Growth of Bulk GaN Crystal by Na Flux Method

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Abstract

With current technologies, dislocation-free bulk shape GaN crystals of centimeter size can be grown from small seed crystals. This technique can be realized by putting a sapphire plate with a small hole (0.5 - 1.5mm in diameter) on a GaN plate seed. Centimeter-sized bulk GaN single crystals with large dislocation-free areas could be fabricated by this technique. Cathodoluminescence measurement at the interface between the seed and the grown crystal has revealed that almost all dislocations propagated from the GaN seed were bent, and terminated at the initial growth stage.

To enlarge the diameter of bulk shape GaN crystals, we have developed the coalescence of GaN crystals from many isolated small seeds. As a first step, we grew two GaN point seeds and coalesced them. Two GaN point seeds were established by mounting a sapphire plate with two small holes. We have found the two GaN crystals grown from two separate seed areas coalesced without generating dislocations at a coalescence boundary. The grown GaN crystal can remove from the substrate easily during the growth. This phenomenon is effective to reduce the stress in the grown GaN crystal. 2-inch GaN crystals have been grown by the coalescence technique. Some of the crystals have very large curvature radius (~100m).

INTRODUCTION

Gallium nitride has attracted significant attention due to its potential applications in ultraviolet light-emitting diodes [1] and laser diodes [2,3], and to high-power, high-frequency electronic devices [4]. However, GaN-based devices have not reached their full potential because of the difficulty in producing high-quality defect-free GaN substrates. In recent year, much effort has been expended in growing bulk gallium nitride (GaN) single-crystals that are dislocation free [5-13]. However, the techniques that have been developed for realizing this suffer from various problems. Fujito *et al.* grew a colorless, freestanding c-plane bulk GaN crystal (diameter: 52mm, thickness: 5.8mm, dislocation density: ~10^6 cm^{-2}) by hydride vapor phase epitaxy [5]. Dwilinski *et al*. reported the ammonothermal growth of large GaN crystals with high crystallinities a radius of lattice curvature greater than 1000m, and a dislocation density of 5 x 10^3 cm^{-2} at 1 inch [8,9]. The Na-flux method is promising for mass producing low dislocation density GaN crystals because a reduction in the dislocation density from 10^8 cm^{-2} in a seed to 10^4 cm^{-2} in liquid-phase epitaxy (LPE) layers and a growth rate of over 20um/h have been attained for 2-inch GaN LPE [12,13]. However, further progress is required to realize dislocation-free GaN single crystals by this technique. Furthermore, the formation of polycrystalline GaN on the crucible wall is one of the issues that is preventing the fabrication of large-size bulk GaN crystals by long-term growth.

In the present study, we developed Na-flux point seed technique (SPST) to grow high-quality and large bulk GaN crystals. Furthermore, stirring the solution was applied to suppress the polycrystal formation on the crucible wall and then promote bulk GaN growth on the seed. Kawamura *et al.* reported that solution stirring using mechanical motion in the Na-flux method improved the growth rate, the flatness, and the uniformity of an LPE layer grown on a GaN template [14]. The resulting crystals were characterized by cathodoluminescence (CL) measurements. We also demonstrated the coalescence growth of GaN crystals grown from many point seeds to effectively enlarge the diameter of GaN crystals [15].

EXPERIMENTAL PROCEDURE

1) Growth by the Na-flux point seed technique (SPST)

As shown in Fig. 1(a), a GaN point seed was produced by freely mounting a sapphire plate (430um in thickness) with a small hold (0.5 - 1.5mm in diameter) on a GaN template, which is a 10-um thick c-face GaN film grown on a c-face sapphire substrate by metalorganic vapor phase epitaxy (MOVPE). The GaN point seed was placed in a ceramic crucible with a diameter of 80mm and a height of 45mm, and the starting materials of metallic Ga (purity: 6N, 1.2 x 10^2g), metallic Na (purity: 4N, 5.8 x 10g) and granular graphite (purity: 6N, 2.6 x 10^{-1}g) were added to the crucible in an Ar-filled glove box. The ratio of the carbon content to the total Ga+Na content was fixed at 0.5 mol%. The granular graphite was added in order to suppress the growth of polycrystalline material on the crucible wall [12]. The starting Ga:Na:C composition ratio was 40:60:0.5.

Growth on the GaN point seed was carried out as follows. After the crucible was transferred into a stainless steel essel in the glove box, the vessel was placed in a resistive heating unit set in a pressure-resistant chamber.

