Transactions of the Materials Research Society of Japan 33[4] 1277-1280 (2008)

Crystal Growth of GaN by the Reaction of Ga_2O_3 with Li_3N in Liquid Ga

Tiansheng Zhang*, Akira Mabuchi, Takashi Sugiura, Hideki Minoura
Environmental and Renewable Energy Systems Division, Graduate School of Engineering, Gifu University, Yanagido 1-1, Gifu 501-1193, Japan
Fax: 81-58-293-2594, e-mail: l3130020@edu.gifu-u.ac.jp

A novel method to synthesize a GaN crystal was studied by the reaction of Ga_2O_3 with Li_3N in liquid Ga. We have already reported that the synthesis of GaN particles by a reaction of Ga_2O_3 with Li_3N. However its particle sizes were limited to be smaller than several micrometer due to the solid-phase reaction. In order to grow bulk GaN single crystals, liquid Ga was used as a Ga source and a reaction bath. We have found that the GaN crystals with about 200 μm size were synthesized under mild condition at the temperature ranging from 650°C to 800°C under N_2 atmosphere.

Keywords: crystal growth, GaN, Ga_2O_3, Li_3N, Ga

1. INTRODUCTION

GaN is a wide band gap semiconductor with crystallographic structure of wurtzite and is used in various electronic devices such as light emitting diodes (LED) and laser diode (LD). GaN is mainly obtained by metal-organic vapor phase epitaxy (MOVPE) on sapphire substrate. Performances of these devices mainly depend on the quality of GaN films. However, it is difficult to grow high quality epitaxial films, due to large mismatch of lattic constant and large difference of thermal expansion coefficient between GaN film and the sapphire substrate [1, 2]. Therefore, bulk GaN single crystal is to be ideal substrate for homoepitaxial growth of high quality GaN films, undoubtedly.

In 1932, Johnson et al. have successfully synthesized GaN by direct reaction of Ga with NH_3 [3].

$$2Ga + 2NH_3 \rightarrow 2GaN + 3H_2 \quad (1)$$

It is difficult to synthesize pure GaN by this technique due to lack of pure Ga sources, slower reaction rate at lower temperatures and decomposition of GaN to its preliminary elements at or above 1000°C.

Lorenz et al. have grown GaN by the reaction of Ga_2O_3 with NH_3 [4].

$$Ga_2O_3 + 2NH_3 \rightarrow 2GaN + 3H_2O \quad (2)$$

However, finding suitable reaction conditions for reaction of Ga_2O_3 and NH_3 was difficult due to partial decomposition of NH_3 under 600°C in addition to above mentioned drawbacks. GaN with a color from yellow to grey has been obtained by this technique at different reaction temperatures.

Whisker, needle-shaped, platelet and prismatic GaN crystals with the size of several millimeters were obtained by the reaction of Ga and NH_3 and the products obtained as reported by Zetterstrom and Ejder [5, 6].

Recently, several attempts have been made to synthesis bulk GaN single crystals at mild growth conditions by so-called flux method [7 - 14]. In these attempts Na, K, Ca, Li were used as fluxes, and Ga and N_2 were used as sources to grow GaN bulk single crystals at temperature of 700 ~ 800°C under N_2 pressure of 10 ~ 100 atm.

All of these methods used NH_3 or N_2 to provide N^{3-} ion for GaN synthesis. We have already reported that the synthesis method of GaN by the use of Li_3N to provide N^{3-} and Ga_2O_3 as a Ga source. GaN particle was synthesized at the temperature of 700°C under N_2 pressure of 0.4 MPa [15].

$$Ga_2O_3 + 2Li_3N \rightarrow 2GaN + 3Li_2O \quad (3)$$

However the size of GaN particles obtained by this method was limited to less than several micrometers because of its solid phase reaction.

Y. Song et al. have grown GaN single crystal by reacting Ga with Li_3N at N_2 atmosphere [16]. They reported that Ga and Li_3N can not react under 700°C and Li_6WN_4 was formed by the reaction of tungsten crucible with Ga and Li_3N at 850°C .

In order to grow bulk GaN crystals, a reaction of Ga_2O_3 with Li_3N in liquid Ga under N_2 atmosphere with mild conditions was investigated in this paper.

