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Synthesis of Bulk GaN Single Crystals Using Na–Ca Flux

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We grew GaN single crystals in Na–Ca flux and found that the presence of Ca in a high-temperature flux system has the following advantages for growing GaN single crystals. First, Ca in solution drastically increased the yield of GaN crystals. Second, transparent GaN single crystals are easy to grow around the gas-liquid interface. Third, the pressure required to synthesize the GaN is reduced. These effects can be interpreted as resulting from increased nitrogen solubility in the flux. In this paper, we report the effects of Ca on the yield of GaN and threshold pressure for growing GaN in Na–Ca flux.
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KEYWORDS: GaN, flux method, single crystal, high pressure, bulk, nitrogen vacancy

GaN-based semiconductors have tremendous potential for blue-to ultraviolet-light-emitting devices and are now commercially available. Many researchers are currently seeking to extend the lifetime of GaN-based semiconductors for fabricating short-wavelength laser diodes. The lack of a lattice-matched substrate is a major problem in fabricating high-quality GaN-based optical devices. GaN-based devices are currently grown on lattice-mismatched substrates, which produces a high dislocation density in films. Recently, success in reducing the dislocation density by applying a buffer-layer technique and epitaxial lateral overgrowth (ELO) has been reported,[1–3] but further improvement is required. GaN single-crystal substrates for homoepitaxial growth are required to solve this problem and to grow high-quality GaN films. However, GaN single crystals for use as substrates are not yet available. Methods for growing bulk GaN single crystals have been reported. For example, Karpinski *et al.* reported a "High-pressure solution growth method" that enabled us to grow a GaN single crystal for the first time.[4] However, the pressure used in this method is too high to apply this technique for commercial use. Yamane *et al.* reported that the pressure required to synthesize GaN single crystals can be drastically decreased by applying the Na flux method[5–8] in which nitrogen reacts with the Na–Ga solution. The Na flux method, however, has problems in that the growth rate is low, nucleation frequently occurs in random positions, resulting in small crystal size of GaN, and crystals synthesized by this method tend to be black. In this research, we attempted to change the flux composition from Na to a Na–Ca system to solve these problems and succeeded in increasing the growth rate and synthesizing transparent GaN single crystals.

Figure 1 schematically illustrates the experimental setup, and the experimental procedures are as follows. 1) A BN crucible is filled with metallic Ga and flux in a glove box, keeping the ratio of the flux to metal Ga constant ($\mathrm{Ga}/(\mathrm{Na}+\mathrm{Ca}) = 0.27(\mathrm{mol})$). The ratio of Ca to the whole flux is changed gradually as indicated in Table I. The amount of Ga is kept constant at 1.0 g throughout the experiment. 2) The BN crucible filled with Ga and flux is transferred in a pressure- and temperature-resistant stainless-steel tube. 3) The stainless-steel tube is transferred in an electronic furnace and then connected to a nitrogen gas cylinder for pressurizing. 4) The temperature is raised to 800°C so the pressure inside the stainless-steel tube reaches the fixed pressure; the temperature and pressure are then maintained for 96 h. In this period, GaN single crystals are grown by continuous dissolution of pressurized nitrogen into the solution. 5) Following the experiment, Na and Ca are carefully decomposed in cold ethanol. After

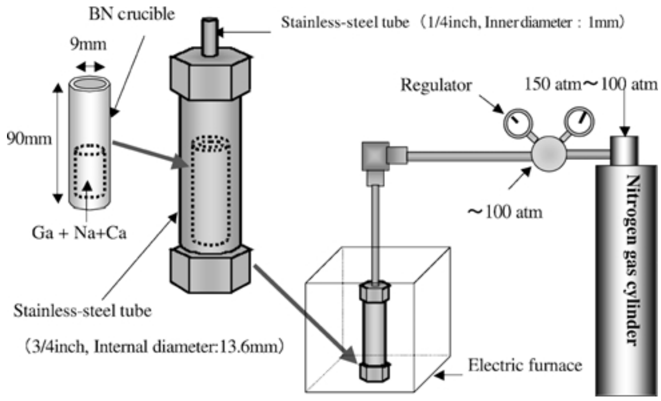
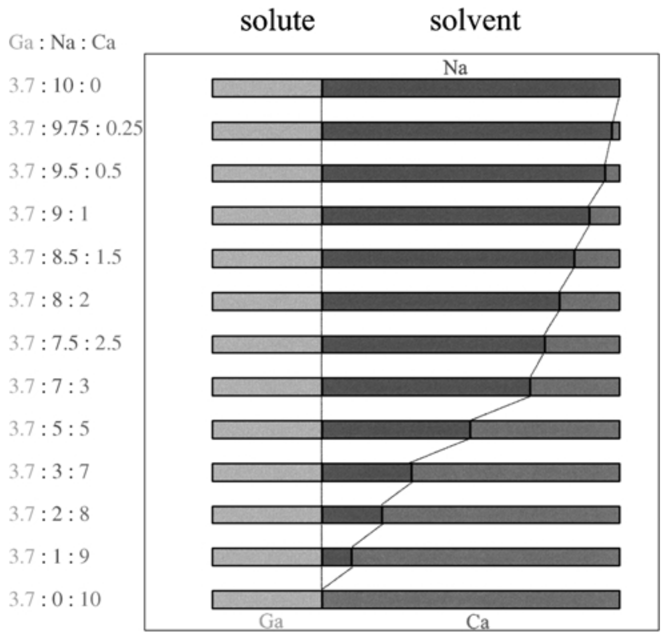


Fig. 1. Schematic illustration of experimental apparatus.

