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Preparation of GaN Single Crystals Using a Na Flux

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Wurtzite structure gallium nitride, GaN, is a wide direct bandgap semiconductor (3.4 eV at 300 K) and regarded as a material for blue light-emitting diodes and laser diodes.[1−4] Recent progress in thin film crystal growth techniques which can control the carrier concentration in GaN films has realized blue light-emitting diodes. Sapphire has been the most widely used substrate for GaN film deposition. However, GaN films on sapphire substrates include many defects owing to the large mismatch of lattice parameters (23%) and difference of thermal expansion coefficients (25%) between GaN and sapphire. Films with low defect concentrations are desired in order to develop blue diode lasers. Buffer layers have been only partially successful in reducing defect densities of heteroepitaxial GaN on sapphire substrates. Other substrates have also been investigated but GaN single crystals are expected to be the ideal substrates for GaN film growth.[2]

Bulk GaN single crystals have been prepared by the reaction of Ga and N_2 under a high N_2 pressure of 8000−17 000 atm and a high temperature of 1300−1600 °C.[5,6] Such extreme conditions are not suitable for industrial mass production. Vapor growth of bulk GaN single crystals has also been carried out above 1100 °C using NH_3 as the source of nitrogen.[5−7] Crystal growth of GaN at 900−1000 °C by flowing a mixture of NH_3 and H_2 over a Ga melt was explained by a vapor−liquid−solid mechanism.[8] These methods still require high temperatures and it is difficult to make large bulk single crystals for substrates in GaN film growth.

Recently, single crystals of new ternary nitrides, Ba_2ZnN_2, Sr_2ZnN_2,[9] $Ba_3Ga_2N_4$,[10] $Ba_5Si_2N_6$,[11] and $Ba_3Ge_2N_2$[12] were prepared at 500−750 °C using a Na flux. In some preparations of ternary Ga containing nitrides, some hexagonal transparent crystals were identified as GaN. We subsequently found that GaN could be prepared as a singe phase in reactions containing only gallium, sodium, and nitrogen.

In the present study, we applied the Na flux method to the preparation of GaN and investigated the conditions of crystal growth. The starting materials used were Ga (Sumitomo Chemical, 99.9999% purity) and NaN_3 (Toyo Kasei Kogyo, 99.9% purity). Thermal decomposition of NaN_3 at 300 °C provides highly purified N_2 and Na: $2NaN_3 \rightarrow 2Na + 3N_2$.[13]

NaN_3 (0.117 g (1.8 mmol) or 0.234 g (3.6 mmol)) and Ga from 0.035 to 1.116 g (0.5−16.0 mmol) were weighed under N_2 atmosphere and sealed in a stainless steel tube (SUS 316, 7.5 mm inner diameter, 9.5 mm outer diameter, and 100 mm inside length) with an arc welder. The sealed tube was heated under N_2 atmosphere in order to prevent the oxidation of stainless steel during heating. The starting materials were heated to 600−800 °C for 24−96 h. After heating, the sample in the tube was cooled to room temperature by shutting off the furnace power. The Na metal which covered the products containing GaN was removed by reaction with 2-propanol and ethanol. After washing with ethanol and drying in air, the products were characterized by X-ray diffraction (XRD). Cu Kα radiation was used on a diffractometer with a pyrolitic graphite monochromator (Rigaku, RINT2000). The samples were observed with an optical microscope and a scanning electron microscope (SEM, Hitachi S2150). Impurities in the single crystals were analyzed with a scanning Auger microscope (SAM, Perkin-Elmer) and a scanning electron microscope (Hitachi X-60) equipped with a wavelength-dispersive X-ray analyzer (WDX) and a energy-dispersive X-ray analyzer (EDAX, Kevex).