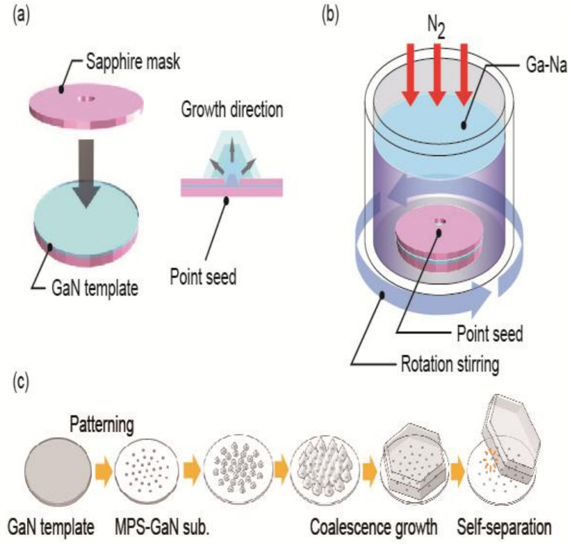

Fig. 1. Schematic illustration of experimental setup. (a) Configuration of GaN point seed and an illustration of crystal growing on the point seed. The GaN point seed was produced by freely mounting a sapphire plate (430um in thickness) with a small hole (0.5 - 1.5mm in diameter) on a GaN template (a 10um thick (0001) GaN film grown on a (0001) sapphire substrate by MOVPE). The crystal grows through the small hole in the sapphire wafer. (b) Arrangement in the crucible. The point seed was placed in a crucible with a diameter of 80um. The nitrogen source gas was pressurized during growth. The solution was stirred by intermittently rotating the crucible. (c) Schematic illustration of the coalescence growth process. The MPS0GaN sub. was produced by patterning a GaN template.

The chamber was then evacuated to below 3.0 x 10^{-1}Pa and N_2 gas was introduced into the vessel through a gas line. The temperature was increased to 870C over a 1-hour period using a resistive heater. The temperature and N_2 pressure in the chamber were then maintained at 870C and 3.4 MPa, respectively, during the growth period of 400h. The solution was stirred by periodically rotating the crucible in a single direction at 20prm for 60s, followed by a stationary period of 30s as shown in Fig. 1(b). Details of the growth procedure have been previously reported [16].

After the vessel cooled naturally, the crucible was removed and immersed in cold ethanol and water to dissolve the residual flux. A c-face wafer was sliced from the grown GaN crystal and subjected to chemical-mechanical polishing (CMP). The dislocation density in the wafer was estimated using panchromatic CL measurements (HORIBA, Imaging CL DF-100).

2) Coalescence growth

As shown in Fig. 1(c), a multi-point seed-GaN substrate (MPS-GaN sub.) was produced by patterning a 10um thick (0001) GaN layer that was grown on a (0001) sapphire substrate by MOVPE. Point seeds were arranged in a hexagonal pattern such that a direction for neighboring point seeds were parallel to the a-direction of the GaN, resulting in the coalescence direction corresponding to the a-direction of the GaN. The diameter of each point seed was 205um, and the distance between the centers of the neighboring point seeds was fixed at 350um. The starting Ga:Na:C composition ratio was 27:73:0.5. Growth on the MPS-GaN sub. was carried out at 870C and 3.2MPa for 144h. Other conditions were the same as those of the growth by SPST.

RESULTS AND DISCUSSION

Well-facetted bulk GaN crystals could be grown on the GaN point seed without the formation of polycrystals on the crucible wall. The crystal size reached diameter of up to 2.1cm and height of up to 1.2cm, corresponding to growth rates of 52um/h in the a-direction (both sides), and 30um/h in the c-direction. These are the largest bulk GaN crystals ever reported using the Na-flux method [17]. In the previous report skeletal growth was confirmed in teh grown crystals, and led to the formation of inclusions in GaN crystals, which degrades their quality. This occurs due to the Berg effect, in which a non-uniform nitrogen supersaturation exists over the seed surface [18]. However, in the present case, no such skeletal growth was evident, possibly because the stirring eliminates such non-uniformity.

Following crystal growth, a c-face wafer was sliced from the bulk crystal and its surface was subjected to CMP as

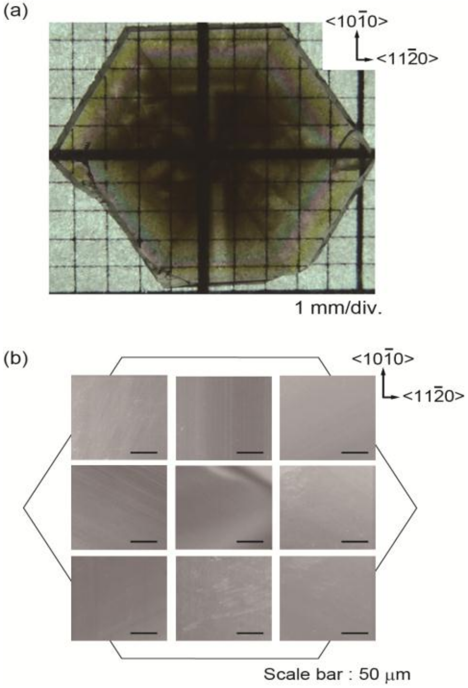

Fig.2 (a) Optical photographs of the c-face GaN wafer sliced from the grown crystal (b) Panchromatic CL images of the c-face GaN wafer sliced from the bulk GaN single crystal. No dark sport associated with dislocations appear in any of the images.

