

Crystal characteristics of bulk GaN single crystal grown by HVPE method with the increase of thickness

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Although GaN has been used in optical materials and power devices, the extent of its application is determined by the crystal quality. Bulk GaN has been reported to produce high-quality GaN. Therefore, it can be used in applications that require high-quality crystals, such as high-brightness light-emitting diode, power devices, etc. We grew a 2-inch bulk GaN crystal, using the hydride vapor phase epitaxy (HVPE) method, on a sapphire substrate to a thickness of ~5 mm. X-ray diffraction (XRD) was used to analyze the structure of GaN. Scanning electron microscopy (SEM) was used to measure the etch pits density (EPD) of GaN after wet chemical etching. In addition, high-resolution XRD (HR-XRD) and Raman spectrometry were employed for radius of curvature and residual strains measurements, respectively.

Key words: HVPE, bulk GaN, dislocation, residual thermal strain, radius curvature.

Introduction

III-nitride compound semiconductors such as GaN, AlN, and InN have been studied for a long time because of their excellent characteristics [1]. In the case of the GaN, it can be applied to optical devices such as light-emitting diodes (LEDs) and laser diodes (LDs), power semiconductors, high-temperature operation devices etc., due to the properties like wide band gap, high breakdown voltage, high electron mobility, and high temperature stability [2,3]. In order to expand the applications of GaN devices for high or ultra-high luminance and high output, it is necessary to be able to control the elements that hinder the basic characteristics. At present, GaN devices are fabricated by epitaxy growth on hetero-substrates such as sapphire, silicon carbide, silicon etc. Among them, the sapphire substrate is mainly used commercially for economic reasons [4]. However, there are inevitable differences in the lattice constant and thermal expansion coefficient between the sapphire single-crystal substrate and the growing GaN epilayer; therefore, internal defects and residual stresses are also induced in the GaN device, which degrades the inherent superior characteristics of the GaN single crystal [5]. The effect of lattice mismatches is significantly reduced when the GaN films are grown to more than several nm in length [6,7]. In the case of the thermal expansion coefficient

of the sapphire single-crystal substrate, a difference of about -25.5% in the a-axis direction and -62.7% in the c-axis direction can be seen when compared to the GaN single crystal. Thus, after growth of the GaN, thermal compressive stresses remain in the GaN single crystal due to the cooling process [8, 9]. It has been reported that residual thermal stresses and defects, generated in the growth process, are relaxed with increasing thickness [6, 10]. Therefore, in order to eliminate these internal defects and residual thermal stresses, homoepitaxy is the best choice of method for bulk GaN single crystal growth. According to reports to date, GaN single crystals grown to a thickness of 5-7 mm have the best quality. The use of such single crystals as a substrate and homoepitaxy of the same type in bulk results in high-power GaN devices with high luminance and power.

In this study, we investigate the defects and residual thermal stresses within a bulk GaN single crystal, grown using the vertical hydride vapor phase epitaxy (HVPE) method, with increasing GaN crystal thickness, and try to establish the processing conditions of a homoepitaxial substrate for GaN devices.

Experiments

GaN single crystal was grown to a thickness of 5 mm on a sapphire substrate (0001) under atmospheric pressure using a vertical HVPE growth method and the growth parameters previously reported [11]. However, when the growth thickness increased to 3 mm or more,

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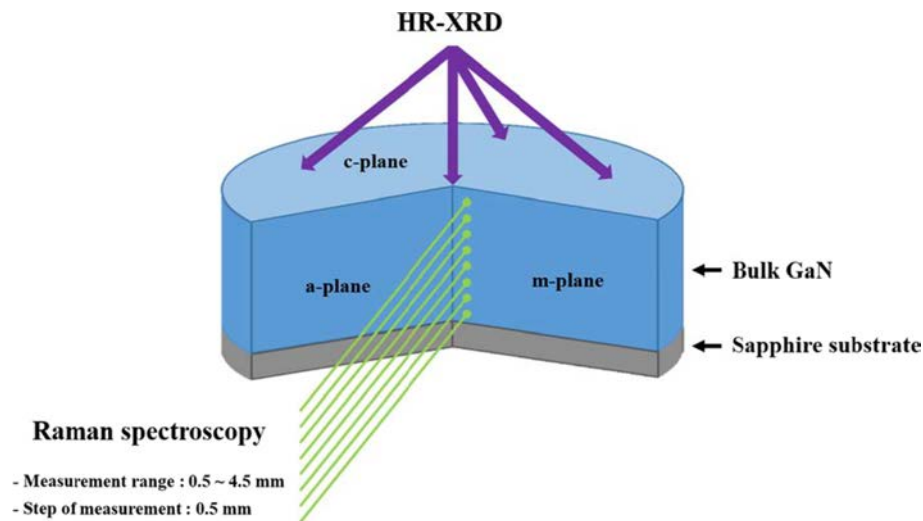