2. EXPERIMENTAL PROCEDURE

Li_3N, Ga_2O_3 and metal Ga were used as the starting materials for the growth of GaN single crystals. For example in the case of molar ratio of Ga_2O_3 , Li_3N and Ga of 1:4:1, 0.806 g (4.30 mmol) of Ga_2O_3, 0.599 g (17.20 mmol) of Li_3N and 0.300 g (4.30 mmol) of metal Ga were weighed and placed into a graphite crucible (15 mm inner diameter, 20 mm depth, Nilaco) in a nitrogen filled glove box. The crucible was put in a sealed stainless steel reaction vessel (inner diameter : 55 mm, length : 309 mm, SUS 316) and it was set vertically in an electric furnace. Before reaction, the vessel was evacuated to a vacuum of about 26 kPa, and then the system was filled with N_2 gas of 0.4 MPa. Then it was heated and kept at the temperature ranging from 650°C to 800°C for 24 ~ 72 hours. After heating, it was cooled to room temperature. The graphite crucible was took out from the vessel into the air, the product was washed by alcoholic HCl solution and distilled water. The samples were characterized by a X-ray diffractometer (XRD, Rigaku Ultama II/PC) with CuKα radiation. The morphologies of samples were observed by scanning electron microscope (SEM, VE-7800, Keyence). The elemental analysis of GaN was determined by X-ray photoelectron spectroscopy (XPS, ESCA-3400, Shimadzu) using a monochromatized Mg Kα X-ray radiation source.

3. RESULTS AND DISCUSSION

3.1 Reaction conditions to grow GaN crystals

We calculated the Gibbs free energy of the reaction of Ga and Li_3N which is +41.3 kJ/mol even at 750°C, hence the reaction does not occur theoretically. However, Δ_rG of the reaction between Ga_2O_3 and Li_3N is -555.7 kJ/mol at the same temperature.

$$Ga_2O_3 + 2Li_3N \rightarrow 2GaN + 3Li_2O \qquad \Delta_rG(1023) = -555.7 \text{ kJ/mol} \quad (4)$$

If Ga_2O_3 reacts with Li_3N in the liquid Ga, Δ_rG of the reaction is converted into minus value.

$$Ga_2O_3 + 3Li_3N + Ga \rightarrow 3GaN + 3Li_2O + 3Li \qquad \Delta_rG(1023) = -514.4 \text{ kJ/mol} \quad (5)$$

In addition, the size of GaN was expected would be larger because this is a liquid-solid phase reaction.

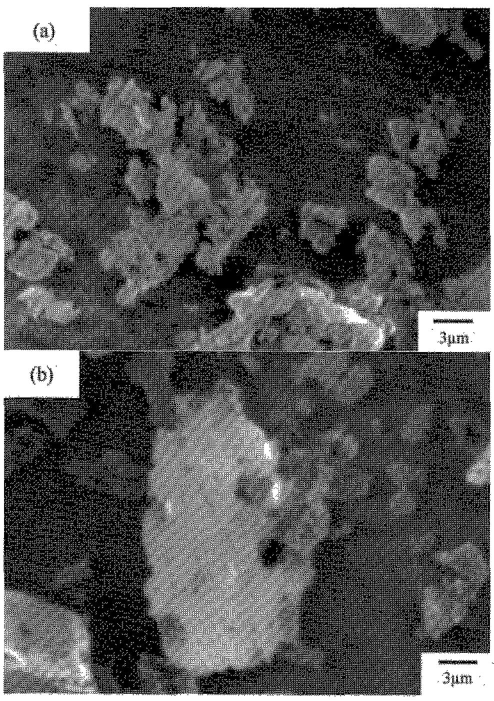

Fig.1 SEM micrographs of GaN prepared without (a) and with (b) Ga

We reacted Ga_2O_3 and Li_3N without(a) or with(b) Ga respectively, and SEM micrographs of obtained GaN were shown in Fig. 1. As compared with the size of GaN crystals, it is confirmed that the crystal growth occurred by the reaction in liquid Ga. In the case of the reaction without Ga, the particle size of product was limited to less than several micrometers. Therefore we studied the influence of reaction conditions.

