

## Effect of annealing temperature on the optical properties of a bulk GaN substrate

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Variation of optical properties in a bulk GaN substrate have experimentally investigated with respect to different annealing conditions of 700 - 1,000 °C. As-annealed GaN was characterized by scanning electron microscopy, photoluminescence, and Raman spectroscopy. The experimental results demonstrated that the crystallinity and internal residual compressive stress of GaN are most effectively improved when heat-treated at 900 °C for three hours. The optical characteristics were also improved by enhancing the quality of the GaN substrate by decreasing both the defect density and the residual stress. It was also confirmed that the effect of the heat treatment was excellent given that impurities were effectively removed by this process.

**Keywords:** Hydride vapor phase epitaxy, Gallium nitride, Optical property, Crystallinity, Residual stress, Defect density.

### Introduction

GaN is a III-V compound semiconductor with a wide band gap. Therefore, it is a material that is expected to be applied to light-emitting devices operating in the blue or ultraviolet range [1, 2]. It has a number of excellent properties, such as very good luminescence, structural stability at high temperatures, high hardness, high thermal conduction, and good chemical stability. Therefore, it can be used in a wide variety of applications, not only in optical devices but also in high-power and high-temperatures devices. Based on these characteristics, numerous studies have sought to apply GaN to high-brightness light-emitting diodes (LED) and laser diodes (LD). Recently, it is also the subject of increasing interest regarding its application to power and communication semiconductors such as those that power RF and other devices [3-7].

The characteristics of the substrate are very important when attempting to produce a GaN device capable of high brightness and high performance. The GaN single crystal difficult the growth for ingot single crystal which can get the substrate of high quality. Because ingot growth requires a pressure above 6 GPa and a temperature above 2,200 °C due to the properties of nitrogen [8]. Therefore, the growth of GaN depends on epitaxial growth, mainly using a heterogeneous substrate. Heterogeneous substrates mainly utilize sapphire substrates for economic reasons [9-11]. Sapphire impedes the acquisition of a high-quality GaN epi-layer due to its

large lattice mismatch and difference in the thermal expansion coefficient from that of GaN. Hence, the interior of GaN single crystal grown on sapphire has a high density (typically in the range of  $10^8\sim 10^9$  cm<sup>-2</sup>) of threading dislocations and residual stress [12-14].

These dislocations and defects play a role in reducing the lifetime and efficiency of these devices by creating, for example, a center of non-radiation recombinations or charge leakage paths [15, 16]. The residual stress changes the crystalline symmetry and exerts an effect the basic physical properties of the materials and the structure of the electronic band [17]. When the residual stress inside the GaN single crystal increases, it generates or propagates cracks to mitigate the stress resulting in new defects. These act the factors that deteriorate the quality of the GaN substrate, including optical and electronic properties [18-20]. In addition, a damage layer is formed under the surface of GaN during mechanical polishing, a step during the substrate manufacturing process, resulting in deterioration of the optical and electrical properties of the device [21, 22]. For use in high-quality electronic and optical devices, there is a need for a method capable of mitigating these problems and improving the properties of GaN. Annealing is known to be a feasible method for improving the electronic and optical properties of nitride semiconductors [3, 23]. However, most of the annealing studies involving GaN focused on dopant implantation. Few studies have concentrated on the effects of a heat treatment on the optical damage recovery of mechanically polished bulk GaN [21, 24]. Therefore, in this work, Therefore, in this work, we investigated variations of the optical characteristics after a heat treatment for bulk GaN substrate grown on a sapphire substrate using the hydride vapor phase epitaxy (HVPE) technique.

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## Experimental

Bulk single-crystal GaN was grown at a thickness of 1.0 mm or more on a c-plane sapphire (0001) substrate using a HVPE system. GaCl gas as a Ga source was formed by reacting metal Ga with HCl gas at 700 - 800 °C. This gas was reacted with NH<sub>3</sub> gas, which was used as an N source, and single-crystal GaN was grown at a sustained growth rate of 100 μm/h at a temperature of 1,000 - 1,100 °C. Fig. 1 shows the bulk single-crystal GaN after growth. The as-grown bulk single-crystal GaN was separated from the sapphire substrate by a laser lift off (LLO) process. The separated GaN was fabricated on a two-inch GaN substrate with a thickness of 1.0 mm after polishing. The GaN substrate was then cut into pieces 10×10 mm<sup>2</sup> in size.

