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GaN single crystal growth from a Na-Ga melt

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GaN single crystals were prepared in a sealed stainless-steel tube container at 650–840°C for 6–300 h using Ga, NaN_3, and Na as starting materials. A thin GaN layer covered Na-Ga melt surface at the initial stage of reaction between Ga in the Na-Ga melt and N_2 given by the thermal decomposition of NaN_3 around 300°C. In the next stage, pyramidal and prismatic GaN single crystals grew under the layer. Prismatic and platelet crystals also grew from the melt which wetted the tube wall. The reaction rate was enhanced by increasing temperature and by increasing Na content in the melt. The maximum size of pyramidal crystals was about 0.7 mm. The platelet crystals were 1–2 mm in one direction and <0.05 mm thick. The platelet single crystals prepared at 650°C exhibited the sharpest cathodoluminescence peak with the strongest intensity at 362 nm. © *2000 Kluwer Academic Publishers*

1. Introduction

Blue light-emitting diodes have already been manufactured with GaN-based nitride thin films and used practically [1–3]. Many research groups are now developing blue and ultra-violet laser diodes, detectors, and high-temperature transistors by using GaN. These devices are usually fabricated on sapphire substrates. However, the films on these substrates contain many defects and dislocations due to the lattice mismatch and the difference of thermal expansion between sapphire and GaN. Other kinds of materials are investigated for substrates for GaN epitaxial growth. GaN bulk single crystals are expected to be the best substrates for the fabrication of high-quality thin film devices. GaN bulk single crystals having mm size were prepared at 930–1100°C under NH_3 atmosphere [4–11]. Recently, GaN single crystals with a size of $2 \times 2 \times 0.03$ mm were grown from a flux at a constant temperature of $\sim$1000°C under N_2 atmosphere at a pressure of less than 2 bar [12]. The basic component of the flux was gallium but the details were not described. High-temperature and high-pressure techniques were applied to the GaN single crystal growth from the reaction between a Ga melt and N_2 gas [13–16]. Porowski *et al.* reported the formation of platelet GaN single crystals of more than 1 cm in the longest direction at 1400–1500°C under an N_2 pressure of 10–20 kbar. We have prepared bulk GaN single crystals with a maximum size of 2 mm at 600–800°C by using starting materials of NaN_3 and Ga in a sealed stainless-steel tube container [17, 18]. This temperature range was lowest among the temperatures of the methods reported previously. In the present study, we prepared GaN single crystals by adding extra Na metal to the starting materials and investigated the process of the GaN crystal growth in the sealed stainless-steel tube container. The GaN single crystals obtained were characterized by cathodoluminescence spectroscopy.

2. Experimental

10 mmol Ga (Sumitomo Chemical, 99.9999% purity), 3.6 mmol NaN_3 (Toyo Kasei Kogyo, 99.9% purity), and 3.6 and 7.2 mmol Na metal (High Purity Chemicals, 99% purity) were weighed and sealed in a stainless-steel tubes (SUS 316, 7.5 mm inner diameter, 80 mm length) with stainless-steel caps on both ends of the tube. This process was carried out in an MBraun MB130 glove box in which the combined O_2 and H_2O content was below 1 ppm. The sealed tube was set vertically in a furnace and heated at 650–840°C for 6–300 h under Ar atmosphere in order to prevent the oxidation of stainless steel during heating. After the heating, the sample in the tube was cooled to room temperature by shutting off the furnace power. The upper part of the tube was cut off using a tube cutter and the Na metal was removed by reaction with 2-propanol and ethanol. Then, a cross section of the tube was obtained by cutting with a ceramic fine cutter. The products in the tube were observed with an optical microscope and a scanning electron microscope (SEM, Hitachi S2150). Some of the samples

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were powdered and characterized by X-ray diffraction (XRD). CuK_α radiation was used on a diffractometer with a pyrolitic graphite monochromator (Rigaku, RINT2000). Impurities in the single crystals were analyzed with a scanning electron microscope (Hitachi X-60) equipped with an energy dispersive X-ray analyzer (EDX, Kevex). Cathodoluminescence (CL) was performed at room temperature in a modified scanning electron microscope (Topcon DS130) [19]. The emitted light was collected with an ellipsoidal mirror, led to a spectrometer (Jobin Yvon HR320) and detected by a charge coupled device (CCD) detector (Jobin Yvon, Spectra View 2D).