Table I. Reagents used in this experiment.



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this process, we can confirm the GaN single crystals on the BN wall.

Ca can be regarded as changing the flux composition from a Na to a Ca–Na system because the molar ratio of flux to the total solution system is constant. Figure 2 presents the changes in the yield of GaN as a function of ratio of Ca, where the yield is calculated as conversion efficiency when GaN is synthesized from metallic Ga.

Figure 2 shows the results of the experiment conducted at 800°C for 96 h. In this figure, yield is indicated as ratio of GaN crystals grown in flux against metallic Ga of starting material. The pressure applied in this experiment was 30 atm throughout the experiment. The yield was 1.3% without Ca but increased with increasing 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 as the Ca ratio increases; GaN was not synthesized when the Ca ratio exceeded 50 mol%. We also checked the effect of Ca at 700°C but found that Ca did not promote GaN synthesis at 700°C over the 96 h period.

Figure 3 illustrates changes in yield as a function of pressure. The dotted line (solid line) indicates the yield synthesized for 10 mol% of Ca (without Ca). Although yield increased with applied pressure with or without Ca, yields obtained in a Na–Ca flux were higher than those obtained in pure Na flux at every pressure applied in this experiment. Furthermore, the threshold pressure for synthesizing GaN was reduced to about 10 atm by using 10 mol% of Ca flux.

Another advantage of using a flux containing Ca is that transparent GaN crystals are easily obtainable. Figure 4(a) illustrates optical microscopic images of GaN single crystals grown in a Na flux, and Fig. 4(b), those grown in a flux containing 5 mol% Ca. The GaN single crystals grown in flux containing Ca were relatively small. This may be attributed to the high nucleation frequency caused by high supersaturation. We emphasize that transparent GaN crystals were grown only around the gas-liquid interface (Fig. 5); crystals grown in the liquid were black with or without Ca.

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

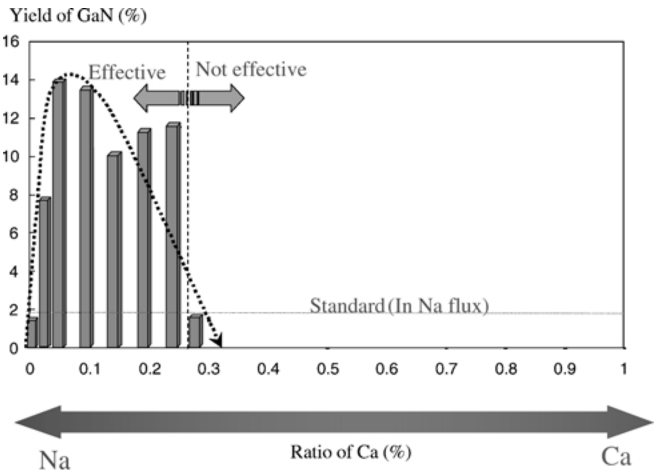


Fig. 2. Relationship between flux composition and yield of GaN grown in various compositional fluxes. Yield is indicated as ratio of GaN crystals grown in flux against metallic Ga of starting material.

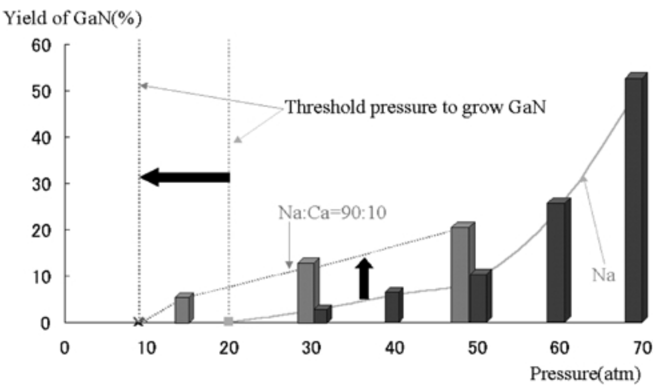
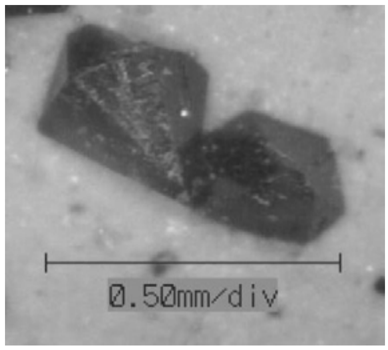
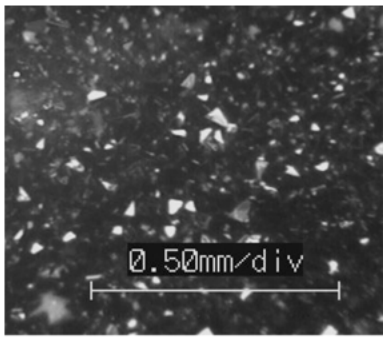