Fig. 1. Schematic of bulk GaN wafer measured by HR-XRD and Raman spectrometer.

it was observed that polycrystalline GaN defects and hexagonal pits were formed on the surface. In order to solve this, the conditions of the process were divided into two steps. In the first step, the V/III ratio was 12 and the growth rate was $\sim 60 \mu\text{m/hr}$. In the second step, the V/III ratio was 10 and the growth rate was set at $\sim 80 \mu\text{m/hr}$. X-ray diffraction, using a Rigaku RAD-C, was used for analyzing the crystal structure of the grown GaN single crystal, and the dislocation density, with increasing thickness, was measured with a molten KOH-NaOH eutectic composition for 25 minutes at 410°C after which the surface was observed through a scanning electron microscope (SEM, JSM-5900LV, Jeol, Japan) [12]. The radius of curvature of the GaN single crystal wafer growth surface was evaluated using a high-resolution X-ray diffractometer (HR-XRD, PANalytical, X'Pert PRO) and the X-ray rocking curve (XRC) was measured at the specimen positions (wafer center and 20 mm up, down, left and right from the wafer center, excluding part of wafer edge). Residual stresses and strains, with increasing thickness, were evaluated using a Raman spectrometer (JASCO, NRS-3100, England). For the preparation of the specimen, the m-plane $(10\bar{1}0)$ of the GaN, grown perpendicular to the c-axis plane (0002) , was used, and the Raman spectrum was observed by moving in 0.5-mm steps in the growth direction from the substrate. The excitation laser source of the Raman spectrometer used has a wavelength of 534 nm and the power is 2.5 mW. The measurement position of the specimen is shown in Fig. 1.

Results and Discussion

Fig. 2 shows the XRD pattern of the grown bulk GaN single crystal. Fig. 2(a) shows XRD peaks at 34° (0002) and 72° (0004) , which proves that the grown

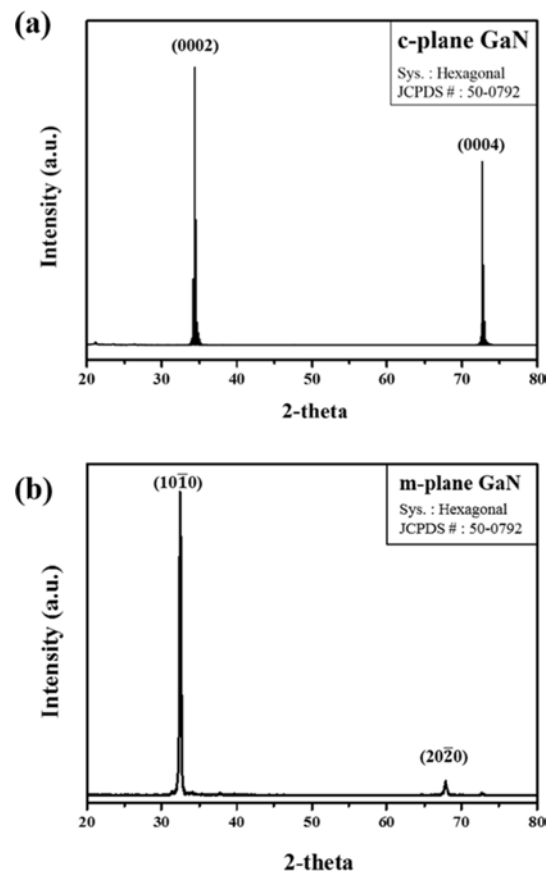


Fig. 2. X-ray diffraction patterns: (a) c-plane GaN, (b) m-plane GaN.