3. Results and discussion

Fig. 1a shows a cross section of the stainless-steel tube container in which 10 mmol Ga was sealed under Ar gas and heated at 750°C for 1 h. The Ga was completely absorbed into the stainless steel and formed alloys. In contrast, crystals of a Na-Ga intermetallic compound were precipitated at the bottom of the tube when Ga of 7.8 mmol and Na of 4.4 mmol were sealed under Ar gas and heated at 750°C for 72 h (Fig. 1b). This compound reacted with water vapor in the air and decomposed quickly. The main peaks in the X-ray powder diffraction pattern of this sample were identified with the structure of $Ga_{39}Na_{22}$ [20]. According to the phase diagram presented by Pelton and Larose [21], the melting temperature of $Ga_{39}Na_{22}$ is 556°C. Judging from the morphology in the tube, the interface between the Na-Ga melt and gas phase at 750°C was convex downward and the melt wetted the surface of stainless-steel tube wall a little more than 10 mm from the bottom of the convex interface.

Tamaki and Cusack characterized the thermodynamic properties of liquid Ga-Na system [22]. The free energy of formation (ΔG) at 570°C for a Na-Ga melt with Na atomic fraction of 0.4 was -1160 cal/mol ($Na_{0.4}Ga_{0.6}$). This may explain the stability of the Na-Ga melt toward a reaction with the stainless steel.

The GaN single crystals prepared in the present study were identified by X-ray powder diffraction as hexagonal wurtzite-type, no cubic phase was found. EDX analysis did not detected any impurity in the crystals (detection limit ~0.3 wt% for Na, Fe, Ni and Cr).

The cross-sectional photographs of the products prepared at 650°C with the starting materials of Ga: 10 mmol, NaN_3: 3.6 mmol, and Na: 3.6 mmol are shown in Fig. 2. Since NaN_3 decomposes into N_2 and Na around 300°C, the Na mol fraction in the melt (r_{Na} = Na/(Na + Ga)) at 650°C was 0.42. Na-Ga crystals were obtained by heating for 72 h (Fig. 2a). Black GaN layers precipitated at the interface between the Na-Ga melt phase and N_2 gas phase. After 200 h heating, GaN single crystals grew from the melt which wetted the tube wall (Fig. 2b). As shown in the scanning electron micrograph of Fig. 3a, the crystals were prismatic grains

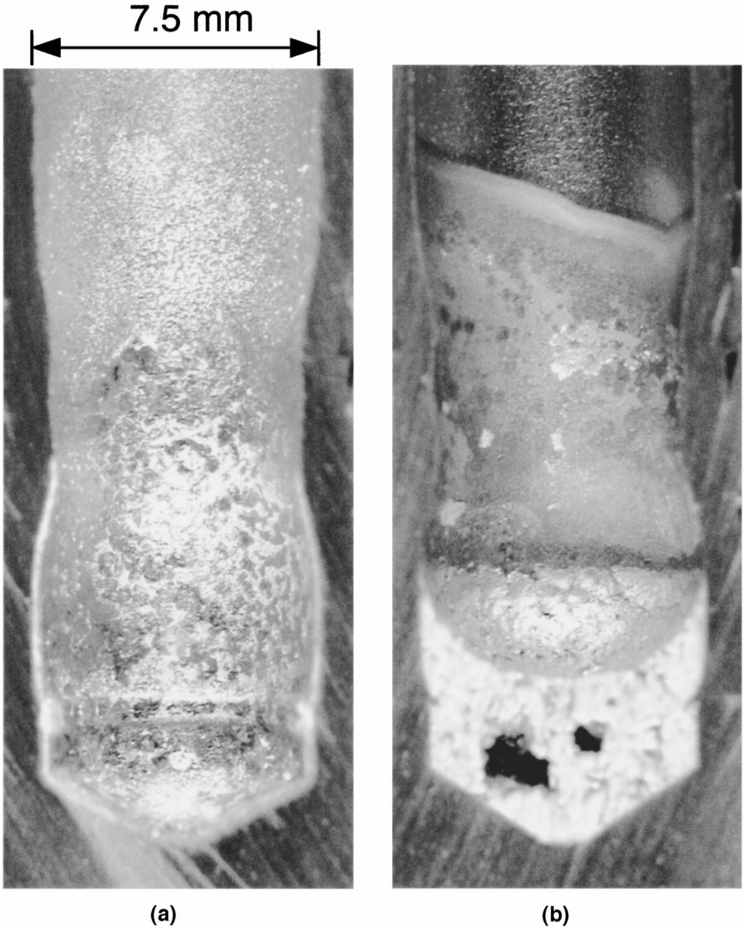
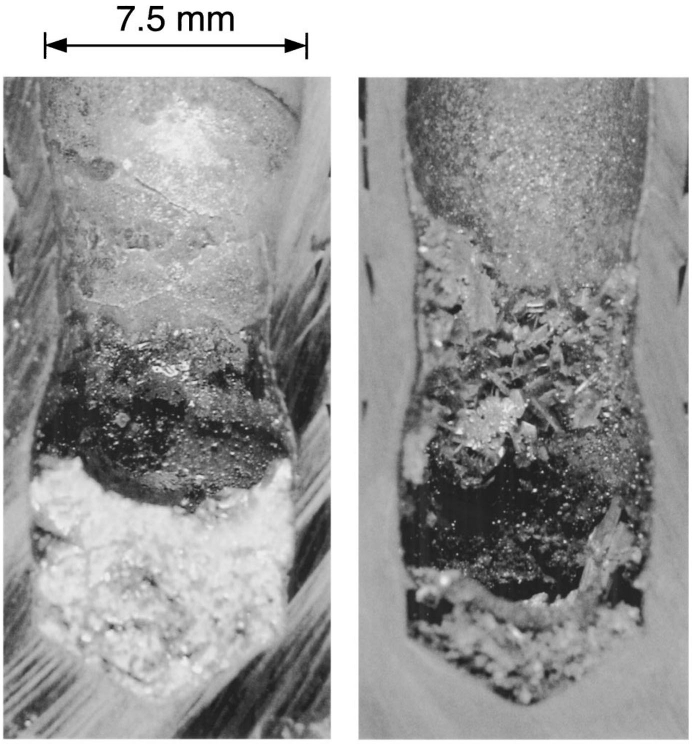