The GaN specimens were annealed in the temperature range of 700 - 1,000 °C for one to five hours using an independently fabricated annealing furnace. N<sub>2</sub> ambient was used to prevent the disassociation of nitrogen at the high temperatures used. We analyzed the defect density of the GaN single crystal according to the heat treatment condition after chemical etching using a melt with a KOH/NaOH eutectic composition [25]. We confirmed etch pits on the surface of the as-etched GaN via scanning electron microscopy (SEM, JSM-5900LV, JEOL, Japan) when analyzing the dislocation density. Raman spectroscopy (JASCO, NRS-3100, England) was used to characterize the residual stress, with the excitation laser source and power level set to 532 nm and 1.3 mW, respectively. The optical properties were analyzed by a photoluminescence analysis (PL, Dongwoo Optron, MonoRa750i, Korea) at room temperature. During this process, the excitation source used was a 325 nm He-Cd laser, of which the energy exceeds that of the band gap energy of GaN. The power of the laser was set to 2.5 mW.

## Results and Discussion

The dislocation density of the GaN substrate is a major measure of the quality of single-crystal GaN, and a lower dislocation density indicates good quality of the single crystal [26]. Etch pits existent in the GaN single crystal are a type of defect deriving from threading dislocations generated at the interface. Therefore, the dislocation density can be obtained by calculating the density using the number of observed etch pits [27]. For the measurement a value of etch pit density (EPD) is calculated from the number of etch pits *N* within the measuring field according to equation (1):

$$EPD = \frac{N}{\alpha_F} \quad (1)$$

Here,  $\alpha_F$  is the measuring field. The value of  $\alpha_F$  must be given in cm to obtain the local EPD in cm<sup>-2</sup> [28]. Fig. 2 presents the results after measuring the variation



Fig. 1. Image of a 2-inch bulk GaN grown by HVPE.

of the etch pit density using an etchant with a KOH/NaOH eutectic composition after the heat treatment. The dislocation density decreased and then increased again with an increase in the annealing time at all temperatures after annealing. In other words, it was observed the same trend which the crystallinity increasing and then decreasing. As shown in Fig. 3, an unstable lattice with high energy in the material move in a direction such that the internal energy is reduced when receiving energy above a critical level thermal energy by annealing. As such, the crystallinity improves as atoms move to stable sites and are rearranged [29]. This is the effect of the annealing. However, the effect of annealing decreases due to the excessive heat energy during the annealing process with increase in the heat treatment time. Therefore, it was considered that the dislocation density was reduced after annealing for five hours. The results of a dislocation density analysis via EPD showed that the lowest dislocation density arose after the sample was annealed for three hours throughout the heat treatment temperature range, meaning that the crystallinity is most effectively improved during the heat treatment at that time.

Fig. 4 shows the PL spectra measured at room temperature for specimens annealed for three hours, at which the effects of the heat treatment were best in all temperature ranges. The strong peak around 3.4 eV in the PL spectra of all samples is nearly identical to that of about 3.41 eV, which is the band gap energy of GaN. This indicates with regard to near-band edge emission (NBE) which the luminescence caused by the death of excitons around the energy gap. The intensity of the NBE peak increased with an increase in the annealing temperature in the PL spectrum, meaning that the quality of the substrate was improved [30]. However, the intensity of the peak decreased again at 1,000 °C because the improved crystal quality was