The results of XRD on the products obtained by heating at 600−800 °C for 24 h are shown in Figure 1 against the r_{Na} = Na/(Ga + Na) molar ratio of the starting mixtures. The maximum N_2 pressure calculated from the amount of NaN_3 is given in the figure. The actual N_2 pressure was probably lower due to the formation of GaN. The broken lines at $r_{Na} = 0.25$ in the figure indicate a Ga:N = 1:1 molar ratio. Intermetallic compounds of Ga_4Na and/or $Ga_{13}Na_7$ and Ga were contained in the samples prepared at the conditions marked with solid circles and shaded circles. The Ga was probably formed from the decomposition of these intermetallic compounds during handling in air. No Na−Ga−N ternary nitrides were found in the present study.

In both cases of NaN_3 = 3.6 and 1.8 mmol, GaN was produced at the high r_{Na} molar ratios.

The region in which GaN was formed spreads toward smaller r_{Na} with increasing temperature. The yields of the GaN decreased with increasing r_{Na} and were from 10 to 60 mol % against the initial Ga at NaN_3 = 3.6 mmol and 0.1−10% at NaN_3 = 1.8 mmol.

Figure 2 shows the X-ray diffraction pattern of GaN powder prepared at $r_{Na} = 0.78$ and 800 °C. All peaks in the pattern were indexed with the wurtzite crystal structure. The lattice parameters refined from the observed peak positions (a = 3.1896(1) and c = 5.1854(2) Å) agreed with the reported values.[1]

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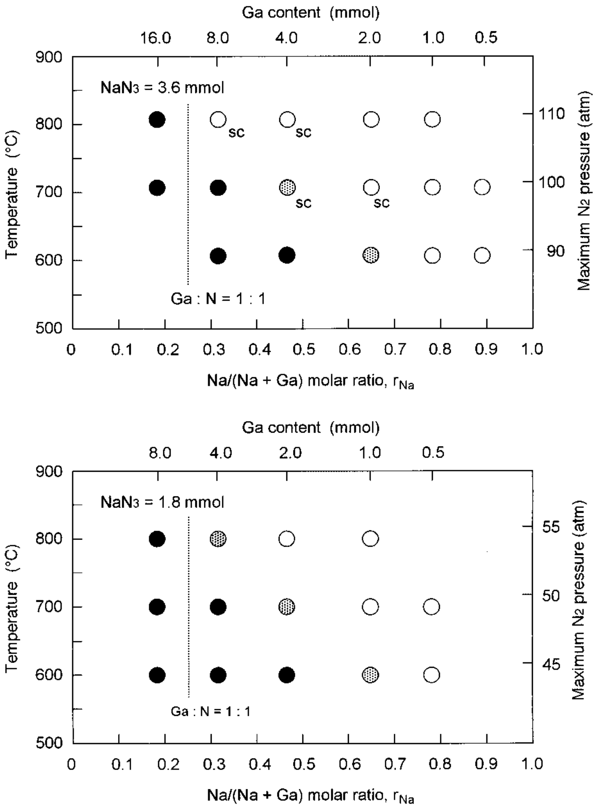

Figure 1. Experimental conditions and products obtained by heating for 24 h and by washing Na with alcohol: (solid circle) Na−Ga compounds, (shaded circle) Ga−Na compounds, and GaN, (open circle) GaN. N_2 pressures calculated from the NaN_3 contents are maximum limits, and actual pressures in the stainless steel tube reactor should be lower than those because of the formation of GaN. SC indicates that the sample contains GaN single crystals with a size over 0.1 mm.

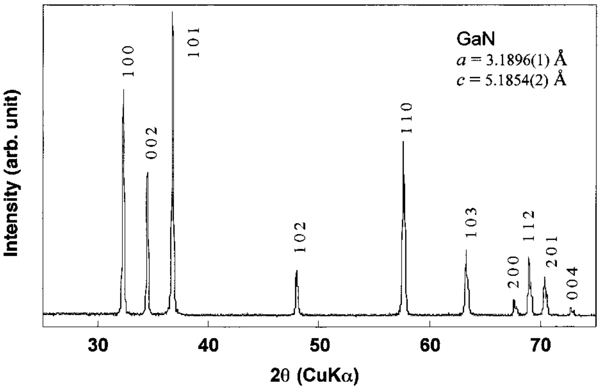

Figure 2. X-ray diffraction pattern of GaN powder prepared at NaN_3 = 3.6 mmol, r_{Na} = 0.78 and 800 °C for 24 h.

