

A Systematic study on the growth of GaN single crystals using the Na-based flux method

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To obtain bulk gallium nitride (GaN) single crystals applicable as the substrate for GaN homoepitaxial growth, we have adopted the Na flux method with some modifications. Assuming that a key reaction of this method is nitrogen dissolution into a flux, we considered both the gas composition and the liquid phase composition. The use of ammonia gas had effects in lowering the threshold pressure for the GaN growth compared with the nitrogen gas which had been used in the original Na flux method. The composition change from pure Na to a mixture of Ca and Na for the flux also brought some favorable effects such as lowering the threshold pressure, and an improvement in the crystal transparency. Finally, the liquid phase epitaxy (LPE) technique along with the Na-based flux method led to the growth of bulk GaN single crystals with much lower dislocation densities than the seed crystals.

Key words: Gallium nitride, GaN, the Na flux method, LPE, bulk, single crystal, dislocation density.

Introduction

Nitride-based semiconductors, represented by gallium nitride (GaN), have recently been paid much attention for their application in optical devices such as blue light emitting diode (LED) and blue/violet laser diode (LD) [1-3]. However, there have been no appropriate substrates for GaN because of its small lattice constant. So it was since the GaN buffer layer technique was established that research on GaN devices have evolved so intensely all over the world. Although comparatively better GaN growth is achieved by the introduction of the buffer layer, the high dislocation density on the heteroepitaxial GaN layer still remains a big problem. GaN bulk single crystals are thus in great demand as substrates for homoepitaxial growth to fabricate GaN thin films with low dislocation density. In general, the solution growth method has advantages for growing high-quality crystals. Porowski *et al.* reported that growing GaN single crystals in a Ga melt requires a high temperature and extremely high N₂ pressures [4, 5], which means that the liquid phase growth is impractical for industrial application. After that report, Yamane *et al.* confirmed that GaN single crystals could be obtained at relatively low temperatures of about 1000-1100 K and pressure of 5.0 MPa using a Na flux [6-9]. However, there are some problems in this method as listed below.

- (1) high nucleation density
- (2) low growth rate
- (3) still severe conditions, especially high pressure
- (4) black-color of the grown crystals.

With the purpose of giving solutions to these problems, we suggest some modifications to the original Na flux method. We would like to report here the series of our studies on the development of GaN growth in the liquid phase. Our final goal is to grow bulk GaN single crystals usable as substrates for the homoepitaxial growth.

The modification of the reaction gas in the Na flux method

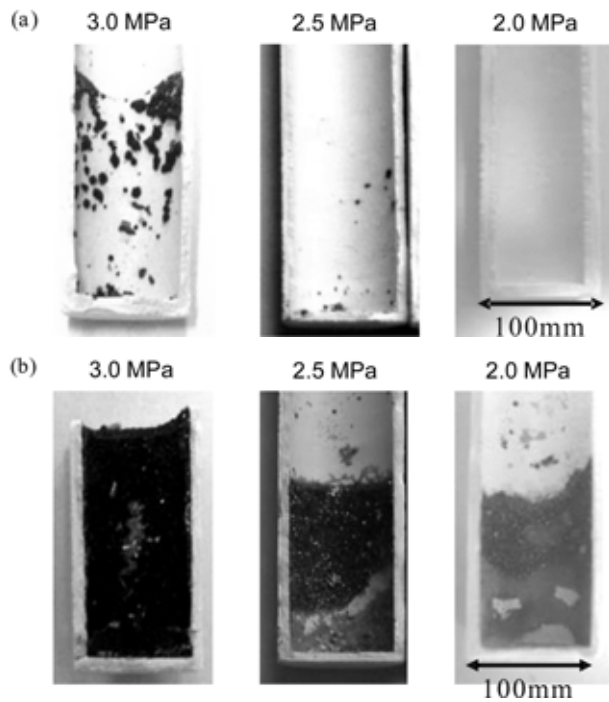
The Na flux method as well as the high pressure solution growth (HPSG) method by Porowski *et al.* supplies the nitrogen solute from the gas phase and so, if the amount of nitrogen dissolved in the solution is increased, the problems concerning the growth rate and the threshold pressure for growing GaN will be solved. Nitrogen dissolution in an iron melt can be increased by two orders of magnitude by dissolving nitrogen radicals instead of nitrogen itself [10, 11]. "Based on this, it should be easier to increase the nitrogen content in a Na-Ga melt by using ammonia as an ambient gas than using nitrogen because ammonia is more readily dissociated into nitrogen radicals and hydrogen". Therefore, we attempted to decrease the threshold pressure necessary for nucleation by using ammonia gas.