Figure 1 Photographs of the samples prepared in the sealed stainless-steel tube containers at 750°C for 1 h with 10 mmol Ga (a), and at 750°C for 72 h with 7.8 mmol Ga and 4.4 mmol Na (b).



(a) (b)

Figure 2 Photographs of the samples prepared in the sealed stainless-steel tube containers at 650°C for 76 h (a) and for 200 h (b) with 10 mmol Ga, 3.6 mmol NaN_3, and 3.6 mmol Na.

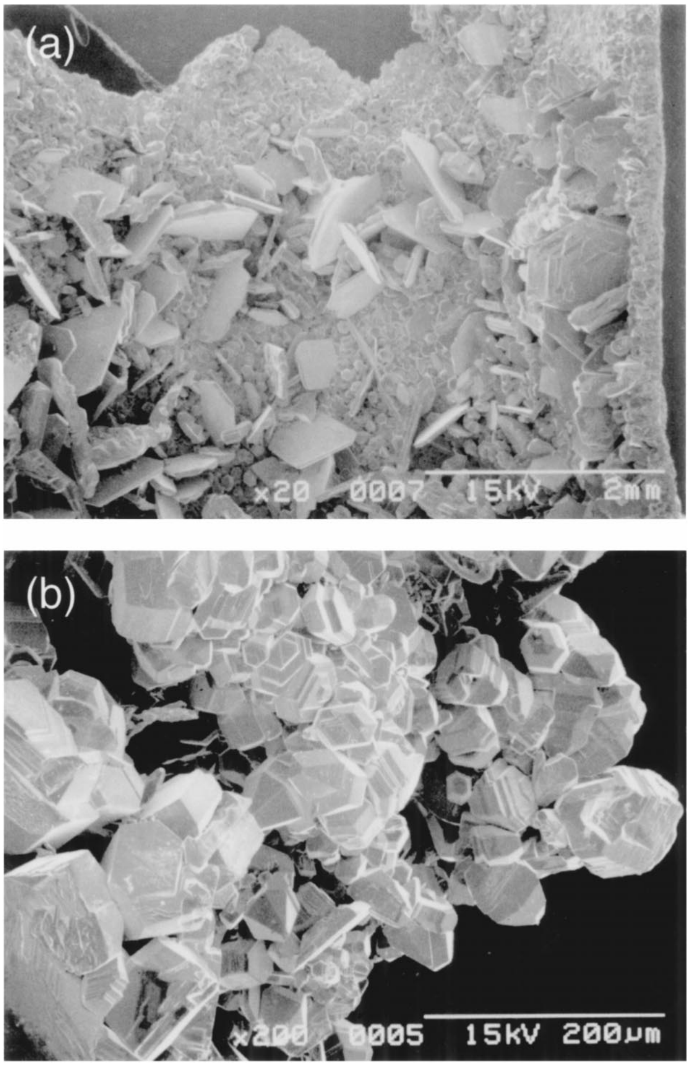


Figure 3 Scanning electron micrographs of GaN crystals prepared at 650°C for 200 h with 10 mmol Ga, 3.6 mmol NaN_3, and 3.6 mmol Na on the tube wall (a) and under the melt surface (b).