GaN grow on the c-axis of wurtzite structure. Fig. 2(b) shows the XRD diffraction pattern of a cross-section plane cut perpendicular to the growth plane using a diamond cutter for obtaining the Raman spectrum. There are only two peaks corresponding to $(10\bar{1}0)$ and $(20\bar{2}0)$, which confirms that it is the m-plane of the

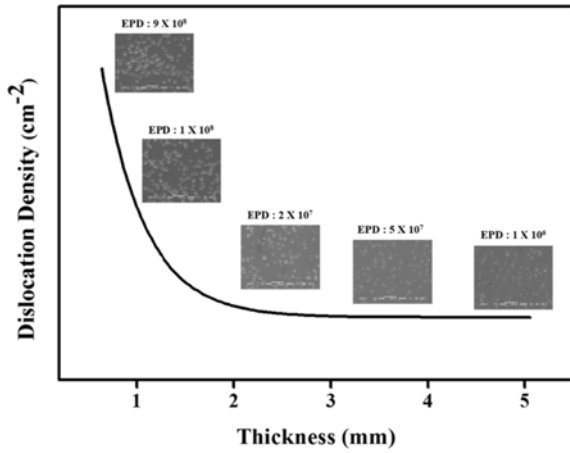


Fig. 3. Variation of dislocation density with increasing thickness of GaN crystal growth.

GaN.

Fig. 3 shows the measurement of the etch pits density (EPD) variation using an etchant of KOH/NaOH eutectic composition [13]. The EPD is about $10^{12}/\text{cm}^2$ near the interface of the sapphire substrate and GaN crystal. It decreases rapidly up to 1 mm of crystal growth thickness. The EPD values are about $9 \times 10^9/\text{cm}^2$ at a thickness of 0.5 mm and $10^7/\text{cm}^2$ on the surface of a crystal grown to 1 mm thickness. In the case of GaN grown to a thickness of 5 mm, the EPD value is $10^6/\text{cm}^2$, while it slightly decreased for thicknesses less than 1 mm. This is the result of dislocations, such as edge, screw, and mixed dislocations, which are generated by the lattice mismatch at the interface which is actively merging. Then, according to the growth, the threading dislocation which grows in the perpendicular direction leaves the GaN single crystal [13]. The difference in thermal expansion coefficient between the sapphire single crystal substrate and the GaN single crystal is about -25.5% in the a-axis direction and -62.7% in the c-axis direction. This causes the occurrence of cracks after growth is completed. Even if no cracking occurs, the GaN single crystal will be bent by the difference in shrinkage rate due to the cooling process that occurs after the growth is completed [8, 14]. The degree of bending is numerically expressed as the radius of curvature, which is calculated by using Eq. (1) [15],

$$R = S/2 \sin\theta \quad (1)$$

where R is the radius of curvature and S is the diameter of the crystal. The radius of curvature decreases as the bending of the GaN single crystal increases, and, in the case of an ideal single crystal which is not bent, the value of the radius of curvature diverges to infinity. So, the bulk GaN single crystal of high quality can be confirmed as having a large radius of curvature using Eq. (1). Fig. 4 shows the XRC measured at the same

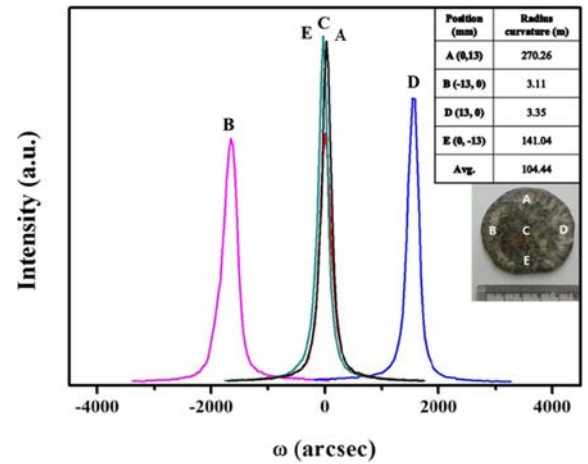


Fig. 4. X-ray rocking curve depending on position.

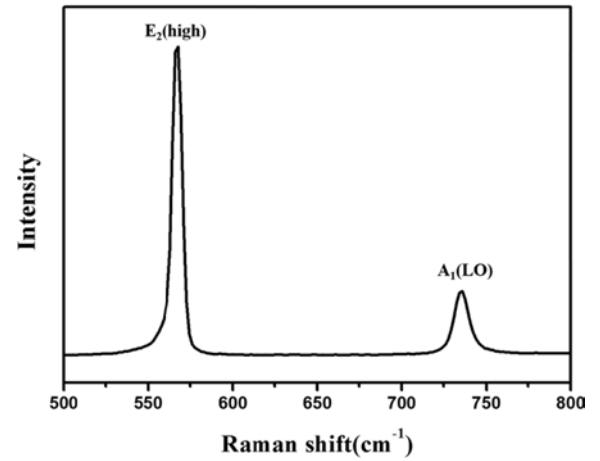


Fig. 5. Raman scattering spectrum of GaN (0002).

distance (up, down, left, and right) from the center of the grown bulk GaN single crystal and the value of the radius of curvature calculated using this approach [14]. The average value of the radius curvature is about 104.44 m. This means that the grown GaN single crystal has a smaller degree of internal bending when compared to values reported in other researchers' research [15]. In this case, the difference in thermal expansion coefficient between the substrate and film decreases with increasing thickness of the GaN film grown on the substrate; therefore, the radius of curvature is considered to increase [16].