The experimental details may be found in [12]. To investigate the threshold pressure necessary for nucleation,

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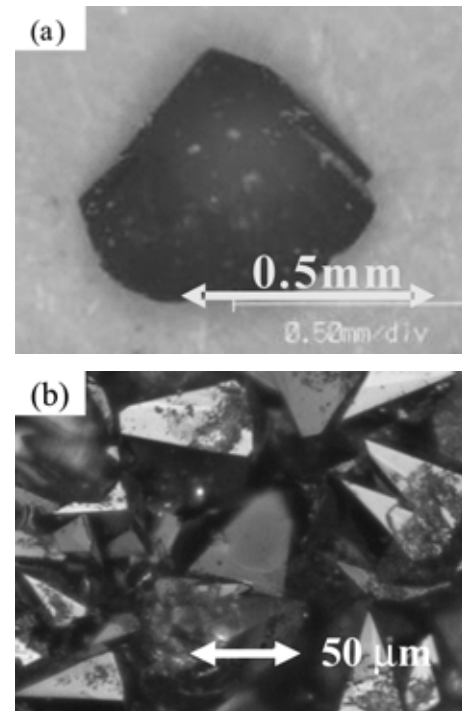
Table 1. The conditions for the experiments with ammonia gas

flux composition	Ga : Na = 0.21 : 0.79
reaction gas	NH ₃ : N ₂ = 4 : 96
temperature	1073 [K]
pressure	1.5, 2.0, 2.5, 3.0 [MPa]
growth period	96 [h]
crucible	BN

**Fig. 1.** (a) GaN single crystals grown on a crucible wall using 100% N₂ gas. (b) GaN single crystals grown on a crucible wall using 4% NH₃ gas diluted with N₂ gas.

we gradually changed the growth pressure. Table 1 shows the experimental conditions. The confirmation of GaN single crystals in this study was made by X-ray powder diffraction (XRD) (Rigaku, RINT 2500) and they were observed with an optical microscope.

Figure 1 shows the GaN single crystals grown on the crucible wall in the growth with 4% ammonia gas and pure nitrogen gas. In Figure 1(a), which shows the results from the growth with pure nitrogen gas, GaN cannot be grown under 2.5 MPa. Meanwhile, 4% ammonia gas is confirmed to generate GaN even at 2.0 MPa, represented in the lower figures in Fig. 1(b). From these results, we can conclude that the ammonia gas decreases the threshold pressure for synthesizing GaN crystals. Figure 2 compares crystals grown in different ambient gases at 2.5 MPa pressure. Figure 2(a) presents an optical micrograph of GaN single crystals grown in pure nitrogen gas Fig. 2(b) presents those grown in nitrogen gas with 4% ammonia gas. Although the amount of GaN synthesized in 4% ammonia gas was much larger than that synthesized in pure nitrogen, the average size of GaN single crystal

**Fig. 2.** (a) Optical micrograph of a GaN single crystal grown using N₂ gas. (b) GaN single crystals grown using 4% NH₃ gas.

grown in 4% ammonia gas (0.1 mm) was smaller than that grown in pure nitrogen gas (0.3 mm). Mixing ammonia into the reaction gas dramatically promoted GaN nucleation. This suggests that ammonia gas dissolved more easily into the Ga-Na melt than nitrogen.

