Enhancement of lateral growth of the GaN crystal with extremely low dislocation density during the Na-flux growth on a point seed

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ABSTRACT Recently, we developed a Na-flux point seed technique for fabrication of large-diameter gallium nitride (GaN) crystals with low dislocation density. It may be possible to further reduce the dislocation density of crystals fabricated by this technique by reducing the point-seed (PS) density, because one dislocation remains on the *c* face of each grain grown on each point seed. Therefore, in order to realize coalescence growth by using a Multi-PS-GaN substrate with a low PS density, namely a long interval between neighboring point seeds, the lateral growth of each grain grown on a point seed must be enhanced. We attempted to promote the lateral growth of GaN crystals grown on a point seed by decreasing the flux thickness. As a result, we realized a high growth rate of 80 $\mu\text{m/h}$ along the *a* direction and a low aspect ratio by the Na-flux point seed technique. Moreover, almost no dislocations could be found in the lateral growth sector. Consequently, growth in a thin flux is applicable for the coalescence growth technique with low PS density and may be an outstanding approach for

reducing the dislocation density in GaN crystals grown by the Na-flux coalescence growth technique.

1. Introduction

Gallium nitride (GaN) has attracted much attention due to its desired properties, which make it applicable for ultraviolet laser diodes and high-power, high-frequency electronic devices [1~3]. However, in order to realize maximum device performance and low manufacturing costs of the devices, large-diameter GaN wafers with low dislocation density are needed [4,5].

In recent years, much effort has been expended in growing large-diameter GaN single crystals with low dislocation. Yoshida *et al.* demonstrated the growth of 4 inch-diameter, colorless freestanding *c*-plane GaN substrates with a dislocation density of $\sim 10^6 \text{ cm}^{-2}$ by a hydride phase epitaxy (HVPE) method [6]. Dwilinski and colleagues demonstrated the ammonothermal growth of GaN crystals with high crystallinity, large radius of lattice curvature ($>1000 \text{ m}$), and low dislocation density ($5 \times 10^3 \text{ cm}^{-2}$) [7,8]. We have attempted to fabricate large-diameter and low-dislocation-density GaN wafers by the Na-flux method and have succeeded in fabricating 2 inch freestanding GaN wafers with low dislocation density ($\sim 10^3 \text{ cm}^{-2}$) using Na-flux growth on a multi-point-seed-GaN (MPS-GaN) substrate [9,10]. This growth technique can effectively enlarge the diameter of GaN crystals by coalescing GaN crystals grown from many point seeds. In this technique, the shrinking of the *c* face in the growth process enables the coalescence of bunched steps, which leads to the gathering of threading dislocations, and results in a dramatic reduction of dislocations propagating from the seed crystal [11]. The dislocation density depends on the point-seed (PS) density because one dislocation remains on the *c* face of each grain grown on each point seed. Therefore, the reduction of the density of PS is one of the candidate approaches for a further reduction of dislocation density. In order to realize the coalescence growth by using MPS-GaN substrate

with a low density of PS, namely a long interval between neighboring point seeds, the enhancement of lateral growth of each grain grown on a point seed is needed.

Here, we attempted to promote the lateral growth of GaN crystals on a point seed by decreasing the flux thickness, a technique we designated Thin-Flux-Growth, which enabled us to promote of supply Ga and N sources in a the lateral direction. As a result, we realized a high growth rate of 80 $\mu\text{m/h}$ along the *a* direction by this technique. Moreover, almost no dislocations could be found in the lateral growth sector.

2. Experimental process

As shown in Fig. 1(a), a point-seed-GaN (PS-GaN) with a diameter of 1 mm was produced by etching an 8- μm -thick (0001) GaN layer (dislocation density: $10^8\sim 10^9\text{ cm}^{-2}$) grown on a (0001) sapphire substrate. The starting materials, namely metallic Ga (purity, 6N), metallic Na (purity, 4N), and graphite grains (purity, 6N), were added to an alumina (Al_2O_3) crucible in an Ar-filled glove box. Graphite grains were added to suppress heterogenous nucleation on the crucible wall [12]. The starting Ga:Na:C composition ratio was 27:73:0.5. Figures 1(b) and (c) show schematic drawings of the conventional method and the Thin-Flux-Growth used in this study, respectively. The thickness of flux, which was controlled by the amount of Ga, Na and C in the crucible, was kept at 2.5, 3.5 and 6.5 mm, respectively, while the conventional thickness is more than 6.5 mm.

After the crucible was transferred into a pressure-resistant stainless steel tube in a glove box, the tube was placed in a resistive heating unit set in a pressure-resistant chamber and connected to a N_2 gas line and the tube was evacuated. N_2 gas was first introduced into the tube at 1.0 MPa and the temperature of the tube was increased to 870°C over a 1 h period. After the temperature reached 870°C, N_2 gas was introduced up to 4.0 MPa and these conditions were maintained during the growth period of 120 h.

