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Thick GaN Epitaxial Growth with Low Dislocation Density by Hydride Vapor Phase Epitaxy

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Thick GaN layers were grown by hydride vapor phase epitaxy (HVPE) with the aim of using these layers as a homoepitaxial substrate to improve device quality of laser diodes or light emitting diodes. HVPE is very useful for thick layer growth since the growth rate can reach from several ten up to one hundred micron per hour. In this experiment, the growth began as selective growth through openings formed in a SiO_2 mask. Facets consisting of $\{1\bar{1}01\}$ planes were formed in the early stage and a continuous film developed from the coalescence of these facets on the SiO_2 mask. As a result, GaN layers with a dislocation density as low as $6 \times 10^7\,\mathrm{cm}^{-2}$ were grown on 2-inch-diameter sapphire wafers. These GaN layers were crack-free and had mirror-like surface.

KEYWORDS: GaN, vapor phase epitaxy, sapphire, dislocation, photoluminescence, selective growth, facet

1. Introduction

Recently, blue- or ultraviolet-light-emitting lasers have been developed using GaN and InGaN-based compound semiconductors.[1–3] These device structures have been grown mainly on sapphire, although its lattice parameter and thermal expansion coefficient differ greatly from those of GaN or InGaN. Due to the lattice-mismatch and the difference in the chemical nature between the sapphire and GaN, many threading dislocations that extend along the *c*-axis of grown GaN films from the interface between the substrate and epitaxial layer have been reported to occur.[4] The dislocation density has been reported to be on the order of $10^{10}\,\mathrm{cm}^{-2}$. Although the effect of these defects on the device characteristics has not yet been investigated, the device quality should be improved by decreasing the number of these defects.

The best way to avoid defect generation at the interface is to use a GaN substrate. Several attempts to grow bulk GaN crystal have been reported. Porowski *et al.* have succeeded in synthesizing GaN bulk crystal by using high pressure (15 to 20 kbar) and high temperature (1400 to 1600°C).[5] These crystals were reported to be practically free of extended defects. However, the crystal size was still limited to less than 17 mm × 10 mm and a long growth time was required. Another approach is to grow thick epitaxial layers. Kurai *et al.* used the sublimation method to obtain small GaN crystal with diameter of a few hundred microns and thicknesses of $\sim 40\,\mu$m on a sapphire substrate.[6] Utilizing hydride vapor phase epitaxy (HVPE) with GaCl and NH_3,[7–9] Detchprohm has grown several-hundred-micron-thick GaN on a sapphire substrate with a ZnO buffer layer.[10] They obtained GaN films that were several millimeters square, which were peeled off from the sapphire substrate. The advantage of the HVPE is high growth rate which is suitable to grow the bulk crystal. In addition, high quality GaN layers can be obtained. Optical properties of these films are among the best ever reported.[7,11] However, it has been reported that the occurrence of cracks was observed in the HVPE-grown GaN layers thicker than $20\,\mu$m.[12]

In this paper, we achieved thick GaN layer growth on a 2-inch diameter sapphire substrate without cracks by using HVPE. The thick layer was grown on a GaN thin layer on the sapphire substrate, where the thin layer was previously grown by MOVPE (metalorganic vapor phase epitaxy). Selective growth was carried out at the beginning of the growth. The coalescence of the selectively grown regions made it possible to achieve flat surface over the entire substrate. As a result, crack-free GaN films with a mirror-like surface were successfully grown in the thickness range of several ten to few hundred microns. In addition, the extended defect density along the *c*-axis was found to be largely suppressed.