GaN particles of about 0.1 μm were observed by SEM in the sample obtained at r_{Na} = 0.78 and 700 °C. Aggregates of GaN grains having facets and a size of about 3 μm were also contained in the sample. The GaN grain size increased with decreasing r_{Na}. The color of GaN powders changed from white gray, yellowish light gray to dark gray.

The samples containing GaN single crystals with a size above 0.1 mm were prepared only at the conditions of NaN_3 = 3.6 mmol and 700−800 °C, as shown in Figure 1 with the label SC. The crystals obtained at 700 °C were colorless and transparent. Figure 3a shows an SEM micrograph of the sample prepared at r_{Na} = 0.64 and 700 °C. Hexagonal crystal plates grew from the container wall into the Na flux. The maximum size of the plate crystals obtained at this condition was more than 0.5 mm in width.

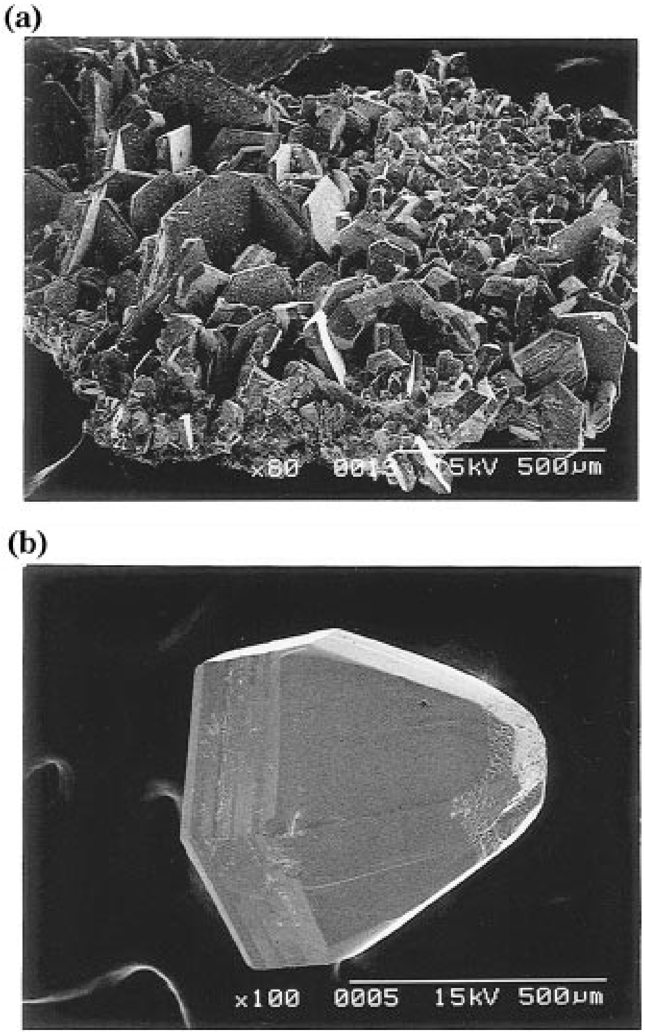

Figure 3. Scanning electron micrographs of GaN crystals prepared at NaN_3 = 3.6 mmol, r_{Na} = 0.64 and 700 °C for 24 h (a, top) and r_{Na} = 0.31 and 800 °C for 24 h (b, bottom).