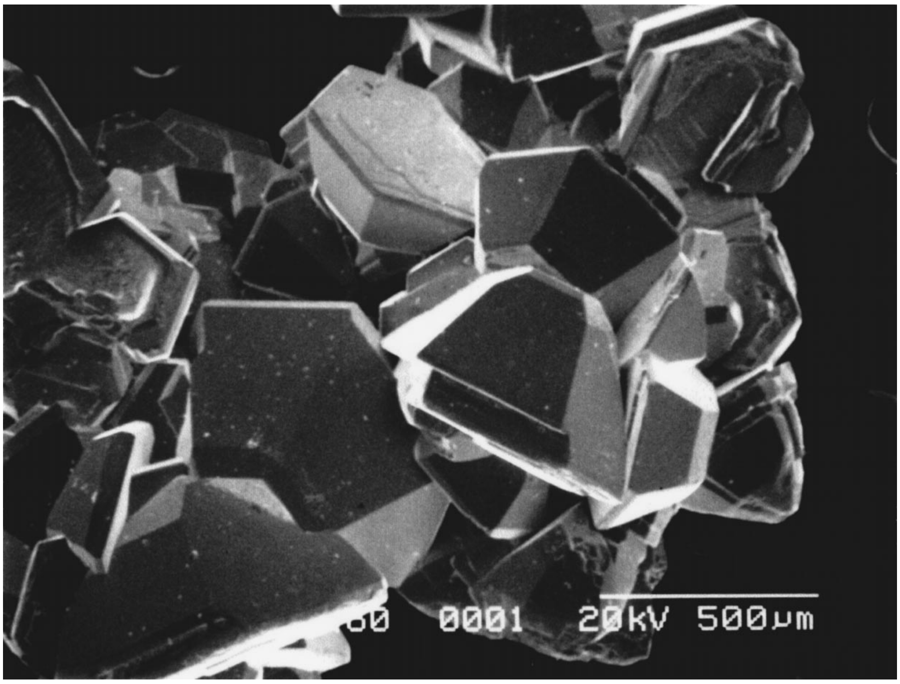


Figure 4 Scanning electron micrographs of GaN single crystals grew under the melt surface at 840°C with 10 mmol Ga, 3.6 mmol NaN_3, and 3.6 mmol Na.

with a size less than 0.5 mm and platelet crystals with a size of about 1 mm. These crystals were transparent, and colorless or light amber. The growth of pyramidal or prismatic GaN single crystals was also observed beneath the liquid surface. The scanning electron micrograph of these crystals is shown in Fig. 3b. The size was from about 50 to 200 μm. Small amounts of the Na-Ga compound remained at the bottom of the tube. Residual Na-Ga compound was not seen in a sample heated for 300 h.

Samples composed of a Na-Ga intermetallic compound and a GaN layer, similar to the sample of 650°C for 72 h, were also obtained at 700 and 750°C for 72 h at $r_{\mathrm{Na}} = 0.42$. However, no Na-Ga compound remained and GaN single crystals grew at 800°C for 72 h and at 840°C for 24 h. Prismatic and platelet single crystals with a size less than 0.5 mm grew on the tube wall. Larger pyramidal GaN single crystals were obtained in the region beneath the interface. As shown in Fig. 4, the maximum size of the pyramidal crystals grown at 850°C was about 0.7 mm. The color of these crystals were dark amber.

Increasing the Na reactant to 7.2 mmol ($r_{\mathrm{Na}} = 0.52$) and heating at 650°C for 72 h resulted in the growth of platelet crystals. The area of the platelet crystal formation spread upward and the Ga-Na compound filled the space between the platelet crystals. In the case of the sample prepared at 800°C for 72 h with $r_{\mathrm{Na}} = 0.52$ (Fig. 5), many platelet GaN single crystals grew on the area up to 15 mm from the position where the bottom of the liquid interface was at the beginning of the reaction. The platelet crystals were a transparent brown color, about 1 mm in the longest direction and below 0.05 mm in thick. These occurrences of the platelet crystals suggested the increase of wettability with increasing Na content. Some of the platelet crystals with a size over 1 mm contained black inclusions. Fig. 6 shows scanning electron micrographs of the platelet crystal