X-ray diffraction analysis was carried out for the products after washing (Fig.2) prepared with a molar ratio of Ga_2O_3 : Li_3N : Ga = 1 : 4 : 1 at different temperatures. As shown in Fig.2, we found that the proper growth temperature should be higher than 700°C. At 650°C, GaN and GaOOH coexist in final products. It may be due to the formation of by-products, $LiGaO_2$ [17] and it transformed into GaOOH in HCl solution. When the temperature is higher than 700°C, only hexagonal GaN is formed and no other by-product is observed. Increasing the reaction temperature, the diffraction intensity of 0002 peak relatively increased. This result shows that the major growth direction of GaN crystal in this reaction is normal to c-axis of wurtzite structure.

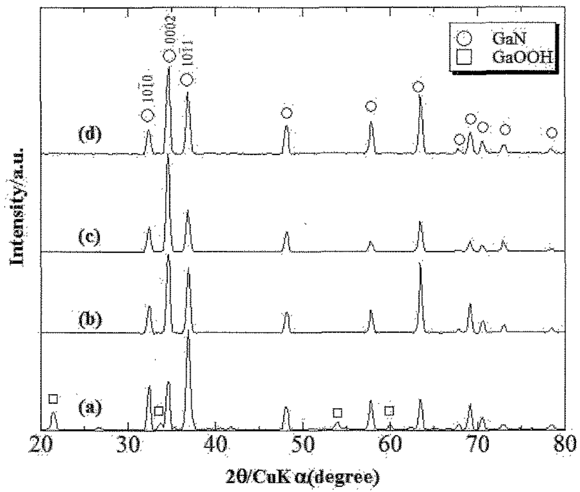

Fig.2 X-ray diffraction patterns of the products prepared with a molar ratio of Ga_2O_3, Ga and Li_3N of 1 : 1 : 4 at (a) 650°C, (b) 700°C, (c) 750°C and (d) 800°C in N_2 pressure of 0.4MPa for 48h.

Table I Yield of products prepared with a molar ratio of Ga_2O_3, Li_3N and Ga of 1 : 4 : 1 at (a) 650°C, (b) 700°C, (c) 750°C and (d) 800°C in N_2 pressure of 0.4MPa for 48h.

No.	Reaction temperature (°C)	Yield of GaN (%)
a	650	9.7
b	700	15.6
c	750	46.9
d	800	47.9

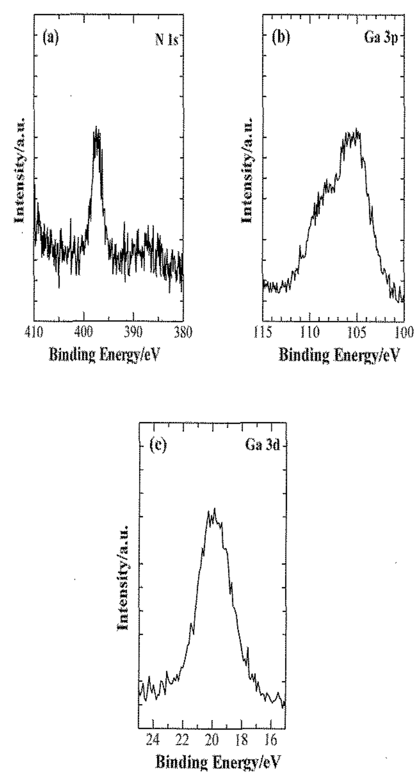

Fig.3 XPS spectra of GaN sample prepared with a molar ratio of Ga_2O_3 , Li_3N and Ga of 1 : 4 : 1 at 750°C in N_2 pressure of 0.4MPa for 24h. (a) N 1s spectrum, (b) Ga 3p spectrum, (c) Ga 3d spectrum.