In order to gauge the applicability of the grown bulk GaN substrate in high-brightness and high-power devices, the residual stress inside the material was evaluated using Raman spectrometry. Fig. 5 shows the Raman spectrum obtained on the growth surface of bulk GaN measured at room temperature. Peaks were observed at $\sim 567.8 \text{ cm}^{-1}$ (E_2 (high)) and 735.97 cm^{-1} (A_1 (low)). Thus, compared to the complete GaN single crystal, the growth surface Raman spectrum shows a blue shift, related to the residual compressive stress components of the residual stresses.

When a compressive stress is applied, the frequency of the phonons decreases because the wavelength is inversely proportional to the phonon frequency, leading to a blue shift in the Raman spectrum. It is known that the residual thermal stresses are generated by the difference in lattice constant and thermal expansion coefficient between the grown GaN single crystal and sapphire substrates; however, the influence of lattice mismatch is lessened when the thickness of GaN is more than a few nanometers [6, 7]. Therefore, the main reason for the residual thermal stress in the GaN single crystal is the difference in thermal expansion coefficients between the sapphire substrate and GaN single crystal during the cooling down after the growth process [6,14]. Since the thermal expansion coefficient of sapphire is larger than that of GaN, more shrinkage occurs during the cooling step. Therefore, existence of residual compressive stress in the GaN single crystal can be predicted, resulting in the peak position being shifted to the right (blue shift) in Fig. 5.

In order to observe the fine deformation of the material with increasing thickness, the Raman spectrum was obtained by laser irradiating the surface perpendicular to the growth surface. Fig. 6 shows the Raman spectrum measured at a constant 0.5 mm step in the growth direction from the interface between sapphire substrate and GaN crystal. As shown in Fig. 6, the change in

Raman shift occurs along the growth direction near the interface, and this facilitates the identification of the atomic vibration modes [7]. In the case of crystals with the III-nitride hexagonal crystal structure, it belongs to the C_{6v}^4 (C63mc) group; therefore, 8 oscillation modes can be predicted, of which two oscillations modes exist for each of A_1 , E_1 , E_2 , and B_1 . Among them, each one of the A_1 and E_1 oscillations is an acoustic vibration mode, oscillating in the same direction of the two atoms. For the remaining six modes, it is an optical vibration mode oscillating in the opposite direction of the two atoms [17]. In the $E_2(\text{high})$ mode, the lattice constant c affects the strain variation because it is the peak due to atomic vibration from the c -plane. Based on the above contents, the frequency of the phonon decreases with decreasing compressive stress; this causes a red shift of the peak. To estimate the approximate value of the residual stress as growth proceeds, the standard specimen selects the edge of the crystal that is relatively less stressed to observe the $E_2(\text{high})$ mode [6]. Residual thermal strain in the GaN single crystal is estimated as follows [7],

$$\Delta\omega = \left(2\alpha_\lambda(x) - \frac{2C_{13}(x)}{2C_{33}(x)}b_\lambda(x) \right) \varepsilon_{//} \quad (2)$$

where a_λ and b_λ represent the values of the phonon deformation potentials of GaN, and C_{13} and C_{33} are the elastic constants. The following value of GaN were used:

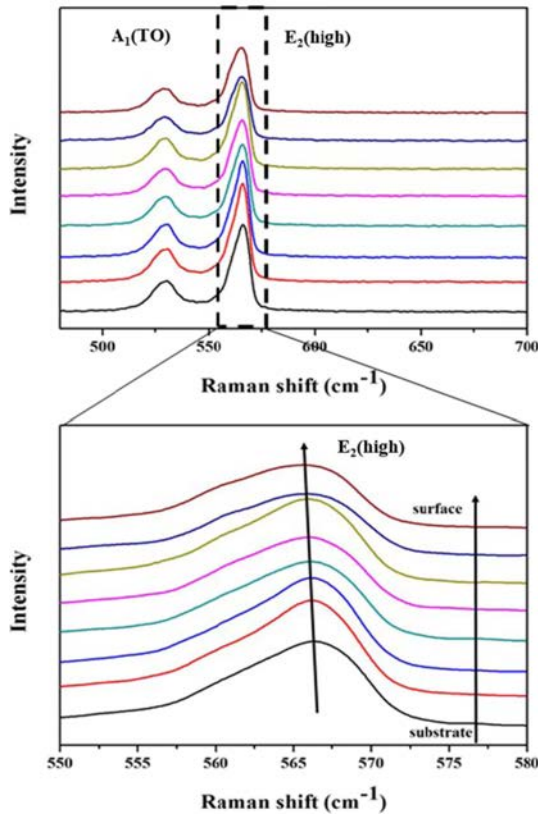


Fig. 6. Cross-sectional Raman scattering spectrum (m-plane GaN).