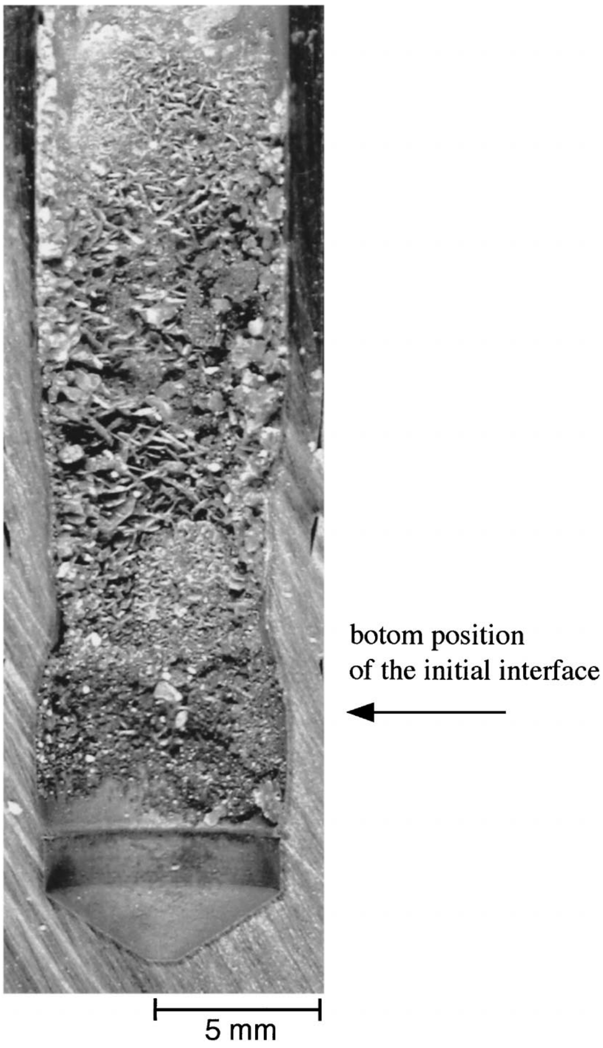


Figure 5 Photograph of the sample prepared in the sealed stainless-steel tube containers at 800°C with 10 mmol Ga, 3.6 mmol NaN_3, and 7.2 mmol Na.

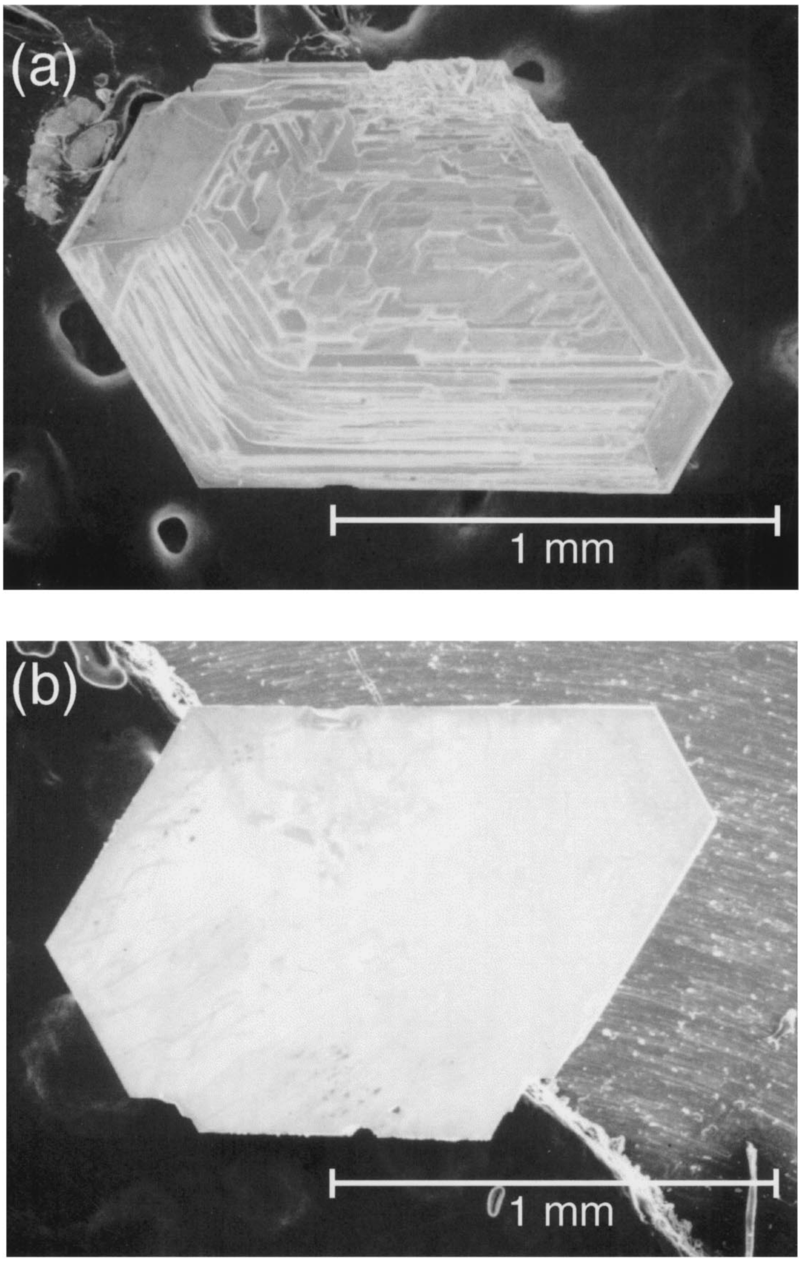


Figure 6 Scanning electron micrographs of GaN platelet crystals prepared at 800°C for 72 h with 10 mmol Ga, 3.6 mmol NaN_3, and 7.2 mmol Na.