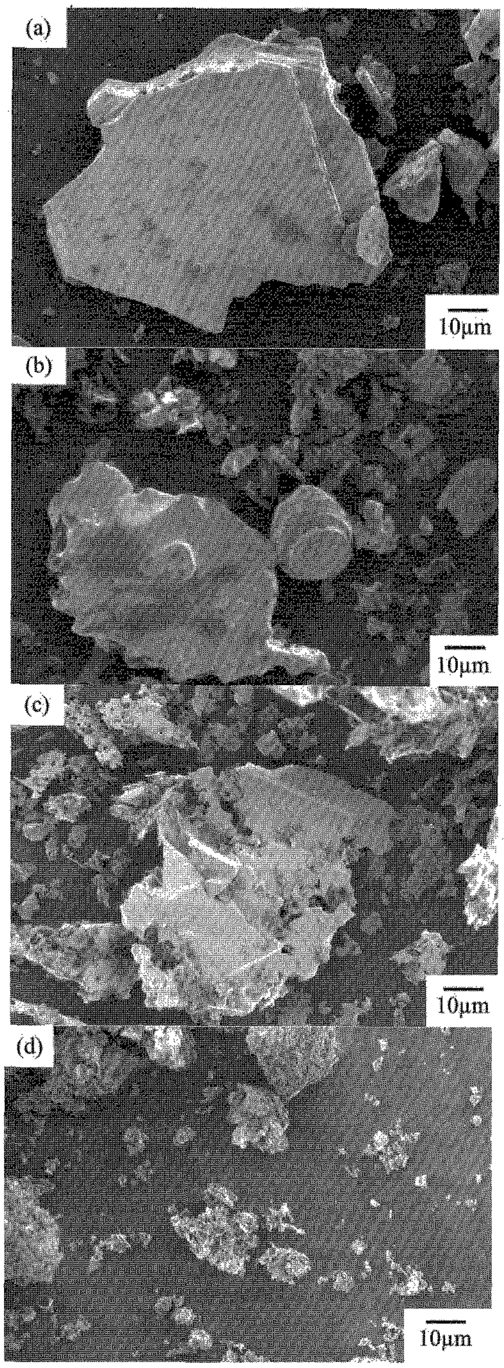

Fig.4 SEM micrographs of GaN prepared with a molar ratio of Ga_2O_3, Ga and Li_3N of 1 : 1 : 4 at (a) 800°C, (b) 750°C, (c) 700°C and (d) 650°C for 48h with N_2 of 0.4MPa.

Yields of products which prepared at different temperatures were listed in table I. The higher temperature leads to the higher yield, because the reaction fully progress at high temperature. However, high temperature(800°C) also will cause the decomposition of GaN crystals. Therefore, we concluded that the optimum temperature is 750°C. Another experiment of the synthesis of GaN with In bath instead of liquid Ga bath at 750°C lead to small yield of GaN which is 6.1%. Therefore we concluded that Ga react as one of the Ga source in this method to grow bulk GaN crystals and lead to high yield of product.

The products were also characterized by XPS. Fig. 3 shows the N 1s, Ga 3p, and Ga 3d core level region spectra. Compare to the standard XPS data, the binding energy of N 1s (Fig. 3a) with 397.3 eV, Ga 3p peak at 105.1 eV (Fig. 3b) and Ga 3d peak at 19.9 eV (Fig. 3c) are consistent with the reference values for

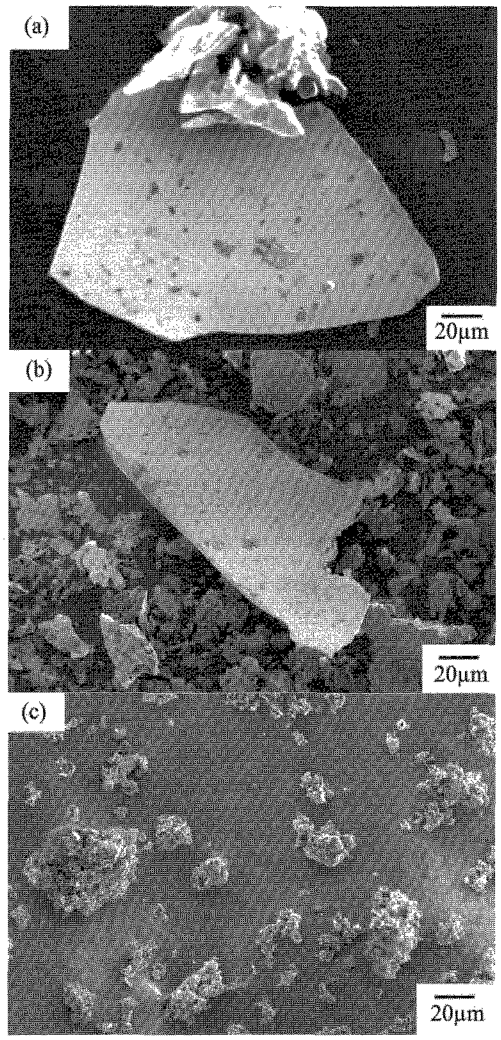

Fig. 5 SEM micrographs of GaN prepared with a molar ratio of Ga_2O_3, Li_3N and Ga of (a) 0.5 : 4 : 1, (b) 1 : 4 : 1 and (c) 1.5 : 4 : 1 at 750°C and N_2 of 0.4MPa for 24h.