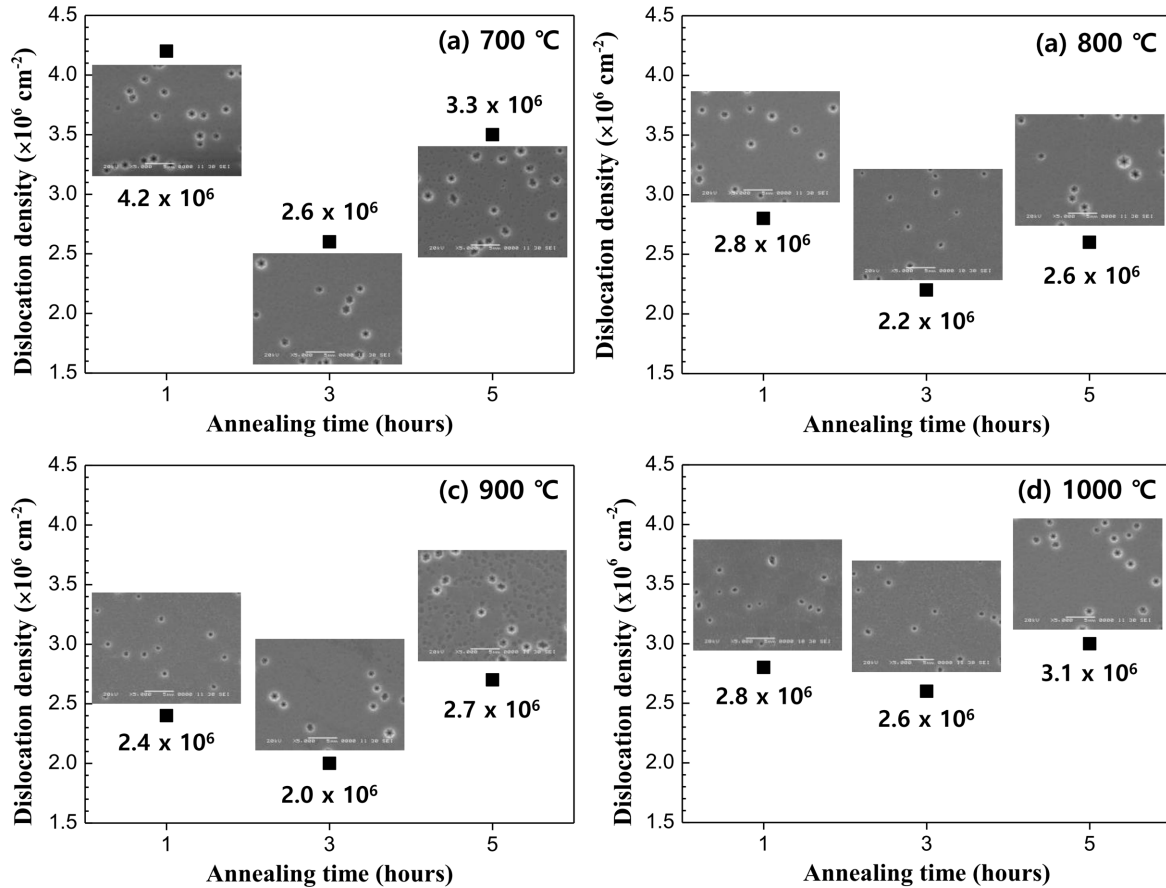


Fig. 2. Etch pit density of the (0002) GaN after annealing at (a) 700, (b) 800, (c) 900, and (d) 1,000 °C.

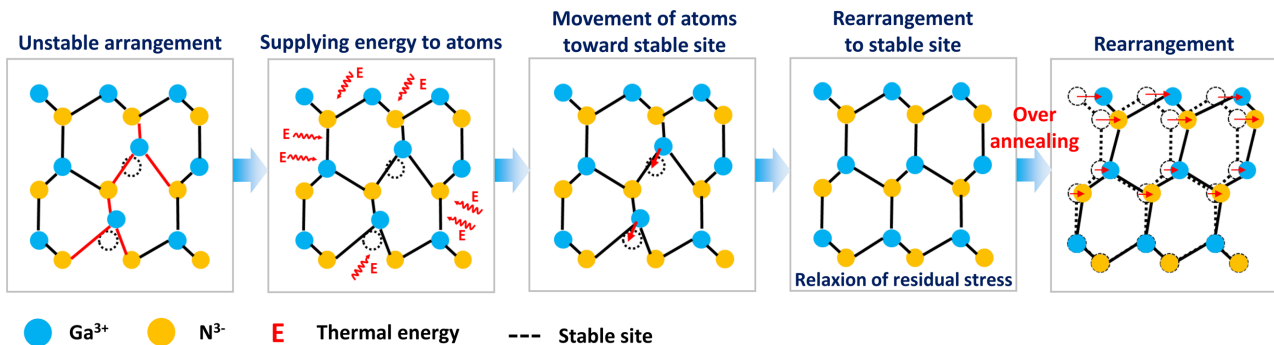


Fig. 3. Schematic of behavior of atoms during heat treatment.

reduced via nitrogen dissociation at a high temperature. The nitrogen can dissociate at high temperatures of 1,000 °C or more below 4.5 GaP [31]. In other words, the nitrogen-vacancy was created due to the thermal decomposition in high temperature and acted as a non-radiative recombination center, resulting in a decrease in the intensity of the NBE peak. These trends match the result of the dislocation density via measurement for EPD.