2. Experimental

The GaN growth was carried out with a conventional HVPE system using a horizontal quartz reactor having an inner diameter of 75 mm. The Ga source was GaCl formed by the reaction between Ga metal and HCl gas. The Ga metal was positioned in the upstream region of the reactor. The temperature of the Ga metal was maintained at 850°C. The substrate holder was set in the downstream region of the reactor, where the GaCl and NH_3 were mixed. GaCl partial pressure in the substrate region was varied from 2.6×10^{-3} to 1.1×10^{-2} atm by changing HCl flow rate over the Ga metal. The NH_3 was supplied as the N source at a partial pressure of 0.26 atm. The total flow rate including the H_2 carrier gas was 3800 sccm. The substrate temperature was kept constant at 1000°C during the growth. A schematic diagram of the substrate structure is shown in Fig. 1. We used 2-inch-diameter sapphire wafers with a 1- to $1.5\,\mu$m-thick GaN layer on top as the substrates. The thin GaN layer was previously grown by low-pressure MOVPE with conventional two-step growth, which consisted of a 20-nm-thick low-temperature GaN buffer layer and a high-temperature GaN layer. After the deposition of a SiO_2 film by CVD at 430°C on the MOVPE-grown GaN layer, window stripes with a period of $7\,\mu$m aligned along the $\langle 11\bar{2}0\rangle$ direction of the GaN layer were fabricated by the standard photolithographic method. The mask width ranged from 1 to $4\,\mu$m. Prior to the growth, the surface was treated with acetone and alcohol in an ultra-sonic cleaning bath, then the wafer was dipped into HCl solution. After being rinsed in deionized water, the

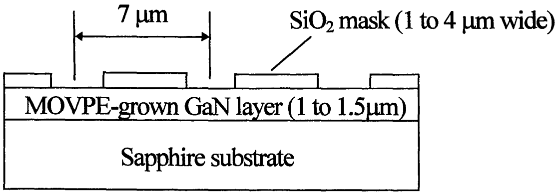


Fig. 1. Schematic diagram of the substrate structure used in this experiment.

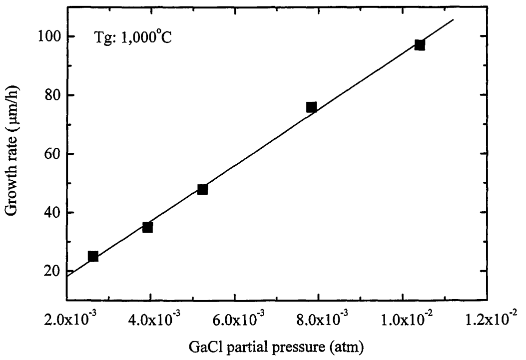


Fig. 2. The dependence of the GaN growth rate on the HCl partial pressure over the Ga metal. The growth temperature was 1000°C.

substrate was dried in a N_2 gas flow. After being set in the reactor, the substrate was heated to 1000°C under the NH_3 atmosphere. The growth was initiated by supplying HCl gas over the Ga metal.

3. Results and Discussions

Figure 2 shows the dependence of the GaN growth rate on the GaCl partial pressure at a growth temperature of 1000°C. The partial pressure of NH_3 was 0.26 atm. The growth rate increased linearly as the HCl partial pressure rose and reached about 97 μm/h at 1.0×10^{-2} atm. However, the surface morphology became rough when the growth rate rose to 75 μm/h or higher. Therefore, the growth was mainly carried out under a growth rate of about 50 μm/h with a HCl partial pressure of 5.2×10^{-3} atm. Figure 3(a) shows an SEM image of the facet structure as it appeared after 2.5 min of growth. Kato *et al.* have already described the GaN selective growth on 10 μm-wide windows in the $\langle 11\bar{2}0 \rangle$ direction of a GaN layer.[13] They found that the sidewalls of the facet consisted of $\{1\bar{1}01\}$ planes. We observed the same structure, as shown in Fig. 3(a). On the sidewall of the $\{1\bar{1}01\}$ facets, a fringe pattern was observed. This pattern appears to consist of giant steps that may have appeared due to the misorientation of window stripes from the $\langle 11\bar{2}0 \rangle$ direction. Figure 3(b) shows an SEM image of the surface after 5 min of growth. The overgrowth of facets was proceeding on the SiO_2 mask, with the facets keeping their shape and the coalescence with neighboring facets was just beginning to occur. As the growth continued, the gap between the $\{1\bar{1}01\}$ facets was filled and finally a flat (0001) surface started to develop, as shown in Fig. 3(c). This SEM image was taken from a sample grown for 10 min. Further growth completely filled the

(a)

(b)

(c)

