec, respectively, which are smaller than the values of 242 and 304 arcsec for high NH_3 flow rate sample. The narrow peak of XRC implies the high crystal quality of GaN when the low NH_3 flow rate is used.

For the purpose of detecting the stress states in GaN layers, the HR-XRD and PL spectra were investigated. Based on the measured 2θ–ω scan peak values, the c and a lattice constants of both GaN samples were calculated by the following formula:

$$c=\frac{\lambda}{\sin(\theta_{00.2}+\Delta\theta_c)} \quad \text{where} \quad \Delta\theta_c=\operatorname{arctg}\left(\frac{\sin\theta_{00.2}-2\sin\theta_{00.4}}{2\cos\theta_{00.4}-\cos\theta_{00.2}}\right) \tag{1}$$

$$a=\frac{cd_{10.2}}{\sqrt{3c^2/4-3d_{10.2}^2}} \quad \text{where} \quad d_{10.2}=\frac{\lambda}{2\sin(\theta_{10.2}+\Delta\theta_a)} \quad \text{and}$$
$$\Delta\theta_a=\operatorname{arctg}\left(\frac{\sin\theta_{10.2}-2\sin\theta_{20.4}}{2\cos\theta_{20.4}-\cos\theta_{10.2}}\right) \tag{2}$$

In Eqs. (1) and (2) λ is the x-ray radiation wavelength, $\theta_{hk.l}$ are the angular positions of the respective symmetric and asymmetric ($hk.l$) peaks, and $\Delta\theta$ is the Bragg angle correction due to the zero setting of instrumental alignment. For the high NH_3 flow rate sample, the c=0.51870 nm and a=0.31857 nm; for the low NH_3 flow rate sample, the c=0.51890 nm and a=0.31833 nm. From those data, the hydrostatic strains were calculated [11], which are much smaller than the biaxial strains in the c-and a-directions. As shown in Fig. 3 2θ–ω scans of (00.2) peak slightly shift to a smaller angle for the low-NH_3 sample than that for the high-NH_3 sample. Both 2θ values are smaller than that of bulk GaN (34.5701°). These results indicate that GaN samples are both

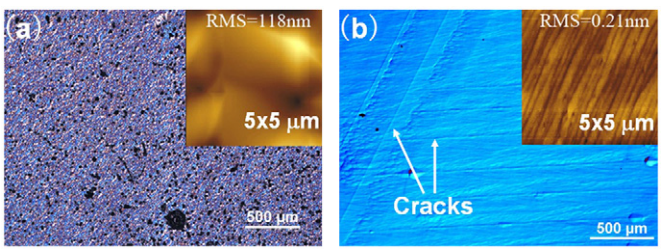

Fig. 2. Differential interference contrast microscopy (DICM) images of (a) the state I sample under high NH_3 flow and (b) the state II sample under low NH_3 flow. The insets are the relatively AFM images of two samples.