GaN. No obvious peak originated from Li was observed (not shown).

SEM photographs of GaN prepared at different temperature were presented as Fig.4. As shown in these photographs, increasing the reaction temperature, the size of GaN crystals increased. The proper growth temperature should be 700 – 800°C. Below 700°C, only GaN particles are obtained.

Fig. 5 shows the SEM images of GaN crystals formed at 750°C with the different molar ratio of starting materials (Ga_2O_3, Li_3N and Ga of 0.5 : 4 : 1, 1 : 4 : 1, 1.5 : 4 : 1, respectively). In the case of Ga_2O_3:Li_3N:Ga = 0.5 : 4 : 1, about 200μm with the size of GaN crystal was obtained (a). Increasing a composition of Ga_2O_3, the size of GaN crystals decreases. Therefore, the amount of Ga_2O_3 has a influence on the crystal size of GaN. A small amount of Ga_2O_3 allows to grow a large crystal.

3.2 Mechanism of the reaction by Ga_2O_3 with Li_3N in liquid Ga

From the calculation of Gibbs free energy, reaction between Ga and Li_3N does not take place. We assume that in the first stage Ga converts to Ga_2O_3 by reacting with Li_2O.

Fig. 6 shows XRD pattern of the product formed by the reaction of Ga with Li_2O. As shown in this figure, formation of Ga_2O_3 was confirmed. Therefore we propose the mechanism of the crystal growth of GaN with two-step reactions as follows.

Step1. Seed Synthesis:

$$Ga_2O_3 + 2Li_3N \rightarrow 2GaN + 3Li_2O \quad (6)$$

Step2. Crystal Growth:

$$2Ga + 3Li_2O \rightarrow Ga_2O_3 + 6Li \quad (7)$$

First Ga_2O_3 react with Li_3N and GaN seed in the size of several micrometers are synthesized as shown in Fig. 1(a). Second, as shown in equation (7) Li_2O reacted with Ga at the surface of liquid Ga. Formed Ga_2O_3 react with Li_3N again to grow bulk GaN single crystal. Although Li was formed as one of by-products, it is unstable and will reacts with a graphite crucible or oxygen which remain in the reaction vessel.

From this mechanism, we make a hypothesis that the bulk GaN crystals can be grown when Li_2O is used as oxygen source and react with Ga and Li_3N. This work is under way by our group.

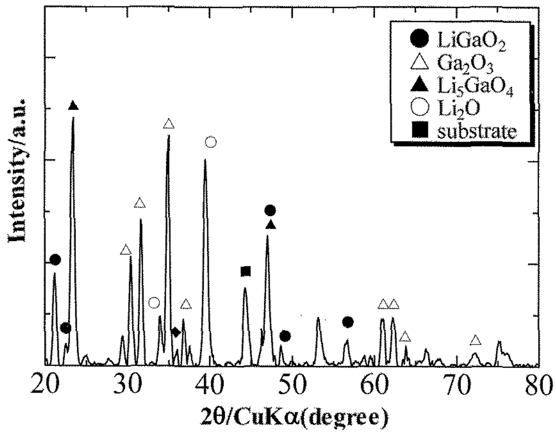

Fig.6 X-ray powder diffraction patterns of the products prepared with a molar ratio of Ga and Li_2O of 1 : 0.25 at 750°C in N_2 pressure of 0.4MPa.

4. CONCLUSION

The size of 200μm hexagonal GaN was prepared by the reaction of Ga_2O_3 with Li_3N in liquid Ga. The reaction mechanism is as follows. In the first stage the seed GaN and the Li_2O were formed by the reaction of Ga_2O_3 with Li_3N. In the second stage Ga_2O_3 was formed by the reaction of Ga with Li_2O continuously, so the crystal growth occurs. A comparison of the yields of GaN using Ga and In for liquid metal bath showed that liquid Ga works not only as a reaction bath but also as a Ga source.

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(Recieved December 8, 2007 ; Accepted March 13, 2008)