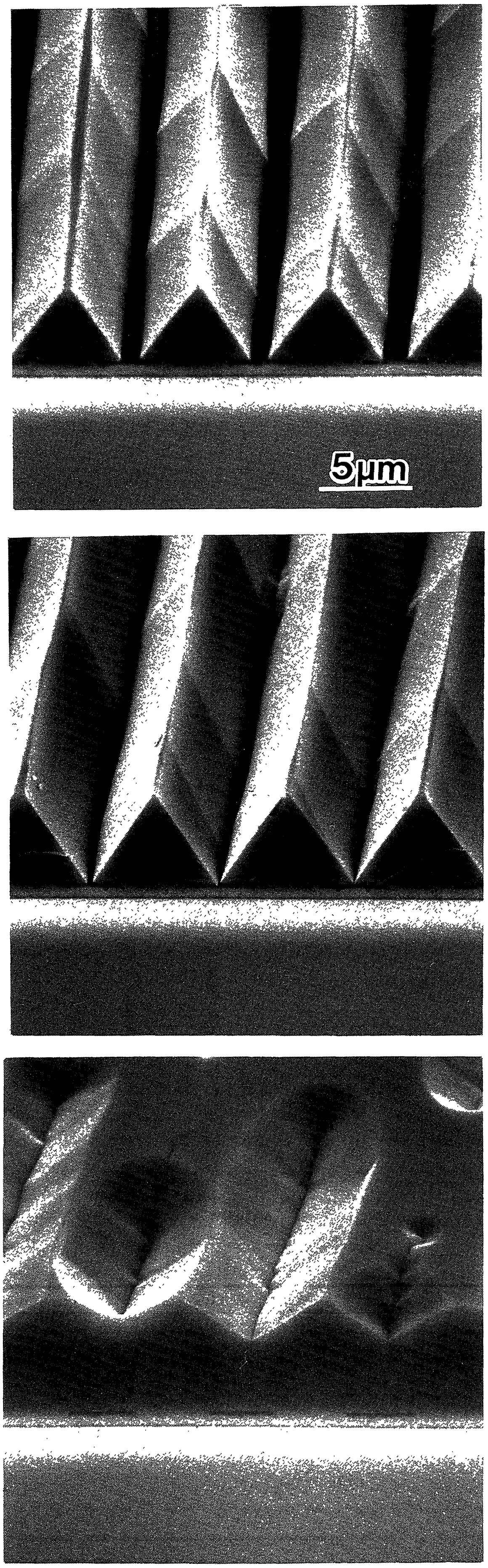
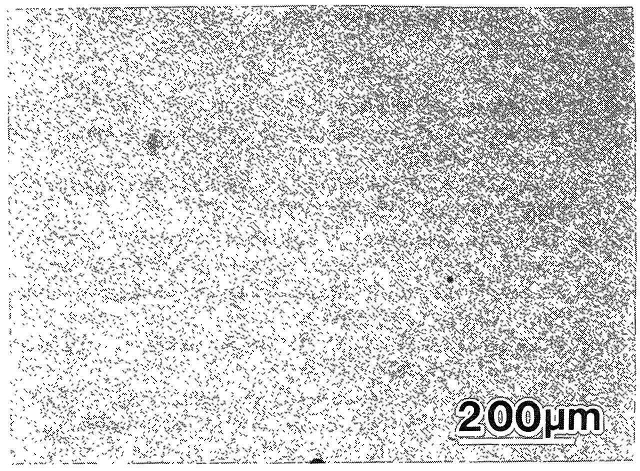
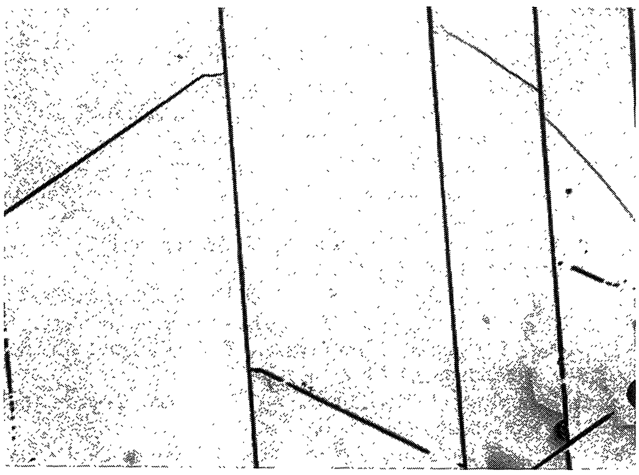


Fig. 3. SEM images of grown surfaces after (a) 2.5 min of growth, (b) 5 min of growth, and (c) 10 min of growth.