Fig. 5(a) shows a blue shift that indicates that the NBE peak shifts toward a lower energy level with an increase in the annealing temperature. A blue shift in the PL spectrum can appear when the interatomic

distance of the material increases, as shown in Fig. 5(c). This is believed to stem from the fact that the interatomic distance was widened because it relaxed the residual compressive stress generated by the difference in the thermal expansion coefficient at the interface between the sapphire and the GaN later via the heat treatment. To confirm this change precisely, we indicate numerically the variation of the position of the NBE peak in Fig. 5(b). The position of the NBE peak decreased with an increase in the annealing temperature, showing its lowest value at the temperature of 900 °C. Therefore, it was considered that annealing at the corresponding temperature most effectively

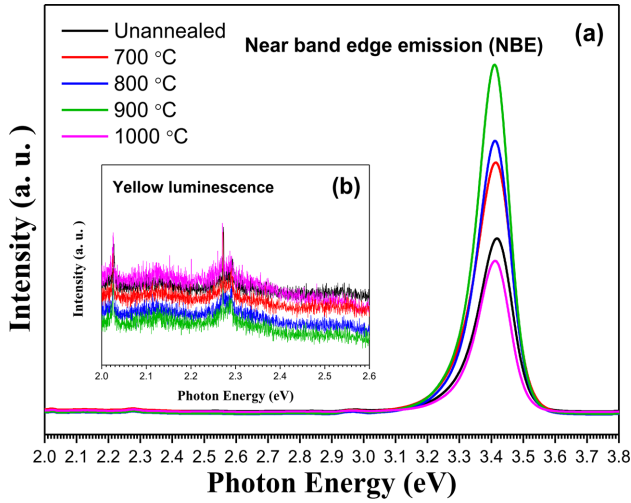


Fig. 4. (a) the PL spectra for specimens annealed for three hours (b) the spectrum of yellow luminescence around 2.2 eV.

relaxed the residual compressive stress.

To characterize the residual stress existing in the internal material after annealing, we undertook Raman measurements, as indicated in Fig. 6(a). The Raman frequency modes of GaN, having a hexagonal symmetric structure (C6v), are  $2A_1$ ,  $2E_1$ ,  $2E_2$ , and  $2B_1$ . For bulk GaN, six phonon frequency modes exist:  $A_1(\text{TO}) = 531.8 \text{ cm}^{-1}$ ,  $E_1(\text{TO}) = 558.8 \text{ cm}^{-1}$ ,  $E_2(\text{low}) = 144 \text{ cm}^{-1}$ ,  $E_2(\text{high}) = 567.2 \text{ cm}^{-1}$ ,  $A_1(\text{LO}) = 734 \text{ cm}^{-1}$ , and  $E_1(\text{LO}) = 741 \text{ cm}^{-1}$ . The  $E_2(\text{high})$  mode of GaN is the mode that most sensitively reacts to stress present inside the crystal or to external pressure. It has been reported that the tensile stress arises during the move to a low phonon frequency and that compressive stress arises when moving to a high phonon frequency based on the  $E_2(\text{high})$  mode value of a stress-free crystal (about  $567.2 \text{ cm}^{-1}$ ) [32]. For example, in the presence of tensile stress, the atomic spacing will increase with

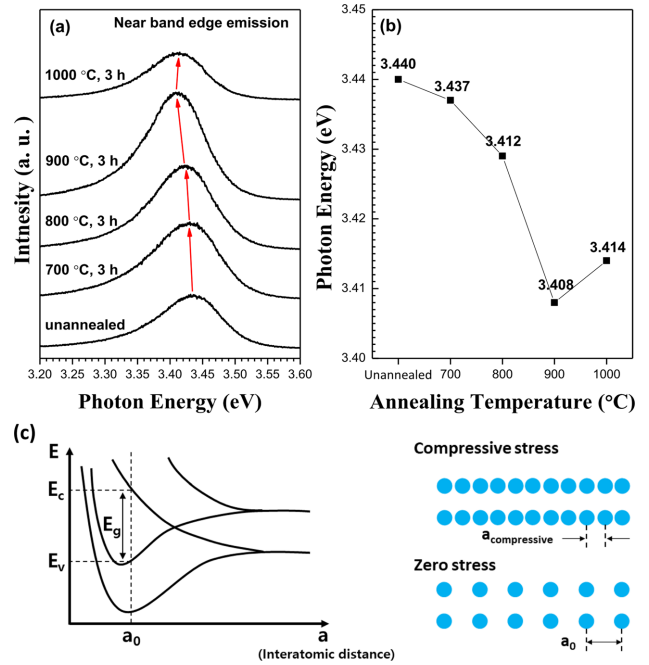


Fig. 5. (a) the shift of NBE peak in PL spectrum for bulk GaN unannealed and annealed, (b) the variation of the position of the NBE peak, and (c) the formation of energy bands in crystals [45, 46].