The modification of the flux composition from Na to the Na-Ca mixed flux

Since it was shown that a consideration of the gas composition is important in the Na flux method, the next question is whether or not the Ga-Na flux is the best choice as the solvent. In this section, the flux composition is changed from Na to a Na-Ca system. Details of the experimental apparatus may be found in [13]. Calcium was chosen as the additive because of its easiness for chemical treatment, the reactivity with the crucible and also the harmlessness when included in the crystals. Ca percentage in the flux was varied from 0 to 35%. Table 2 presents the experimental conditions for varying the Ca ratio. Also the threshold pressure for the Na-Ca system was investigated. The experimental conditions for the determination of the threshold pressure are summarized in Table 3.

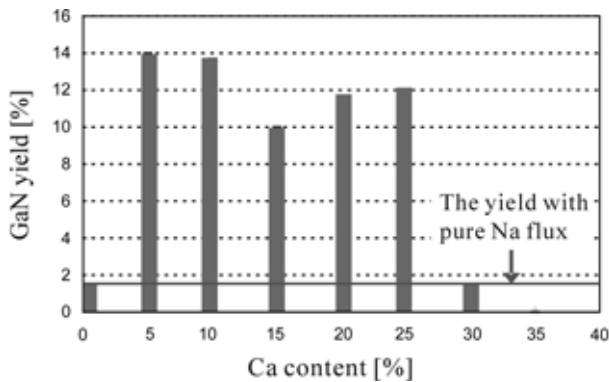
Figure 3 presents the changes in the yield of GaN as a function of the ratio of Ca, where the yield is calculated as the conversion efficiency when GaN is synthesized from metallic Ga. The pressure applied in this experiment was 3.0 MPa throughout. The yield was 1.3% in the pure Na and increased with increasing

Table 2. The conditions for the experiments varying the Ca ratio in the Ca-Na mixed flux

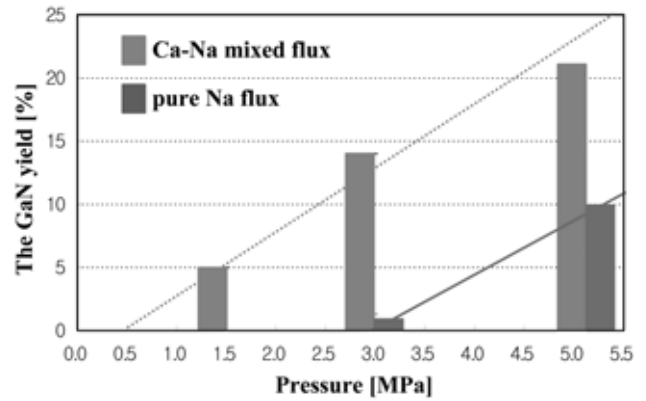
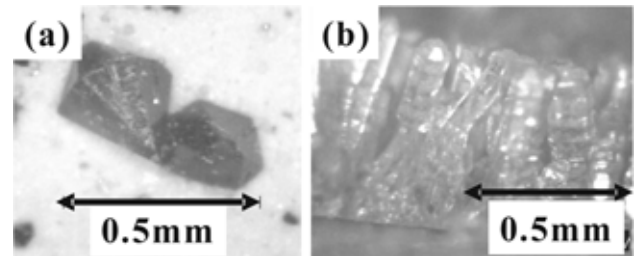
starting materials	Ga : flux = 0.27 : 0.73
flux composition	Na : Ca = 100 : 0
	95 : 5
	90 : 10
	85 : 15
	80 : 20
	75 : 25
	70 : 30
	65 : 35
ambient gas	N ₂
temperature	1073 [K]
pressure	3.0 [MPa]
growth period	96 [h]
crucible	BN

Table 3. The conditions for the experiments varying the pressure applied for the growth in the 10% Ca mixed flux

starting materials	Ga : flux = 0.27 : 0.73
flux composition	Na : Ca = 90 : 10
ambient gas	N ₂
temperature	1073 [K]
pressure	1.5, 3.0, 5.0 [MPa]
growth period	96 [h]
crucible	BN