shown in Fig. 2(a). The wafer was blackened, which is often observed in a seeded growth by the Na-flux method [17]. We speculate that the cause of the blackening is the N vacancy, because in our previous works, we demonstrated that transparent GaN crystals could be obtained from teh solution with high N solubility such as high temperature solution and the Na-Ca and Na-Ca-Li flux [19,20]. Unfortunately, to our knowledge, there are no experimental approaches for detecting the N vacancy up to now, thus there is no conclusive scientific evidence for blackening at present. Figure 2(b) shows CL mapping results carried out on the wafer to estimate the dislocation density. I panchromatic CL images, dislocations appear as dark spots and lines, due to the occurrence of non-radiative carrier recombination, which is strongly localized because of the short hole diffusion length in GaN [21]. Therefore, the density of such features is close to the true dislocation density. As shown in Fig 2(b), no dark spots can be seen in any of the 150um x 150um regions, indicating the the wafer is almost free from dislocations. Details of the dislocation geometry and the growth mode are given in our previous paper [18].

The colaescence growth of GaN crystals grown from many point seeds was also attempted. As shown in Fig. 3, a coalesced GaN crysatl with a 1mm thickness unified over the entire 2-inch range was obtained. The sapphire substrate separated naturally from the MPS-GaN sub.

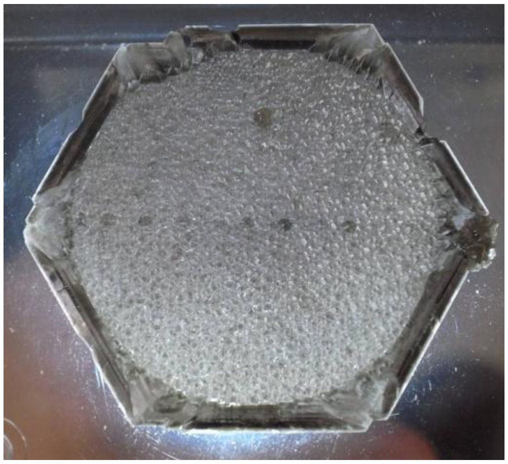

Fig. 3. Photograph of the 2-in GaN crysatl grown by the coalescence growth method. GaN crystals grown from many point seeds coalesced and unified. The sapphire substrate separated naturally from the MPS_GaN sub.

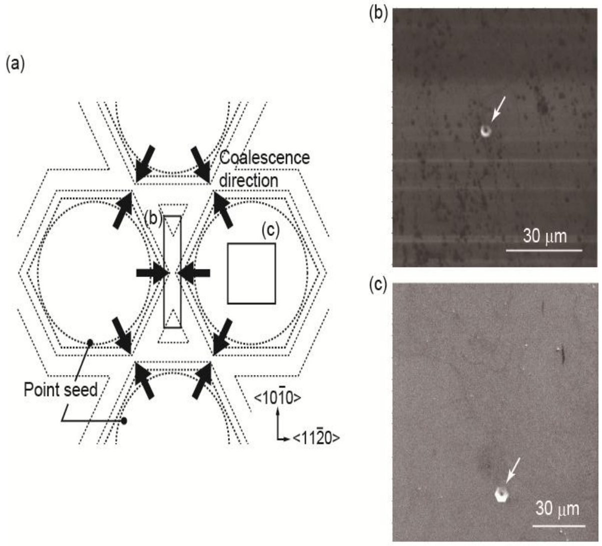

Fig. 4(a) Illustration of coalescing crystals grown from each point seed. Surface SEM images of the coalesced GaN after CMP and NaOH-KOH etching at 450C for 20m (b) at the coalescence regions and (c) away from the coalescence region.

The dislocation density was estimated by using the etch-decoration technique. Figure 4(a) is an illustration of coalescing crystals grown from each point seed. Figs. 4(b) and (c) show SEM images after NaOH-KOH etching at 450C for 20m, which were taken close to the coalescence boundary and away from the coalescence boundary, respectively. Note that Figs. 4(b) and (c) are focused on the regions that etch pits (white arrows in Figs. 4(b) and (c)) exist, and no other etch pits existed in the area of 500um x 500um, indicating the dislocation density is on the order of 10^2 cm^{-2} both at the coalescence boundary and away from the coalescence boundary. Radius of lattice curvature of the coalesced GaN crystal was also evaluated from the shift of peak top angle of 002 GaN XRCs, showing that the radius of lattice curvature was large than 100m. Details of structural properties of coalesced GaN crystals are described in [22].

CONCLUSIONS

In summary, bulk GaN single crystals could be grown by newly developed SPST. For 400h growth, GaN crysatls reached dimensions as large as diameter of 2.1cm and height of 1.2cm. Panchromatic CL images showed that no dark spots were observed in large areas of the sliced c-face GaN wafer. In addition, we have advanced SPST to the coalescence growth and demonstrated the growth of 2-in GaN with low dislocation density and curvature, which shows the possibility of effectively enlarging the diameter of GaN crystals grown by SPST.

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