Synthesis of GaN crystals through the reaction of gallium with lithium amide

Tiansheng ZHANG*, Takashi SUGIURA†, Wenhui LU, Fan WU, Junwen MAO, Peizhen QIU and HUGEJILE

Laboratory of Optoelectronic and Devices, Faculty of Science, Huzhou University,
No.1 Xueshi Road, Huzhou City, Zhejiang Province, China
†Environmental and Renewable Energy Systems Division, Graduate School of Engineering, Gifu University,
1-1 Yanagido, Gifu 501–1193, Japan

Gallium nitride (GaN) crystals were synthesized through the reaction of Ga with LiNH₂ at temperature ranging from 450 to 800°C under NH₃ atmosphere. Hexagonal GaN crystals with a diameter of approximately 100 μm were obtained. A mechanism that can increase the crystal size during the synthesis of GaN crystals has been discovered. Ga reacted with LiNH₂ to form GaN particles at the first step. Afterward, Li₃GaN₂ was formed through the reaction of GaN particles and LiNH₂. At the second step, the growth of GaN crystals continuously occurred through the reaction of Li₃GaN₂.

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1. Introduction

Gallium nitride (GaN) has gained significant attention because of its wide band gap corresponding to blue and ultraviolet ray emissions, which makes it suitable for optoelectronic devices. Recent studies have investigated some techniques for growing bulk GaN single crystals from solutions with the Na-flux and the ammonothermal methods as representative examples. GaN single crystals have been grown through the Na-flux method at a low temperature (700 to 900°C) and a low pressure (0.1–7 MPa) with the Ga-Na mixed melt or with the Ga melt in Na vapor under N₂ atmosphere. The idea of the ammonothermal technique, which uses ammonia as a solvent, has also been developed to grow GaN crystals at a pressure ranging from 100–300 MPa and a temperature ranging from 400–600°C. A high-pressure ammonothermal method was also developed to grow GaN single crystals with high quality at a pressure of 5–20 kbar and a temperature ranging from 600 to 1000°C.

Li₃N was used as a highly reactive nitrogen source to develop a new technique for synthesizing low-cost GaN crystals under moderate conditions, to improve the reaction rate and to lower the reaction temperature. We have developed a synthesis method by using Li₃N and Ga₂O₃. GaN particles were synthesized at a temperature of 700°C and an N₂ pressure of 0.4 MPa, which is a moderate condition. However, the size of GaN particles obtained through this method was limited to less than several micrometers because it reacted in a solid phase. Ga (melting point: 29.8°C) was added into the reaction system to synthesize bulk GaN crystals. Afterward, the reaction transformed to a liquid-solid phase. Hexagonal bulk GaN crystals with a size of several micrometers were formed by this method. The size of GaN was limited by the amount of Li₃N. Therefore, the atmosphere of the reaction was changed from N₂ to NH₃ to continuously supply nitrogen. Ga₂O₃ and Li₃N were then heated under NH₃ atmosphere. However, with this method, GaN crystals have not been synthesized. Only LiGaO₂ and Li₃GaO₄ were observed. Ga was used as the gallium source instead of Ga₂O₃ and was reacted with Li₃N under the NH₃ atmosphere to prevent the oxide formation. The GaN crystals with a diameter of approximately 100 μm were then synthesized. However, in this reference paper, it also presented that LiNH₂ was used as a nitrogen source instead of Ga₂O₃ and was reacted with Li₃N under the NH₃ atmosphere to prevent the oxide formation. In this study, we have investigated the mechanism of synthesizing GaN through the reaction of Ga with LiNH₂ under the NH₃ atmosphere. In this mechanism, the bulk GaN single crystal can be obtained if the reaction time is long enough.

2. Experiment

Ga (Nacalai Tesque. Inc., 99.9999%) and LiNH₂ (Kishida Chemical Co. Ltd., 99.9%) were used as the starting materials and added into a graphite crucible (Φ 15 mm × H 20 mm). The molar ratio of Ga and LiNH₂ was set to 1:6. The crucible with starting materials was then placed in a sealed stainless steel reaction vessel and was set vertically in an electric furnace. The vessel was evacuated and then filled with NH₃ (Taiyo Nippon Sanso, 99.999%) before the reaction. The vessel was heated and kept at a temperature ranging from 400 to 800°C and under various reaction times under the NH₃ atmosphere of 0.1 MPa. After the reaction, the vessel was cooled to room temperature. The products were successively washed with a 1.0 M alcoholic HCl solution and distilled water.

The crystallographic structure and crystallinity of the samples were examined by X-ray diffraction (XRD, Rigaku, RINT-Ultima II/PC) with CuKα radiation. The morphology of the samples was observed through a scanning electronic microscope and compositional analysis was performed through energy dispersive X-ray analysis (SEM/EDX, Hitachi, S-4800).
3. Results and discussion

Ga was used as the gallium source and was heated with LiNH₂ under the NH₃ gas atmosphere of 0.1 MPa, and the reaction temperatures varied from 400 to 800°C with the same reaction time (12 h). The XRD patterns of each sample are depicted in Fig. 1. At 400°C, all products were dissolved in the alcoholic HCl solution. The existence of LiGaO₂ was confirmed from the XRD spectrum of the products before washing, and they can be removed by the HCl solution. At 450°C, the XRD peak of GaN was clearly observed after washing. Therefore, the synthesis method of GaN through the reaction of Ga and LiNH₂ occurs at a temperature higher than 450°C. The major diffraction peaks of the products, which were synthesized at 450–800°C, can be indexed to a hexagonal GaN, which agreed with the data listed in the JCPDs (No. 89-8624). No peaks of other by-products were detected. These results have shown that the products contained only GaN crystals, and no other by-products were produced.