**Fig. 3.** A relationship between the flux composition and the yield of GaN.

Ca ratio and reached 13.9 mol% at a Ca ratio of 5 mol%. However, when the Ca ratio exceeds 10 mol%, the yield decreases with the Ca ratio increasing. Finally GaN was not synthesized when the Ca ratio exceeded 35 mol%. Figure 4 illustrates changes in the yield as a function of pressure. The dotted line indicates the yield synthesized with 10 mol% of Ca and the solid line without Ca. Although the yield increased with applied pressure with or without Ca, the yield obtained in the Na-Ca flux was higher than that obtained in the pure Na flux at every pressure applied in this experiment. Furthermore, the threshold pressure for synthesizing GaN was reduced to about 1.0 MPa by using 10 mol%

**Fig. 4.** Changes in the yields of GaN synthesized in pure Na flux and Ca 10 mol% mixed flux according to the reaction pressure. Dotted line: Ca 10 mol% mixed flux. Solid line: Pure Na flux.**Fig. 5.** (a) Optical micrograph of GaN single crystals grown in the Na flux. (b) GaN single crystals grown in the Ca-Na mixed flux.

of Ca flux. Another advantage of using the Ca-mixed flux is that transparent GaN crystals can be easily obtained. Figure 5(a) illustrates an optical microscopic image of GaN single crystals grown in a Na flux, and Fig. 5(b), the crystals grown in the flux containing 3 mol% Ca. The crystals grown in the mixed flux become much more transparent than those in the pure Na flux. We have not discovered why Ca has such a function yet. Note that the crystals grown in the flux containing Ca were relatively small. Ca might somehow cause a high supersaturation in the flux. Then the transparency can be attributed to modifying the nitrogen vacancy concentration and also the smaller crystals may be attributed to the high nucleation frequency caused by high supersaturation.

The effects of Ca in the flux system on growth of GaN are summarized as follows.

- 1) If the flux composition is changed from Na to Na-Ca and the ratio of Ca to flux is below 10 mol%, the yield of GaN grown at 1073 K is much higher than that grown in pure Na flux.
- 2) Excessive Ca in the flux system decreases the yield of GaN.
- 3) GaN single crystals grown in the flux containing Ca tend to be transparent.

Results 2) and 3) can be explained by examining the phase diagram, which shows that solids and liquids coexist at 1073 K in a 10% Ca-Na system. Although the state of the Ca-Ga-Na system at 1073 K is not clear

because of the absence of the phase diagram, dissolution of nitrogen in the flux system seems to be prevented by the solid-state compound at high Ca molar ratios. Furthermore, solid-state Ca reacts to form Ca_3N_2 in a nitrogen atmosphere at high temperatures. This could be why the crystal growth is prevented at the higher Ca ratio. However, for 10 mol% of Ca at 1073 K, the effect of Ca on promoting the growth of GaN in the flux system is quite clear. This can be considered as a result of promoting dissolution of nitrogen in the flux due to Ca in the solution. We suspect that the strong reduction power of Ca promotes nitrogen dissolution. These mechanisms will be a future issue. Another effect of Ca is to synthesize transparent GaN. Some researchers have reported that GaN with many nitrogen vacancies tends to be black [14]. If Ca promotes nitrogen dissolution into a flux, the nitrogen concentration should increase considerably, which results in the synthesis of transparent GaN crystals with few nitrogen vacancies.

Application of the LPE technique to the Na-based flux method

The combination of the LPE technique and the Na flux

We have succeeded in relaxing the GaN growth conditions and also improving the transparency of the crystals by considering the composition of both the gas and the liquid phases. However, it is still difficult to obtain large bulk GaN single crystals. In this section, we report our attempt to apply the liquid phase epitaxy (LPE) method with the Na flux to grow large, high-quality GaN single crystals. A (0001) 3 μm -thick GaN thin film for the LPE substrate grown on a sapphire (0001) substrate by the metal organic chemical vapor deposition (MOCVD) method was used as a substrate for the LPE growth. The experimental details are given in [15]. The experimental conditions are summarized in Table 4.