an expansion of the lattice, and the phonon frequency will decrease. On the other hand, in the presence of compressive stress, the atomic spacing will decrease with a contraction of the lattice, and the phonon frequency will increase [33]. Fig. 6(b) shows the variation of the  $E_2(\text{high})$  mode peak. The  $E_2(\text{high})$  mode, which appears strongly in the Raman spectrum, shifted to a lower frequency with an increase in the heat treatment temperature. We confirmed that the  $E_2(\text{high})$  value after annealing at 900 °C was closest to the value indicated by the dotted line in a stress-free condition which has a

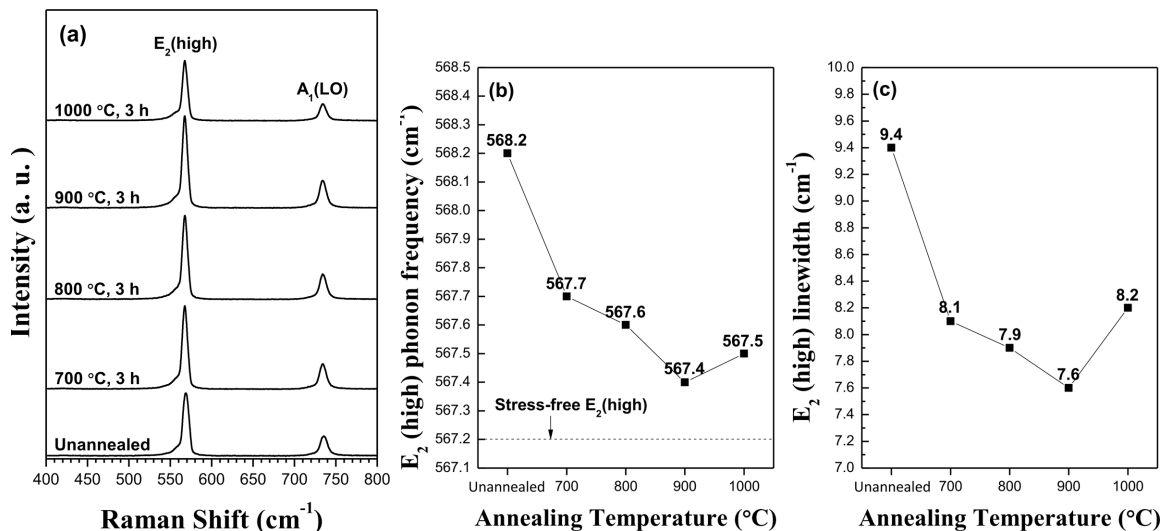


Fig. 6. (a) Raman spectra of GaN single crystal unannealed and annealed, the variation of (b) the  $E_2$  (high) and (c) the FWHM of the  $E_2$  (high) mode.

value when the internal stress of bulk GaN is free. This means that the residual compressive stress of GaN substrate was relaxed with an increase in the annealing temperature. This matches the result showing the blue shift of the NBE peak in the previously described PL spectrum. Also, the intensity of  $E_2(\text{high})$  mode peak varies with crystallinity, as the phonon vibrations are sensitive to atom compositions. Therefore, higher crystal quality revealed more distinct  $E_2$  high phonon vibration peaks [34]. We observed that the intensity of the  $E_2(\text{high})$  mode peak was most strongly at 900 °C in Fig. 6(a). This is considered that due to the crystallinity improved with relaxing residual stress. Moreover, the full width at half maximum (FWHM) of  $E_2(\text{high})$  is affected by the quality of the crystal [35]. Defects in the crystal decrease the effective wavelength of phonons by contributing to the scattering of phonons, and the FWHM of the phonon peak is reduced with a decrease in the defect density [36]. Fig. 6(c) indicates the variation of the FWHM of the  $E_2(\text{high})$  mode. The FWHM of the  $E_2(\text{high})$  mode shows a decreasing trend with an increase in the temperature to 900 °C, past which it increased again at 1,000 °C. This is consistent with the result of the dislocation density described above. Thus, we confirmed that the crystallinity was most improved at a heat treatment temperature of 900 °C.