(a)



(b)

Fig. 4. Photomicrographs of grown surfaces (a) grown by the proposed method, and (b) grown by conventional HVPE.

gap and a flat surface appeared. Figure 4(a) shows a surface photomicrograph of a 26-μm-thick GaN layer grown by this method, and the surface morphology of a 30-μm-thick GaN layer grown by conventional method without the selective growth is shown in Fig. 4(b). The surface in Fig. 4(a) was mirror-like and no cracks were observed. In contrast, many cracks, which were appeared as dark lines in Fig. 4(b), were observed in the conventional-growth sample. A part of the grown layer was peeled off along cracks. Thus, our proposed growth method prevented formation of cracks in the GaN layer, which are considered to be induced by the thermal-expansion-coefficient difference between the sapphire substrate and the GaN layer.

We examined the defect density by TEM observation. By plan-view TEM observations, we determined the threading dislocation density in the grown film. Figure 5 is a typical plan-view image showing the region in the vicinity of the surface of a 140 μm-thick GaN film. The end-on dislocations are imaged as dark dots or short-segments and they are accompanied by bend-contours. The dislocation density of this sample was determined to be as low as $\sim 5 \times 10^7$ cm^{-2} from this figure. The average value was found to be around 6×10^7 cm^{-2}. As the

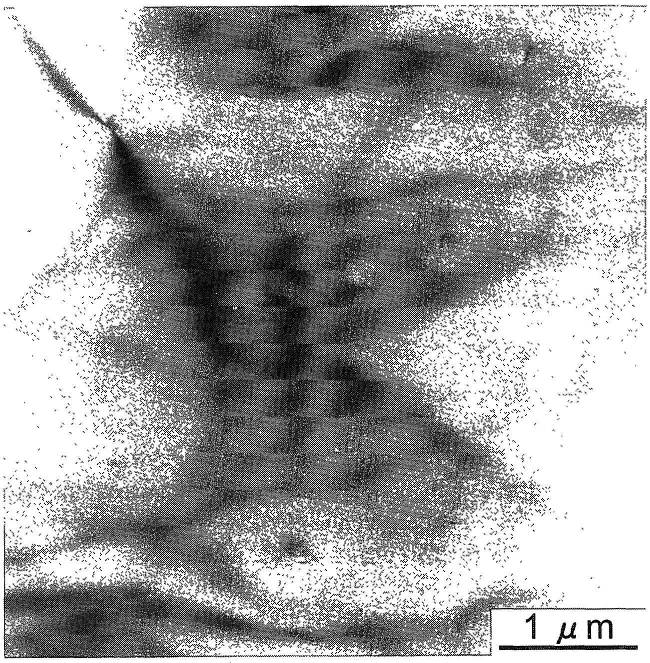


Fig. 5. Plan-view TEM image showing the region in the vicinity of the surface of a 140 μm-thick GaN film. Dark dots or short-segments show the end-on dislocations.

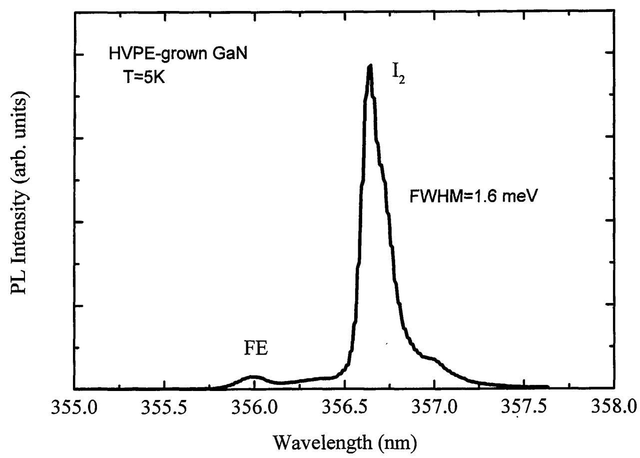


Fig. 6. Low temperature PL spectrum of 80-μm-thick GaN grown by HVPE.

dislocation density of the conventional GaN was in the 10^9 to 10^{10} cm^{-2} range, we believe that the crack formation is related to the dislocation density. It has been reported that the coalescence of small GaN islands produce a large number of dislocations that extend through grown layers.[14] Therefore, such a GaN layer will have little resistance to the strain caused by the thermal-expansion-coefficient difference. However, the reduction in the number of threading dislocations when our proposed method is used should make the GaN layer harder. Mechanism responsible for this reduction will be discussed elsewhere.