Figure 6 depicts a cross-sectional optical microscopic image of a GaN crystal grown at 5.0 MPa with pure nitrogen gas. The GaN crystal grew much larger than the MOCVD-GaN thin film in the horizontal direction, and grew to a thickness of 500 μm in the vertical

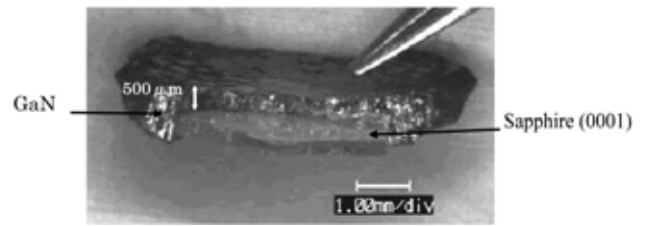


Fig. 6. Cross-sectional image of the bulk GaN single crystal grown on 3 μm -thick GaN thin film.

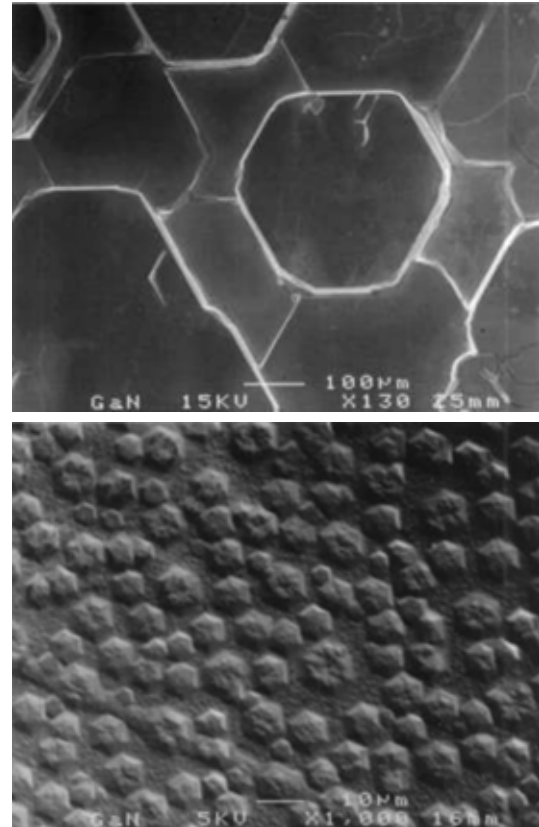


Fig. 7. (a) Surface morphology of bulk GaN treated in 503K with $\text{H}_2\text{PO}_4\text{-H}_2\text{SO}_4$ (1:1) solution for 10 minutes. (b) Etch pits on MOCVD-GaN produced by chemical etching in $\text{H}_2\text{PO}_4\text{-H}_2\text{SO}_4$ (1:1) solution for 10 minutes.

direction (c-direction). However, the grown GaN layer was black as the nuclei grown at other locations and on the crucible wall.

Dislocation density of the bulk LPE-GaN was investigated by a chemical-etching method. The grown bulk GaN and 3 μm -thick MOCVD-GaN film were etched chemically at 503 K for 10 minutes with an etchant, a mixture of H_2PO_4 and H_2SO_4 in the ratio of one to one. Figure 7(a) and 7(b) present scanning electron microscope (SEM) images of the bulk GaN grown by the LPE technique and MOCVD-GaN film after the etching treatment, respectively. Despite a large number of etch pits ($1.3 \times 10^6/\text{cm}^2$) on the MOCVD-GaN film, no etch pits were observed on the bulk LPE-GaN surprisingly. Given the etching conditions, these etch pits seem to represent screw dislocations included

Table 4. The conditions for the LPE experiments using the pure Na flux

starting materials	Ga : Na = 0.27 : 0.73
the seed crystal	3 μm -thick (0001) MOCVD-GaN grown on sapphire substrate
ambient gas	N_2
	1073 [K]
	5.0 [MPa]
growth period	96 [h]
crucible	BN