Fig. 3. Changes in yields of GaN synthesized in pure Na flux and Ca 10 mol% mixed flux according to the reaction pressure. Dotted line: Ca 10 mol% mixed flux. Solid line: Pure Na flux. Yield is indicated as ratio of GaN crystals grown in flux against metallic Ga of starting material.



(a)



(b)

Fig. 4. (a) Optical micrograph of GaN single crystal grown in pure Na flux. (b) GaN single crystals grown in pure Ca 5 mol% mixed flux.

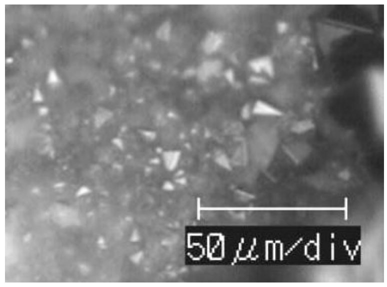


Fig. 5. Transparent GaN single crystals grown near the gas-liquid interface in Ca 5 mol% mixed flux.

and the ratio of Ca to flux is below 10 mol%, the yield of GaN grown at 800°C is much higher than that grown in pure Na flux.

2) Excessive Ca in the flux system decreases the yield of GaN.
3) Ca does not promote GaN synthesis when GaN is synthesized at 700°C.
4) GaN single crystals grown near the gas-liquid interface in flux containing Ca tend to be transparent.

Results 2) and 3) can be explained by examining the phase diagram. When the ratio of Ca exceeds 10 mol% in a Na–Ca system at 800°C, solids and liquids coexist according to the phase diagram of the Ca–Na system. Although the state of the Ca–Ga–Na system at 800°C is not clear because of the absence of a 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 is nitrided in a nitrogen atmosphere at high temperatures, resulting in the formation of Ca_3N_2. This may be why crystal growth is prevented. An alloy of Ca–Na at 700°C exists as a solid throughout almost the entire compositional region. Although the state of the Ca–Na–Ga alloy at 700°C is not clear either, an increase of the solid-state part with increases in the Ca ratio seems to reduce the yield. However, for 10 mol% of Ca at 800°C, the effect of Ca on promoting the growth of GaN in the flux system is quite clear. This can be considered a result of promoted 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 considered and reported.

Another effect of Ca is that synthesizing the transparent GaN becomes possible only around the gas-liquid interface, as mentioned above. Nitrogen vacancies can be considered to cause GaN grown away from the gas-liquid interface to be black. For example, some researchers have reported that GaN with many nitrogen vacancies tends to be black.[9] When Ca promotes nitrogen dissolution, the concentration of nitrogen at the gas-liquid interface increases considerably, which results in the synthesis of the transparent GaN crystals in areas with few nitrogen vacancies.

Experimental results obtained in this study lead to the following conclusions.

1) The yield of GaN grown in a Na–Ca flux increased drastically compared with yields in Na flux.
2) Transparent GaN single crystals can be synthesized around the gas-liquid interface using a Na–Ca flux system.

We believe that these results are due to the nitrogen dissolution promoted by changing the flux composition from Na to Ca–Na.

1) A. Sakai, H. Sunakawa and A. Usui: Appl. Phys. Lett. **71** (1997) 2259.
2) I. Akasaki, H. Amano, Y. Koide, K. Hiramatsu and N. Sawaki: J. Cryst. Growth **98** (1989) 209.
3) S. Nakamura, T. Mukai and M. Senoh: J. Appl. Phys. **71** (1992) 5543.
4) J. Karpinski, J. Jun and S. Porowski: J. Cryst. Growth **66** (1984) 1.
5) H. Yamane, M. Shimada, T. Sekiguchi and F. J. DiSalvo: Chem. Mater. **9** (1997) 413.
6) M. Onda, T. Iwahashi, M. Okamoto, Y. K. Yap, M. Yoshimura, Y. Mori and T. Sasaki: J. Cryst. Growth **237–239** (2002) 2112.
7) M. Yano, M. Okamoto, Y. K. Yap, M. Yoshimura, Y. Mori and T. Sasaki: Jpn. J. Appl. Phys. **38** (1999) L1121.
8) M. Yano, M. Okamoto, Y. K. Yap, M. Yoshimura, Y. Mori and T. Sasaki: Diamond Relat. Mater. **9** (2000) 512.
9) Bell Telephone Lab: J. Mater. Sci. **5** (1970) 1102.