At r_{Na} = 0.47 and 800 °C, the products contained agglomerates composed of colorless and transparent granular GaN crystal plates with sizes around 0.3 mm. At r_{Na} = 0.31 and 800 °C, the products included dark amber granular crystals and greenwish transparent crystal plates of 0.5−1.0 mm in size. Figure 3b shows the SEM photograph of a dark amber color single crystal which has a hexagonal pyramidal shape. The {1011} planes were well developed and the {1012} planes were observed at the top edge. Adsorbed carbon and oxygen peaks were seen in the differential Auger electron spectrum taken for the surface of the dark amber color crystals and greenish transparent crystals (Figure 4a). After 6 min of Ar beam sputtering, only the peaks from Ga, N, and Ar sputtering gas were observed in the spectrum (Figure 4b). EDX and WDX analyses also did not detect any impurity elements.

The size of GaN crystals obtained at 600 °C for 24 h was less than 0.1 mm. But after 40 h heating, colorless transparent hexagonal single-crystal plates with a size more than 0.2 mm were obtained at r_{Na} = 0.64. As shown in Figure 5, hexagonal islands and steps were observed at the surface of the crystals. The product at r_{Na} = 0.47 after heating at 700 °C for 96 h contained

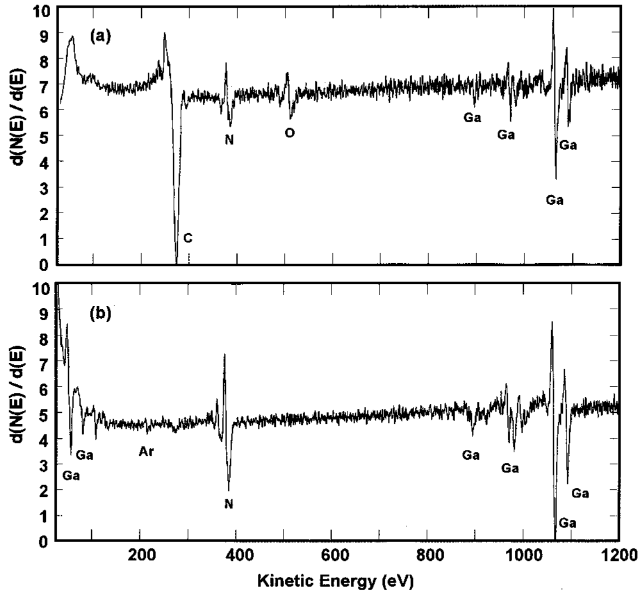

Figure 4. Scanning Auger microscope spectra obtained from the surface of the GaN single crystal prepared at $r_{Na} = 0.31$ and 800 °C for 24 h (a) and from the surface after 6 min Ar ion beam sputtering (b). It should be noted that the oxygen and carbon were only detected before the sputtering.