The tube was allowed to cool naturally, and the crucible and crystal were removed from the tube and immersed in cooled ethanol and water to dissolve the residual flux. The growth rate

was determined by the growth length in the a direction and growth period (120 h). The aspect ratio was calculated as the c axis length over the a axis length. Then, the crystal was sliced at the center parallel to the m face. Both samples were treated with chemical mechanical polishing (CMP) on the c - and m -faces to estimate the dislocation density of the c face, and to clarify the habit hysteresis, respectively. The dislocation density on the c face was estimated using an etch-decoration technique on the CMP surface. A eutectic alloy of KOH-NaOH (50% KOH and 50% NaOH) heated at 450°C was used as the etchant [13]. Etch pits were observed using a scanning electron microscope (SEM). The habit hysteresis was evaluated by panchromatic cathodoluminescence (CL) measurements on the m -face.

3. Results and discussion

Pyramidal or platelike crystals could be grown under each condition. Figures 2(a)~(c) show photographs of crystals grown at the flux thickness conditions of 2.5 mm, 3.5 mm and 6.5 mm, respectively. We called the crystal grown at the flux thickness conditions of 2.5, 3.5 and 6.5 mm samples A, B and C, respectively. These crystals were black in color, probably; due to the interband absorption of free electrons arising from point defects, such as oxygen impurities. The impurity concentrations in the crystal grown by Thin-Flux-Growth (Flux thickness: 2.5 mm) were [O]: 2×10^{18} atoms/cm³, [Si]: 1×10^{16} atoms/cm³, [C]: $<1 \times 10^{16}$ atoms/cm³ and [H]: 3×10^{16} atoms/cm³. On the other hand, the impurity concentrations in the crystal grown by the conventional method (Flux thickness: >6 mm) were [O]: 9×10^{19} atoms/cm³, [Si]: $<1 \times 10^{16}$ atoms/cm³, [C]: $<1 \times 10^{16}$ atoms/cm³ and [H]: 3×10^{16} atoms/cm³. Therefore, the oxygen concentration in the crystal grown by Thin-Flux-Growth was much lower than that of conventional method. Therefore, we assumed from this result that Thin-Flux-Growth enables the crystal to grow near the gas-liquid-interface leading to the high nitrogen concentration around the growing surface and suppression of the incorporation of the oxygen substituted at nitrogen site in the crystal. Pimputkar *et al.* reported that an indirect, phonon-assisted process

occurs and significantly contributes to the optical losses. For electrons residing in the conduction band of GaN, this would require the simultaneous absorption of a photon and a phonon of the proper energy to cause an intraband transition [14]. Figure 3(a) shows the dependence of the growth rate along the *a* axis on the flux thickness. As we can see from Fig. 3(a), the growth rate increased as the flux thinned and reached 80 $\mu\text{m/h}$ in sample A, which is the highest value in a crystal grown by the Na-lux point seed technique [15,16]. As shown in Fig. 3(b), the aspect ratio (*c* axis length/*a* axis length) decreased with thinning of the flux, and the aspect ratio of sample A was 0.18, which resulted in a platelet shape. In the Na-flux growth, the growth rate is determined by the nitrogen concentration around the growing surface [17]. In the present study, the fact that the growth rate increased as the flux thinned (Fig. 3(a)) indicates that the reduction of the flux thickness promoted the supply of nitrogen in the lateral direction. This was likely due to the suppression of the vertical growth at the gas-liquid interface.

In order to investigate the dislocation distribution, the etch decoration technique with KOH-NaOH was performed on the *c* face of samples A and B. Figures 4(a) and (b) show the distribution of the etch pit density of samples A and B, respectively. As shown in Figs. 4(a) and (b), almost no etch pits were observed in the large area of the lateral growth sector in both samples. There were some areas with $\sim 10^5 \text{ cm}^{-2}$ dislocation density in the lateral growth sector in both samples. Although the origin of these dislocations is still unclear, it is possible that they propagated from the periphery of a point seed [10]. Etch pit density at the region above the point seed of the sample A was as high as $\sim 10^7 \text{ cm}^{-2}$ (Fig. 4(d)), but no etch pits were observed in the same area in sample B. Next, we will consider the possible reasons for this difference.

Figures 5(a) and 5(b) show the cross-sectional CL images parallel to the *m*-face of samples A and B, respectively. Figures 5(c) and (d) show schematic drawings of the habit hysteresis of each sample estimated from the CL images. We can see from Figs. 5(a) to (d), the growth region above the point seed shows a skeletal shape with some voids. This morphological instability may be due to nonuniform supersaturation over the growing surface, which is known

1 as the Berg effect [18]. As shown in Figs. 5(a) and (c), the size of the skeletal growth sector
2 above the point seed of sample A grew larger during growth. Although dislocation density is
3 generally reduced to 10^6 cm^{-2} during the initial growth stage in the Na-flux method [19], the
4 skeletal growth sector causes propagation of the remaining dislocations toward the c direction
5 without a further reduction in the dislocation density, as reported Imanishi *et al.* [10]. On the
6 other hand, the size of the growth region of sample B gradually shrank, and a pyramidal habit
7 was formed in the initial growth stage (Figs. 5(b) and (d)). This growth habit is reported to be an
8 effective growth mode for dramatic reduction of the dislocation on the c face, because the
9 dislocations gather at the center of grains on a point seed by bunched steps during the
10 shrinking of the c -face.