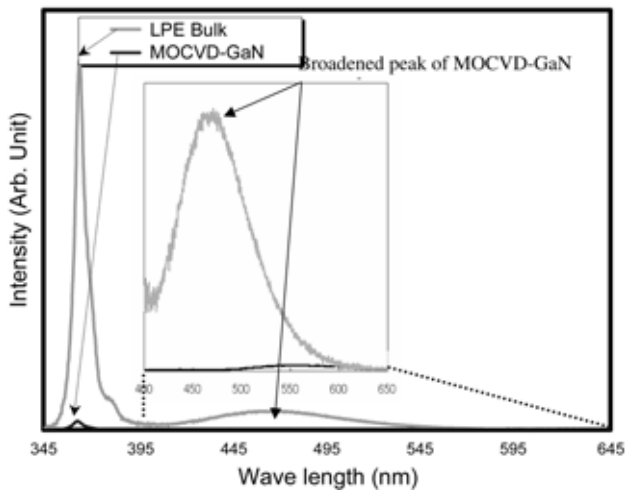


Fig. 8. Photoluminescence spectra of bulk GaN grown by LPE and MOCVD-GaN. PL spectra without band-edge luminescence are separately indicated with a changing vertical scale in the box.

in the GaN crystal. Although we cannot precisely determine the dislocation density, the dislocation density of the bulk LPE-GaN seems extremely low for an unknown reason.

Figure 8 depicts the results of photoluminescence (PL) measurements of the MOCVD-GaN thin film used as a substrate, and the LPE-GaN. A He-Cd laser (10 mW, 325 nm) was used as the pumping source and the measurement was conducted at room temperature. The PL intensity of the bulk LPE-GaN crystal was 40 times stronger around 360 nm than that of the MOCVD-thin film, indicating that the crystal quality of GaN grown by LPE was much greater than the MOCVD-GaN substrate. It was reported that screw dislocations included in GaN crystals affected the PL intensity [16]. A broadened peak around 550 nm was detected in the MOCVD-GaN, while the LPE-GaN did not emit at the same position. However, the LPE-GaN had a strong broadened peak at around 470 nm. The strong green luminescence of LPE-GaN was visually confirmed when the He-Cd laser irradiated the samples. Currently we are investigating the origins of the conspicuous increase of PL intensity and of the strong broadened peak at around 470 nm of the bulk LPE-GaN. These observations indicate that the LPE method can give GaN single crystals with commercially-usable quality. The bulk GaN grown at 5.0 MPa with pure nitrogen gas can be used as the substrate for growing GaN film in the vapor phase because this large crystal had few dislocations.

The LPE technique with the Ca-Na mixed flux

We have reported that in the Na flux method, a change in the flux composition to Ca-Na enables us to grow transparent GaN crystals. Concerning the size problem, it was confirmed in the previous section that large GaN single crystals can be grown by applying the

Table 5. The conditions for the LPE experiments using the Ca-Na mixed flux

starting materials	Ga : flux = 0.27 : 0.73
flux composition	Na : Ca = 97 : 3
seed crystal	3 μ m-thick (0002) MOCVD-GaN grown on sapphire substrate
ambient gas	N ₂
temperature	1073 [K]
pressure	1.0, 5.0 [MPa]
growth period	96 [h]
crucible	BN

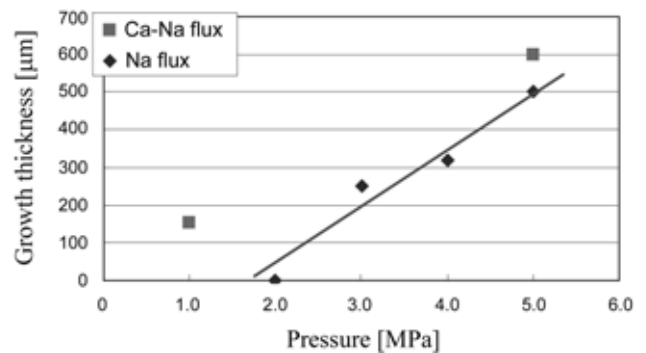


Fig. 9. Relationship between applied nitrogen pressure and LPE-GaN thickness grown in a Na and a Ca-Na mixed flux system.

liquid phase epitaxy (LPE) method in a Na flux. So it is natural to attempt the LPE growth in the Ca-Na mixed flux system.

The experimental setup is given in [17]. The flux used in this study was Ca, Ga and Na in the ratio of 38 to 3 to 100, respectively. 3 μ m-thick MOCVD-GaN film grown on sapphire was placed in a Boron Nitride (BN) crucible. The experimental conditions are shown in Table 5.