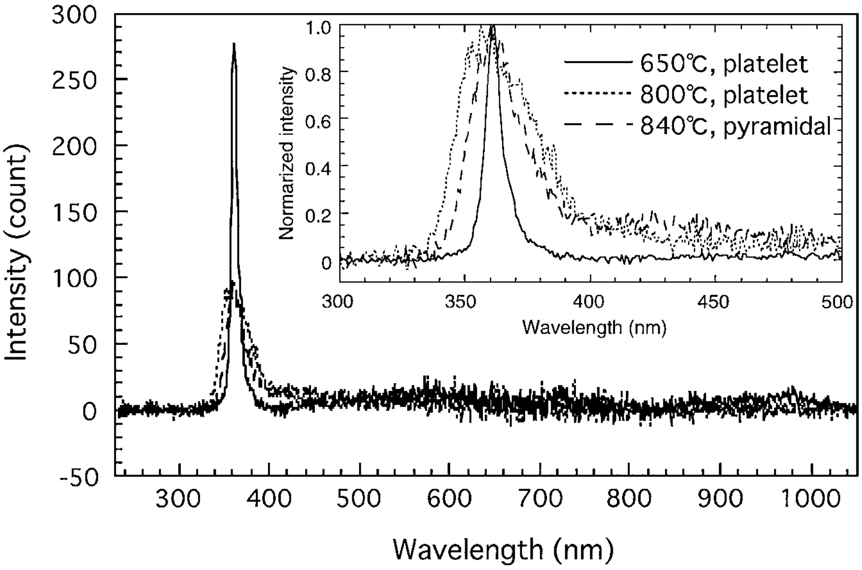


Figure 7 Cathodoluminescence spectra of GaN platelet single crystals prepared at 650°C for 200 h and 800°C for 72 h, and the pyramidal crystal prepared at 840°C for 72 h. The graph inserted is the normalized spectra in the wavelength range of 300 to 500 nm.

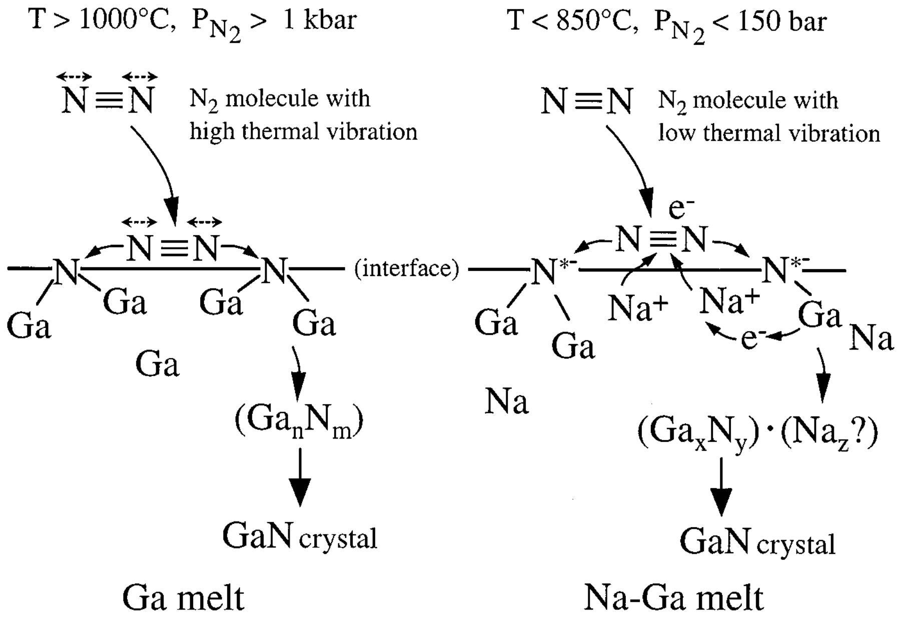


Figure 8 Schematic drawing of the models proposed for the reaction between N_2 gas and Ga melt under a higher temperature-pressure condition, and for the reaction between N_2 gas and Na-Ga melt under a lower temperature-pressure condition.

prepared at 800°C. The platelet crystals obtained in the present study had mirror surfaces in one side, which corresponded to the N plane according to our previous study on the polarity of GaN determined by the X-ray anomalous dispersion method [23]. The other side, the Ga plane, was bumpy and many steps were seen.