The mask width was varied from 1 to 4 μm while the stripe period remained 7 μm. However, this change affected the growth very little.

Figure 6 shows the 5 K photoluminescence (PL) spectrum of an 80-μm-thick GaN layer that was separated from a sapphire substrate. PL measurements were per-formed by using the 325-nm line of He–Cd laser. Excitation power was about 2 mW. The strong band-edge emission due to excitons bound to neutral donors, I_2, was observed at 356.6 nm. The peak had a full width at half maximum (FWHM) as narrow as 1.6 meV. The free-exciton emission, *FX*, was also clearly observed. The intensity of the deep emission was three orders of magnitude lower than that of the main peak. These results indicate that thick GaN with excellent optical quality can be fabricated by our proposed method.

4. Conclusion

Using a hydride VPE system, thick GaN with a dislocation density as low as $6 \times 10^7\,cm^{-2}$ was successfully grown. The growth began with selective growth at stripe openings formed in a SiO_2 mask. The continuous film was grown by the coalescence of a selectively grown facet structure. A crack-free mirror-like surface was obtained on a 2-inch-diameter wafer. Photoluminescence measurements showed a very strong band-edge emission with a narrow FWHM of 1.6 meV and distinct free-exciton emission was observed. By using the thick GaN as a substrate, the crystalline quality for InGaN/GaN laser diodes and light emitting diodes could be significantly improved.

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1) S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku and Y. Sugimoto: Jpn. J. Appl. Phys. **35** (1996) L74.
2) I. Akasaki, S. Sota, H. Sakai, T. Tanaka, M. Koike and H. Amano: Electron. Lett. **32** (1996) 1105.
3) K. Itaya, M. Onomura, J. Nishino, L. Sugiura, S. Saito, M. Suzuki, J. Rennie, S. Nunoue, M. Yamamoto, H. Fujimoto, Y. Kokubun, Y. Ohba, G. Hatakoshi and M. Ishikawa: Jpn. J. Appl. Phys. **35** (1996) L1315.
4) S. D. Lester, F. A. Ponce, M. G. Craford and D. A. Steigerwald: Appl. Phys. Lett. **66** (1995) 1249.
5) S. Porowski, J. M. Baranowski, M. Leszczynski, J. Jun, M. Bockowski, I. Grzegory, S. Krukowski, M. Wroblewski, B. Lucznik, G. Nowak, K. Pakula, A. Wysmolek, K. P. Korona and R. Stepniewski: *Proc. Int. Symp. Blue Laser and Light Emiting Diodes, Chiba, 1966* (Ohmsha, Tokyo, 1966) p. 38.
6) S. Kurai, Y. Naoi, T. Abe, S. Ohmi and S. Sakai: Jpn. J. Appl. Phys. **35** (1996) L77.
7) K. Naniwae, S. Itoh, H. Amano, K. Itoh, K. Hiramatsu and I. Akasaki: J. Cryst. Growth **99** (1990) 381.
8) W. Götz, L. T. Romno, B. S. Krusor, N. M. Johnson and R. J. Molnar: Appl. Phys. Lett. **69** (1996) 242.
9) Yu. V. Melnik, I. P. Nikitina, A. S. Zubrilov, A. A. Sitnikova, Yu. G. Musikhin and V. A. Dmitriev: Inst. Phys. Conf. Ser. **142** (1996) 863.
10) T. Detchprohm, K. Hiramatsu, H. Amano and I. Akasaki: Appl. Phys. Lett. **61** (22) 2688.
11) D. Volm, K. Oettinger, T. Streibl, D. Kovalev, M. Ben-Chorin, J. Diener, B. K. Meyer, J. Majewski, L. Eckey, A. Hoffmann, H. Amano, I. Akasaki, K. Hiramatsu and T. Detchprohm: Phys. Rev. B **53** (1996) 16543.
12) K. Hiramatsu, T. Detchprohm and I. Akasaki: Jpn. J. Appl. Phys. **32** (1993) 1528.
13) Y. Kato, S. Kitamura, K. Hiramatsu and N. Sawaki: J. Cryst. Growth **144** (1994) 133.
14) X. J. Ning, F. R. Chien, P. Pirouz, J. W. Yang and M. A. Khan: J. Mater. Res. **11** (1996) 580.