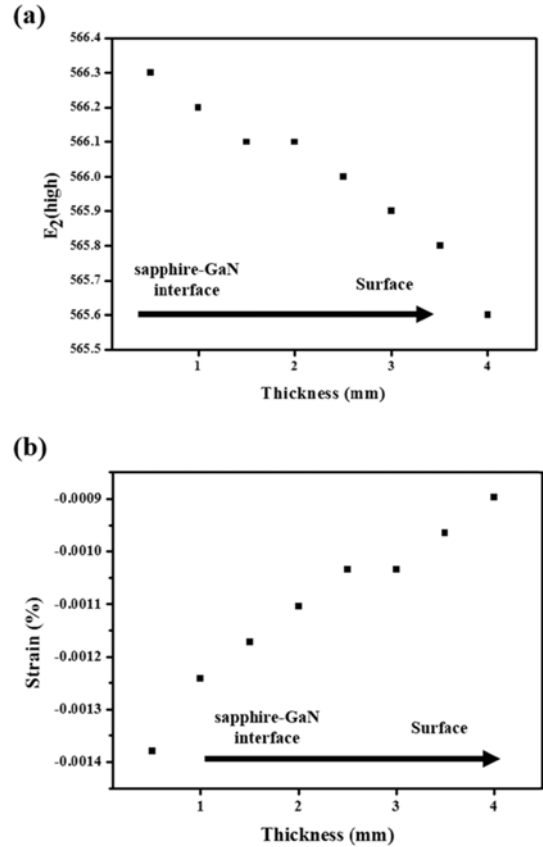


Fig. 7. Variation of (a) $E_2(\text{high})$ and (b) strain with increasing depth of the bulk GaN.

$\alpha_{\lambda}(E_2(\text{high})) = -850 \text{ cm}^{-1}$, $b_{\lambda}(E_2(\text{high})) = -920 \text{ cm}^{-1}$ [18], $C_{13}(E_2(\text{high})) = 106 \text{ GPa}$ and $C_{33}(E_2(\text{high})) = -850 \text{ cm}^{-1}$ [19]. Fig. 7(a) shows the variation of the $E_2(\text{high})$ peak with relation to the depth from the grown GaN surface vicinity to the interface between sapphire substrate and GaN single crystal. This shows that the peak undergoes a blue shift as it enters the bulk from the surface, and Fig. 7(b) shows the calculated value of residual strain based on $E_2(\text{high})$ variation. The fact that the resultant value has a negative sign means that compressive stresses act inside the material. Thus, the value gradually decreases from the grown surface to the interface with the substrate. According to the results of Wang et al., who carried out similar experiments for GaN film of $\sim 4 \mu\text{m}$ thickness, strains of about -0.18 were measured at a depth of $4 \mu\text{m}$ from the growth surface [6]. In contrast, the results of this experiment show much lower strains than this value. This means that the stress in the GaN crystal is relaxed and the strain is lowered with increasing thickness of the GaN single crystal.

Conclusions

The bulk GaN single crystal grown to a thickness of about 5 mm by the HVPE method was confirmed to be a GaN single crystal grown to [0002] using XRD. Through the wet chemical etching process, it was confirmed that the value of EPD decreased according to increasing thickness, and that, at the final thickness of 5 mm, the bulk GaN crystal had a dislocation density of $10^6/\text{cm}^2$. We measured the radius of curvature using HR-XRD and its value was approximately 104.44 m on average. Considering that the radius of curvature of the current, commercially used GaN substrate is 10 m, this numerical value can be understood to be a single crystal of excellent quality. Upon measuring the residual thermal strain using Raman spectrometer, very fine deformations were observed when compared to other researchers' results. This was due to thickness of the crystal growth. Based on the above results, we confirm that the bulk GaN single crystal, grown by using the vertical HVPE method, produces a high-quality single crystal. It is expected that high-output and high-brightness GaN devices can be manufactured using this fabrication method.

Acknowledgments

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