The cathodoluminescence spectra of the platelet single crystals prepared at 650°C for 200 h and 800°C for 72 h, and of the pyramidal crystal at 840°C for 72 h are shown in Fig. 7. The platelet single crystal prepared at 650°C exhibited a peak of near band-edge emission at 362 nm (3.4 eV) having the narrowest peak width and highest intensity among these samples. A week band was observed at 410–420 nm for the samples obtained at the higher temperatures. The broadness of the peaks and the week band, suggest the presence of some levels near band edge that might be due to defects or imperfection of the crystal lattice owing to the fast growth rate at high temperatures.

The results of the present study on the effect of Na content on the crystal growth of GaN is consistent with those where only NaN_3 and Ga were used as starting materials [17, 18]. In these studies, the yields of GaN increased with decreasing Ga content at constant NaN_3 content for a 24 h reaction. Platelet crystals were obtained at lower Ga contents and the products became powder at a much lower Ga content.

Madar *et al.* reported that below 950°C and above the equilibrium N_2 pressure of GaN, Ga does not react with N_2 and its surface remains clean and shiny and gives no residue after dissolution [13]. At 1000°C, they observed very thin GaN film on the surface of Ga melt. The solubility of GaN in Ga at 1200°C and 8 kbar was determined to be about 1×10^{-3} mol fraction. Grezegory *et al.* also reported 10^{-3} mol fraction for the solubility of GaN in Ga melt at 8 kbar and 1427°C [15]. These results indicated that the reaction between Ga melt and N_2 gas needs high temperature. One of the possible reason we think is the strong binding energy of diatomic N_2 molecule (945 kJ/mol) [24].

N_2 reacts with Ga of the Na-Ga melt and form GaN single crystals below 850°C. The role of the Na should be a catalysis which enhances the reaction between N_2 and Ga or the Na-Ga intermetallic melt. Na is one of the alkali metals which release electrons easily as seen by their low work functions or their low ionization potentials. We speculated that a N_2 molecule adsorbed on the surface of Na-Ga melt could receive electrons from Na (Fig. 8). Since the bonding orbitals of $1\pi_u$ and $3\sigma_g$ are already filled in the N_2 molecule, the electrons from Na go into the next level of antibonding $2\pi_g^*$ orbitals. This could weaken the bonding and the N_2 molecule might dissociate into negatively charged N atoms. Because there is no sodium nitride and no ternary nitride containing Na and Ga [25], in addition to the extremely low solubility of nitrogen in liquid sodium (7.1×10^{-9} mol% N at 600°C) [26], Ga is the only element which can catch N and form a nitride. The Ga atoms in the melt presumably make bonding with the dissociated N^{*-} atoms near the interface and form soluble species with or without Na atoms: $(Ga_xN_y)\cdot(Na_z)$. Electrons released by Na are presumably taken up to produce N^{3-} as species like $GaN_2{}^{3-}$. Note the similarity of $GaN_2{}^{3-}$ of $BN_2{}^{3-}$ a well known species in compounds such as Li_3BN_2. Hubbersty reported the increase of N solubility and speculated on a soluble species of $Ba_xN(Na)(x \sim 4)$ in a Na-rich Na-Ba melt, where Ba forms Ba_2N and Ba_3N_2 in the solid state.

The maximum N_2 pressure estimated from the amount of NaN_3 and the inner volume of the container was about 120 bar at 700–800°C. The N_2 pressure should decrease during the formation of GaN. On opening reaction tubes containing GaN single crystals and no Na-Ga intermetallic compound, N_2 pressures of a few bar in the tube were apparent by hearing the sound of gas leak. The crystal growth of GaN continued under N_2 pressure of at least a few tens bar at the growth temperature.

Fig. 9 shows the equilibrium N_2 partial pressure of GaN versus temperature determined by Karpinsiki *et al.*