11 The difference in the size of the growth region above the point seed between two samples is
12 likely caused by the difference in the nitrogen concentration around growing crystals, because
13 the habit of the GaN crystals in the Na-flux growth is strongly dependent on the nitrogen
14 concentration. Yamane *et al.* reported that the habit of the GaN crystals changed from
15 pyramidal to prismatic, and finally to thin platelets with increasing growth temperature and N_2
16 pressure i.e. with high nitrogen concentration in a flux. In this study, the Thin-Flux-Growth
17 technique, which enables crystals to grow near the gas-liquid interface, led to a higher nitrogen
18 concentration around growing crystals, because nitrogen dissolved into the flux through the
19 gas-liquid interface and its concentration was much higher than at the bottom of the crucible.
20 Therefore, the nitrogen concentration around the crystal placed in a 2.5 mm-thick flux seemed
21 to be higher than the nitrogen concentrations around crystals placed other various conditions.
22 Hence, the pyramidal habit, which is a smaller size of the skeletal growth sector, is favored by
23 the condition of thinner flux.

24 Based on the above considerations, we propose an ideal growth mode for realizing a high
25 growth rate and suppressing the propagation of dislocations above the point seed; the mode is
26 a two-step process as follows. First, the crystal is grown in a thick flux or under low nitrogen

pressure (low nitrogen concentration) to promote the pyramidal growth mode and reduce dislocation density. Second, the flux thickness is reduced, or the nitrogen pressure is increased, in order to raise the nitrogen concentration around a growing crystal to promote lateral growth. As reported by Imanishi *et al.*, the use of a small-diameter point seed is also a promising approach to gather and dramatically reduce dislocations above the point seed [10]. Investigating this possibility remains a challenge for a future study.

4. Summary

In this work, we succeeded promoting lateral growth in the Na-flux method by the Thin-Flux-Growth technique. The *a* axis growth rate reached 80 $\mu\text{m/h}$, which is the highest value reported to date by the Na-flux method. In addition, the etch decoration technique showed that almost no etch pits were observed in the lateral growth sector. However, the dislocation density at the region above the point seed was as high as $\sim 10^7 \text{ cm}^{-2}$ in the crystal grown in a thin flux. On the other hand, no dislocations were observed in the crystal grown in a thick flux. The growth region above the point seed of the crystal grown in a thick flux showed a pyramidal habit, which is the effective growth mode for reducing dislocation density. These results led us to propose a new, ideal growth mode to realize a high growth rate and lower dislocation density, the two-step growth mode. We concluded that Thin-Flux-Growth can be applied to the coalescence growth technique with low PS density and may be an outstanding approach for fabricating GaN crystals with large-diameter and lower dislocation density.

Acknowledgement

We gratefully acknowledge funding from the Ministry of the Environment and the Japan Science and Technology Agency. We would like to thank E. Sawai (Frontier Alliance, LLC) for slicing and polishing specimens.

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Figure captions

Fig. 1. Schematic drawings of (a) the process used to prepare a point seed, and the growth setup used for (b) the conventional growth and (c) the Thin-Flux-Growth in this study. We defined the flux thickness as the distance between gas-liquid interface and bottom of crucible.

Fig. 2. Optical photographs of GaN crystals grown at the flux thickness conditions of (a) 2 mm (sample A), (b) 3 mm (sample B) and (c) 6 mm (sample C). The height of crystals was 1.9 (sample A), 3.5 (sample B) and 4.6 mm (sample C), respectively.

Fig. 3. Flux-thickness dependence of (a) the growth rate along the *a* direction and (b) the aspect ratio. The growth rate was determined by the growth length in the *a* direction and growth period (120 h). The aspect ratio was calculated as the *c* axis length over *a* axis length.

Fig. 4. Distribution of the etch pit density on the *c* face of (a) sample A and (b) sample B. Open squares, solid squares and a solid triangle represent the areas with dislocation densities of 0 cm^{-2} , $\sim 10^5 \text{ cm}^{-2}$ and $\sim 10^7 \text{ cm}^{-2}$, respectively. Typical SEM images of each area are shown in (c) to (h).

Fig. 5. Cross-sectional CL images of (a) sample A and (b) sample B at the *m* face. Schematic drawings of the habit hysteresis evaluated by CL images of (c) sample A and (d) sample B are also shown.

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1 **Fig. 4.**
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1 **Fig. 5.**

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(b)

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(d)