Figure 9 indicates a dependency of the growth rate on the applied nitrogen pressure. Although quantitative consideration is impossible since the ratio of Ga in the solution varies with the consumption of Ga, it was found that the growth rate of the LPE growth in the Na-based flux method is almost proportional to the nitrogen pressure and that the threshold pressure needed to generate GaN in the Na flux is about 2.0 MPa. On the other hand, in the Ca-Na mixed flux, 150 μ m-thick-GaN film could be grown even at 1.0 MPa (in Fig. 10), at which GaN growth was impossible with the Na flux. 600 μ m-thick GaN film was grown at 5.0 MPa in the Ca-Na mixed flux. We have previously reported that most of the LPE films are black in color, which is attributed to the nitrogen vacancies. Figure 11 shows a photograph of the LPE film grown at 5.0 MPa in the Ca-Na mixed flux system. A portion of the early stage of LPE growth was somewhat colored because that is the growth in a low nitrogen concentration. However, the major part of the crystal was completely

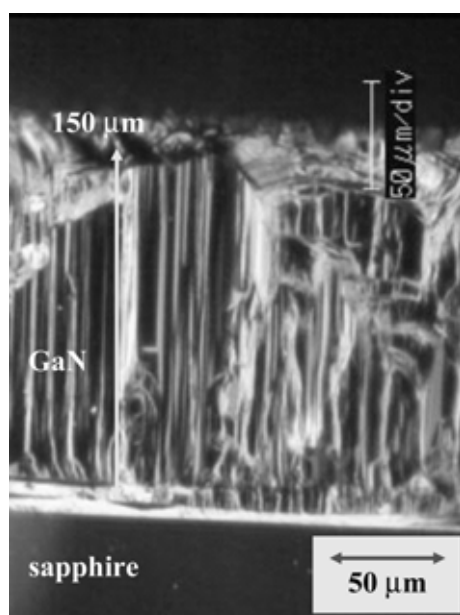


Fig. 10. A cross-sectional image of the LPE-GaN film grown at 1.0 MPa in the Ca mixed flux. Under 1.0 MPa, we cannot obtain GaN single crystals using the Na flux.

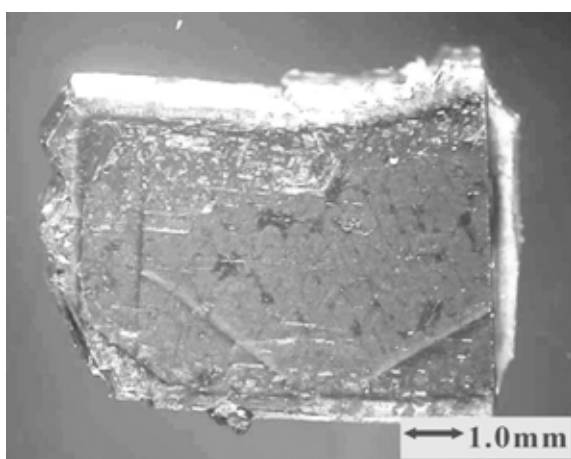


Fig. 11. Transparent LPE-GaN film grown in a Ca-Na mixed flux.

transparent. Figure 12 shows a differential interference microscope (DIM) photograph of the surface of an LPE crystal etched chemically at 503 K with an acidic etchant for 10 minutes. This crystal was grown in the Ca-Na mixed flux system under 5.0 MPa for 96 h. Although the etch pits on the surface are distributed randomly, it was found that there is a partial area with no etch pits, i.e. an area free from dislocation density. Considering the dislocation density to be of the order of $10^8/\text{cm}^2$ for the MOCVD-GaN used as the substrate, dislocations in GaN were remarkably reduced by the LPE growth. Figure 13 indicates the results of PL intensity of the LPE-GaN grown in the Ca-Na mixed flux under 5.0 MPa, that grown in the Na flux under 5.0 MPa, and that of the MOCVD-GaN. A He-Cd laser (325 nm, 10 mW) was used as a pumping source. The