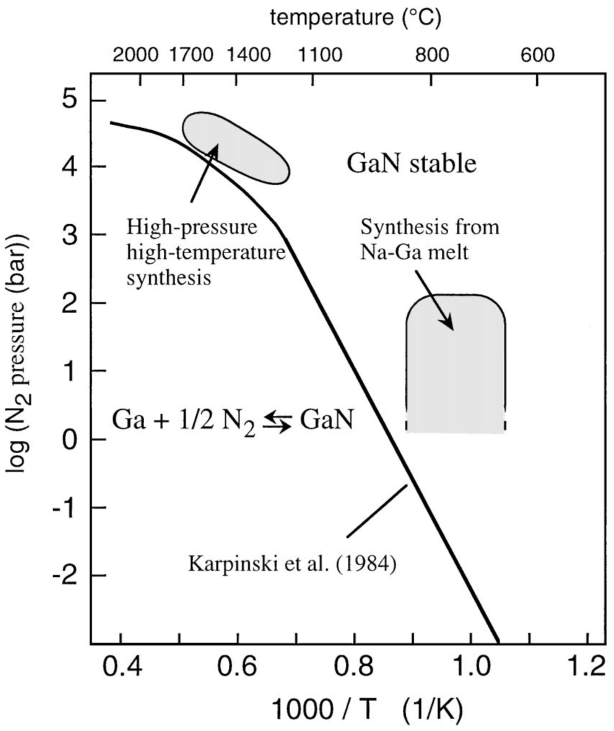


Figure 9 Equilibrium pressure of N_2 over GaN reported by Karpinski *et al.* [14]. The conditions of GaN single crystal growth are indicated.

[14]. In this figure, the equilibrium line curves due to the deviation of the ideal gas behavior at high pressure. The conditions of the GaN single crystal growth in the present study are in the stability field of GaN. In order to determine the lower limit of N_2 pressure and to control the crystal growth, we are attempting to introduce N_2 gas into the container from the outside. However, Tamaki and Cusack reported problems of Na vaporization from the Na-Ga melt above 600°C [22]. We are working on solving this problem.

4. Conclusions

GaN single crystals were prepared at 650–840°C for 24–300 h in sealed stainless-steel tube containers by using Ga, Na and NaN_3 as starting materials. From the observation of the products, the reaction process between Na-Ga melts and N_2 is as shown schematically in Fig. 10. The melt has a concave surface and wet the stainless-steel tube wall. At the first step of the reaction, the Na-Ga melt surface is covered with a GaN layer. Ga is consumed and Na content relatively increases near the interface. At the second stage, the melt with higher Na content wet well the surface of GaN crystals on the stainless-steel tubing, and caused the crystal growth of platelet single crystals perpendicular to the tube wall. The growth rate along the direction perpendicular to the *c*-axis seemed to be faster than other direction under these conditions. Pyramidal and Prismatic crystals grow beneath the melt surface. As the Na content of the initial melt increased, the time period of the 1st stage becomes shorter and the area of the platelet crystal growth spread upward.

Because of the good wettability of Na-Ga melt on stainless steel, the interface was convex downward and crystal growth area spread toward the container wall. We tested other metals such as Nb and Mo for containers. But all of them we tried were wetted well with the Na-Ga melt. On the contrary, boron nitride has a poor wettability against the melt. The melt surface was convex upward and did not spread on the BN container wall. We are now studying the single crystal growth in BN containers.

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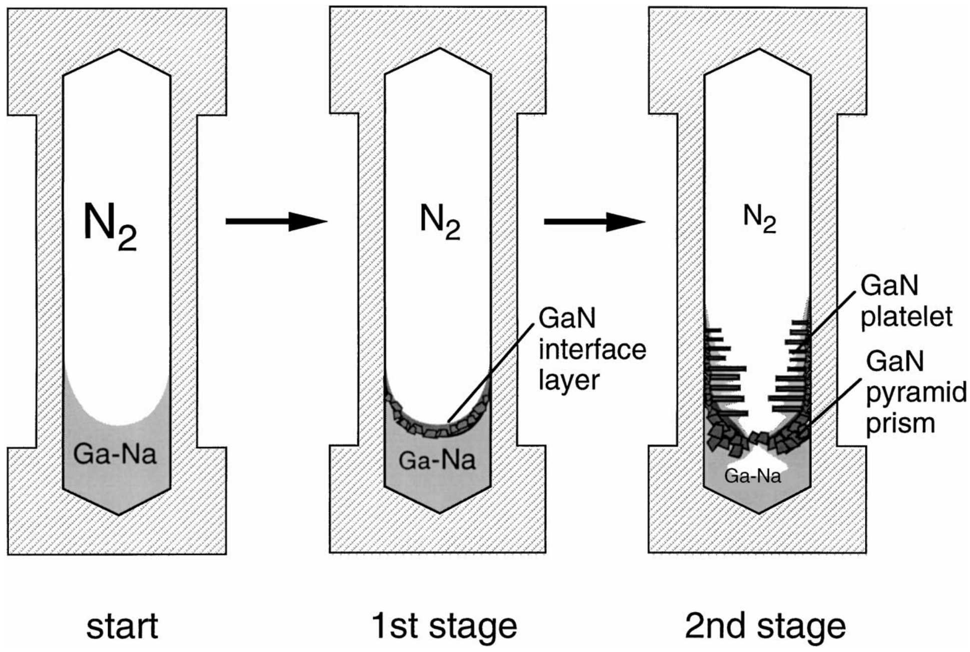

Figure 10 Schematic drawing of the proposed process for the formation of GaN crystals in a stainless-steel tube container.

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