SEM was used to observe the morphology of GaN particles, which were synthesized at different temperatures for 12 h. The micrographs are illustrated in Fig. 2. The photographs show that the size of GaN crystals increased as the reaction temperature increased. At 450°C, the size of GaN crystals was approximately several nanometers and still increased up to several micrometers at 550 and 650°C. The increase of the reaction temperature to 750°C resulted in the increase of the size of the crystals to approximately 100 μm, and the shape of these crystals became plate-like. The shape was consistent with the result that the (0002) peak intensity in the XRD spectrum at 750°C (Fig. 1) is relatively strong. Considering the results of XRD spectra and crystal shapes, the direction of the crystal growth in this reaction at 750°C is perpendicular to the c-axis of the hexagonal GaN to create the plate-like crystals, and the growth direction was set to parallel to the substrate. However, at 800°C, the size of the crystals and the yield of GaN decreased. Therefore, the decomposition of GaN was confirmed to occur at a higher temperature.

In Fig. 3, the full width at half maximum (FWHM) of the (0002) diffraction peak in Fig. 1 for the obtained hexagonal GaN crystals as a function of the reaction temperatures is illustrated. The FWHM decreased the increasing reaction temperature to a minimum value and then increased. The minimum FWHM value was obtained at 750°C. The maximum yield of 90% was obtained at this temperature. Therefore, the optimum temperature is 750°C in terms of the size of the crystals and the yield.

The SEM micrographs of the GaN crystals that were synthesized at 750°C under different reaction times are presented in Fig. 4. In these photographs, increasing the reaction time, resulted to the increase of the size of the GaN crystals. The yield was calculated by the molar ratio of GaN and Ga and is shown in Fig. 5. The yield increased until 6 h and reached a constant value of approximately 80%. However, the size of the GaN crystals increased with the increase of the reaction time. From these results, the Ga reacted with LiNH₂ to form small GaN particles at the first step, and then the growth of the GaN crystals occurred at the second step.

Considering that the reaction of Li₃GaN₂ and H₂ has also been reported.20)
The obtained GaN particles then reacted with LiNH₂ to form the intermediate Li₃GaN₂, and then Li₃GaN₂ reacted to form GaN, Li₃GaN₂, and Li₂O were observed in this condition [Fig. 6(a)]. The results show that Ga reacted with LiNH₂ to form the intermediate Li₃GaN₂, and then Li₃GaN₂ reacted to form GaN under the NH₃ atmosphere. Moreover, the mechanism of the growth of the GaN crystals through the reaction of Ga and LiNH₂ was confirmed.

\[
\text{Li₃GaN}_2 + 2\text{H}_2 \rightarrow \text{LiNH}_2 + 2\text{LiH} + \text{GaN}
\]
\[
\leftrightarrow \text{Li}_2\text{NH} + \text{LiH} + \text{GaN} + \text{H}_2
\]  

The mechanism of this study was proposed as follows.

First, Ga reacted with LiNH₂ to form small GaN particles according to the following reaction.

\[
2\text{Ga} + 2\text{LiNH}_2 \rightarrow 2\text{GaN} + 2\text{LiH} + \text{H}_2
\]  

The obtained GaN particles then reacted with LiNH₂ to form Li₃GaN₂.

\[
\text{GaN} + 2\text{LiNH}_2 + \text{LiH} \rightarrow \text{Li}_3\text{GaN}_2 + \text{NH}_3 + \text{H}_2
\]  

Li₃GaN₂ reacted similar to reaction Eq. (1), and the growth of GaN crystals continuously occurred at the second step.

Ga and LiNH₂ were heated at 750°C for 12 h under the N₂ atmosphere of 0.1 MPa to confirm this mechanism. GaN, Li₃GaN₂, and Li₂O were observed in this condition [Fig. 6(a)]. The yield of GaN was calculated as follows:

\[
\text{Yield} \% = \frac{M(\text{GaN})}{M(\text{Ga metal})} \times 100\%
\]

which is 34.3%. After being heated under the N₂ atmosphere, the mixture, including GaN, Li₃GaN₂, and Li₂O, were heated at 750°C for 12 h under the NH₃ atmosphere. The yield of GaN was up to 82.7%, and no peaks of Li₃GaN₂ were observed in the XRD pattern [Fig. 6(b)]. The results show that Ga reacted with LiNH₂ to form the intermediate Li₃GaN₂, and then Li₃GaN₂ reacted to form GaN under the NH₃ atmosphere. Moreover, the mechanism of the growth of the GaN crystals through the reaction of Ga and LiNH₂ was confirmed.

4. Conclusion

Hexagonal GaN crystals with a diameter of 100 µm were synthesized through the reaction of Ga with LiNH₂ under the NH₃ atmosphere. The reaction temperature of approximately 750°C was determined as an optimum condition in terms of the size and yield of the GaN crystals. Li₃GaN₂ was obtained through the reaction of Ga and LiNH₂ under the N₂ atmosphere, and the yield of GaN increased when the mixture was heated under the NH₃ atmosphere. Therefore, the reaction mechanism was suggested as follows. At the first step, Ga reacted with LiNH₂, and the intermediate Li₃GaN₂ was obtained. At the second step, Li₃GaN₂ was reacted, and GaN crystal growth occurred.

Acknowledgment

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Table 1. Atomic ratio of GaN before and after LiNH₂ treatment

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Ga (at%)</th>
<th>N (at%)</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>before</td>
<td>69.77</td>
<td>30.23</td>
<td>2:1</td>
</tr>
<tr>
<td>after</td>
<td>50.37</td>
<td>49.63</td>
<td>1:1</td>
</tr>
</tbody>
</table>

Reference

7) F. Kwamura, M. Morishita, M. Tanpo, M. Imade, M.