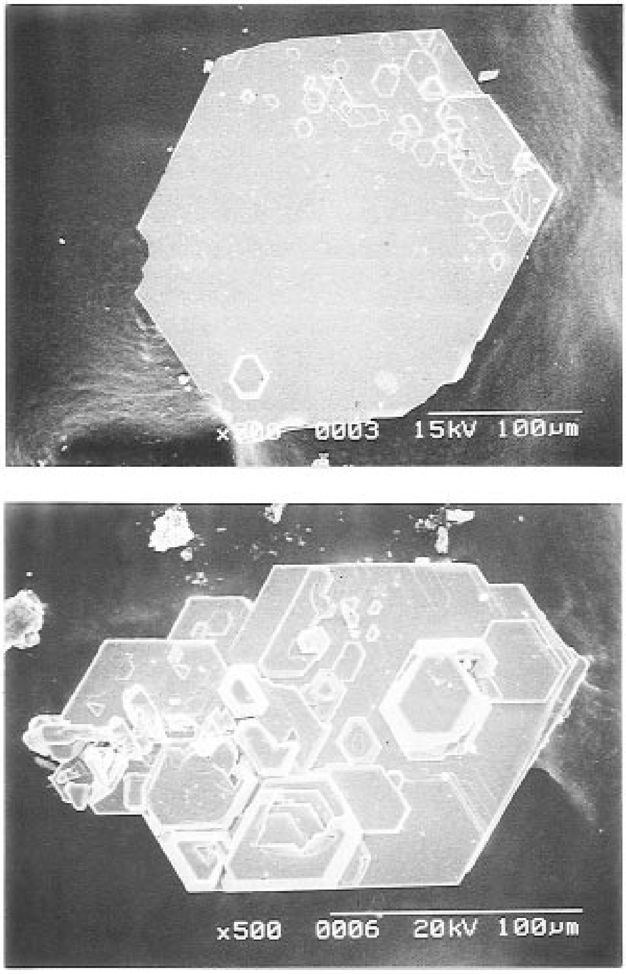

Figure 5. Scanning electron micrographs of GaN single crystals prepared at $NaN_3 = 3.6$ mmol, $r_{Na} = 0.64$ and 600 °C for 40 h.

GaN crystals with a size of 1.0−2.0 mm. The crystals were slightly brownish translucent. No GaN was detected by XRD at $r_{Na} = 0.31$ and 700 °C for 24 h. But after 96 h heating, the product mainly consisted of black GaN grains with a size around 0.1 mm.

The preparation of GaN from the reaction of a Ga melt and N_2 is prevented below 1000 °C by a skin formed on the Ga melt surface.[14] In the Ga−Na binary phase diagram,[15] only liquid is found above 556 °C. The XRD did not detect GaN in the samples prepared by heating 24 h at Ga-rich compositions. The r_{Na} conditions of GaN formation are not related to the N_2 pressure, although the yields and grain sizes of GaN depended on the N_2 pressure. We surmise that the Na activity at the Ga−Na melt surface, depending on the melt composition and temperature, mainly governs the initiation of GaN formation. Judging from the formation of GaN at 700 °C and $r_{Na} = 0.47$ after the longer heating time of 96 h, crystal growth occurs either by slow reaction of N_2 or by secondary recrystallization using the melt as a diffusion medium.

The solubility of nitrogen in liquid sodium is extremely low (3.2×10^{-11} mol % N at 600 °C and $P_{N_2} = 90$ atm).[16] The nitrogen solubility in liquid gallium estimated from the measured solubility data[6,17−19] is also low at 600 °C and $P_{N_2} = 90$ atm (1.0×10^{-7} mol % N), although the solubility in liquid Ga is 10^4 times greater than that in liquid Na. Hubbersty reported the enhancement of the solubility in Na-rich Na−Ba solution, hypothesizing a soluble species of $Ba_xN(Na)$ ($x \sim 4$).[20] Since the yields of GaN decreased with increasing r_{Na} at constant nitrogen content and pressure in the tube, it may be that similarly soluble $Ga_xN(Na)$ species are formed in the Na-rich melt. Some of the GaN products at high r_{Na} were fine powders which seemed to be from homogeneous nucleation in the solution, perhaps on cooling. The GaN single crystals obtained at low r_{Na} were probably grown through the inhomogeneous nucleation at the surface of the Ga−Na melt. During the crystal growth, the Ga component was supplied from the Ga−Na melt and the total melt composition shifted to Na-rich compositions.

GaN single crystals prepared by the previous studies[5,7,8] were not always colorless as expected from the wide bandgap. The colors reported in the previous GaN crystals were slightly yellowish,[5] dark green,[7] pale amber, and black.[8] All colors were attributed to nitrogen deficiency. The colored GaN single crystals of the present study were prepared at $r_{Na} = 0.31$ and 800 °C for 24 h (greenish transparent and dark amber), at $r_{Na} = 0.47$ and 700 °C for 96 h (pale brownish, translucent), and $r_{Na} = 0.31$ and 700 °C for 96 h (black). Under these conditions, the Ga/N ratios were small and close to Ga:N

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= 1:1. During the crystal growth, N_2 was consumed and the crystals grew under lower nitrogen pressure. These colors were presumably caused by nitrogen deficiency as speculated in the previous studies.

To summarize, GaN single crystals can be grown using Na flux at 600−800 °C. This process may become a promising way to produce GaN single-crystal substrates soon because it does not require the conditions of high temperature and high pressure, because it can grow GaN single crystals in readily available containers, and because it is readily scaled up as we are now doing.

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