On the other hand, the yellow luminescence (YL) band at around 2.2 eV in the PL spectrum and the  $A_1(\text{LO})$  mode at about 734  $\text{cm}^{-1}$  in the Raman spectrum are peaks caused by defects and impurities. Fig. 4(b) shows the spectrum around 2.2 eV, in which YL is generated by defects or impurities of the crystal at a deep level. These YLs greatly degrade the optical properties of GaN because they are related to structural defects such as stacking defects and dislocations [37, 38]. In particular, this is a factor that interferes with the realization of full color via the saturation of blue emission during the manufacturing of LEDs [39]. We confirmed that the intensity of the YL band decreased with an increase in the heat treatment temperature and that it scarcely appeared at 900 °C. Recently, it has been reported that nitrogen vacancies [40], C-O-related impurities [41], and Si impurities exist in dislocations [42] and cause this YL band. However, this has not been clearly verified.

The  $A_1(\text{LO})$  mode in the Raman spectrum changes of its frequency according to the number of impurities contained in the internal defects [43]. The intensity of the  $A_1(\text{LO})$  mode decreases with an increase in the carrier concentration when the number of impurities increases [44]. Fig. 7(a) shows the variation of the  $A_1(\text{LO})$  mode peak before and after annealing. The intensity of the  $A_1(\text{LO})$  mode peak increased with an increase in the heat treatment temperature. Fig. 7(b) presents a graph that quantifies the variation of the intensity of the  $A_1(\text{LO})$  mode peak. The intensity of the  $A_1(\text{LO})$  mode increased the most after annealing at 900

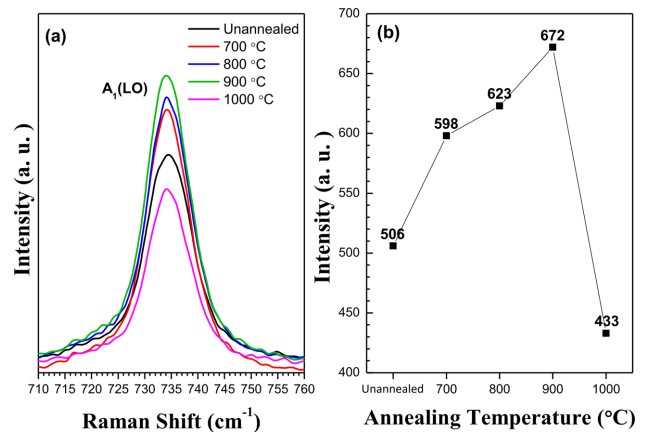


Fig. 7. (a) the spectra of  $A_1(\text{LO})$  mode for the GaN unannealed and annealed and (b) the variation of the intensity of the  $A_1(\text{LO})$  mode peak.

°C. Thus, it can be determined that defects in the crystal decreased because the number of impurities decreased after annealing under the this conditions. However, the intensity of the peak of the  $A_1(\text{LO})$  mode decreased after annealing at 1,000 °C. This is considered to have occurred because the carrier concentration was increased due to nitrogen vacancies, leading to the disassociation of nitrogen at a high temperature. In other words, it is likely that the heat treatment effect deteriorated as nitrogen vacancies acted as defects.

## Conclusion

We annealed a bulk GaN under various conditions. We confirmed that the dislocation density of a bulk GaN substrate was reduced when a heat treatment at all temperatures for three hours via an EPD analysis. Based on this, we analyzed the optical characteristics of specimens annealed for three hours in the temperature range of 700 - 1,000 °C. It was observed that the optical properties of annealed bulk GaN were best after annealing at 900 °C with an increase in the intensity of the NBE peak as the temperature was increased up to the temperature range of 700 - 900 °C. As a result of Raman measurements, the residual compressive stress was found to be relaxed with an increase in the heat treatment temperature, showing a value closest to the stress-free value at 900 °C. This confirmed that impurities in the crystal were effectively controlled under this condition via the variation for the YL band of the PL and  $A_1(\text{LO})$  Raman modes. When annealing at a temperature of 1,000 °C, the effect of annealing was found to have decreased upon an evaluation of the optical properties and residual stress. This likely occurred due to nitrogen vacancies which were generated given the nitrogen dissociation that occurred at a high temperature and functioned as defects. All things considered, the relaxation of the residual stress and the crystallinity are superior when the heat treatment takes

place at 900 °C and lasts for three hours in the case of a bulk GaN substrate with a thickness of 1 mm. Therefore, it could be confirmed that the optical properties were most effectively improved because the effect of annealing was best under the this condition.

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