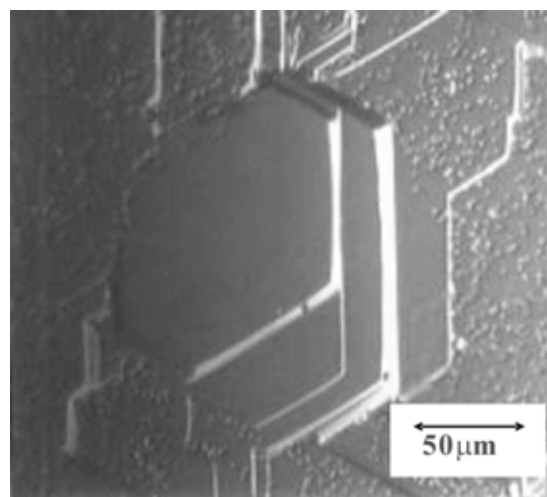


Fig. 12. DIM photograph of LPE-GaN surface etched in 503K with phosphoric- and sulfuric mixed acid.

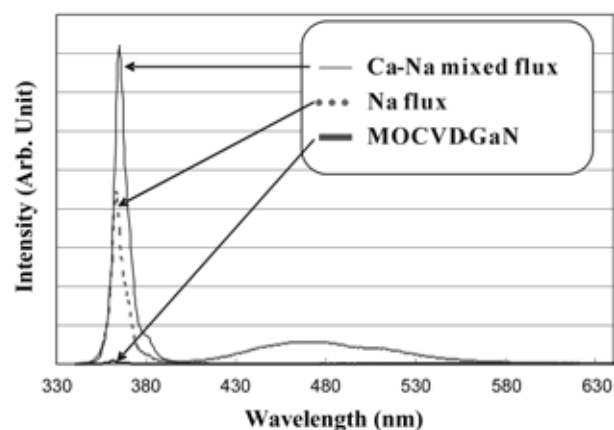


Fig. 13. Comparison of photoluminescence measurements of LPE-GaN grown in a Na or a Ca-Na flux and MOCVD-GaN.

intensities of the band-edge emission of the LPE-GaN grown in the Ca-Na mixed flux and that grown in the Na flux were 86 times and 47 times greater than that of MOCVD-GaN, respectively. A drastic increase of PL emission intensity by the LPE growth of GaN on MOCVD-GaN was confirmed. A PL emission of around 470 nm which was confirmed in the LPE-film grown in a Na flux disappeared by changing the flux composition to the Ca-Na mixed system for a still unknown reason. The results of LPE growth of GaN in a Na flux and a Ca-Na mixed flux carried out under the various pressures led to the following conclusions.

- 1) The threshold pressure of the LPE growth in the Na flux is about 2.0 MPa
- 2) In the Ca-Na mixed flux system, the LPE growth can progress at about 1.0 MPa.
- 3) A transparent LPE-GaN film is easily obtained by the growth in the Ca-Na mixed flux system.
- 4) The dislocation density in GaN can be drastically reduced by applying the LPE growth.
- 5) The intensity of the PL emissions of the LPE-GaN

is several ten-times greater than that of MOCVD-GaN.

Conclusions

We have carried out a study on how to obtain large GaN single crystals. Considering the reaction gas in the gas phase and the composition of the liquid phase leads us to the idea that nitrogen dissolution is a key process in the Na flux method. Using ammonia gas enables us to ease the growth conditions, especially pressure that is lowered to 1.0 MPa. Addition of Ca into the Na flux improves the crystal color and transparency and also decreases the threshold pressure for the growth. Finally the LPE technique was applied to the Na-based flux method. We succeeded in growing bulk GaN single crystals both in the pure Na and the Ca-Na mixed flux system. The dislocation densities of those crystals were much lower than the MOCVD grown seed crystal. The PL intensity of the LPE-GaN with the Na flux is 47 times greater than that of the seed crystal and the LPE-GaN with the mixed flux shows even greater PL intensity, 86 times as great as that of the seed crystal. We confirm that the Na flux method with our series of modifications is very effective in obtaining the large GaN single crystals with low dislocation densities.

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