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Synthesis of gallium nitride nano-particles by ammonia nitridation of mixed β -gallium oxide and gallium nitride powders

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Gallium Nitride nano-particles (GaN NPs) are synthesized by a simple nitridation method. A mixture of commercially available β -Gallium Oxide (β -Ga₂O₃) and GaN powders with about 5 μ m particle size was heated at temperatures ranging from 700–1,000 °C in an ammonia (NH₃) atmosphere for 1 h. In the powder mixture, the β -Ga₂O₃ particles converted to GaN NPs agglomerates, while the GaN particles are slightly grown. When the mixture was heated in the NH₃ atmosphere at 900 °C, GaN NPs varying from 30 to 50 nm and micro-sized GaN particles were obtained.

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1. Introduction

Gallium nitride (GaN) is a promising wide-band gap ($E_g = 3.4$ eV) semiconductor for blue-light-emitting diodes, laser diodes, high-speed field-effect-transistors, and high temperature electronic devices.^{1)–4)} Recently, its utilization as solar cell material is also envisaged.⁵⁾ Metal and semiconductor nano-structured materials are recently gaining significant attention because of their size dependent optical, magnetic, and electronic properties.^{6),7)}

Of these, GaN nano-particles (NPs) are synthesized by multiple methods. Lan et al. reported synthesis of GaN NPs (30–70 nm) by the ammonothermal method at 350–500 °C.⁸⁾ Wan et al. synthesized NPs (45 nm) by ammonia (NH₃) nitridation of a Ga₂O₃/Ga mixture at 950 °C,⁹⁾ with the reaction tube pressure maintained at 100 Torr. Ogi et al. proposed the salt-assisted spray pyrolysis method to produce NPs (25 nm) from a Ga(NO₃)₃-containing solution.^{10),11)} Azuma et al. applied a metal–organic chemical vapor deposition process of trimethyl gallium for the synthesis of NPs (<10 nm) at 800–1,000 °C.¹²⁾ Also, You et al. synthesized NPs (10–40 nm) by the gallium particle trapping effect in N₂ nonthermal plasma with Ga vapor.¹³⁾ However, most of these methods require expensive or

unstable reagents and/or complicated equipment, whereas the synthesis of the GaN NPs necessitates a cheap and simple method. Qaeed et al. reported chemical synthesis of highly crystalline GaN NPs (50 nm) at low temperature (90 °C) under atmospheric pressure.¹⁴⁾ Previously, we introduced a simple method for GaN NPs synthesis by NH₃ nitridation of mixed β -Gallium Oxide (β -Ga₂O₃) and GaN powders,¹⁵⁾ but the optimal synthesis conditions and characterization were not examined. In this study, the synthesis of GaN NPs by a simple nitridation method is demonstrated and the NPs obtained are characterized.

2. Experimental procedure

Commercially available β -Ga₂O₃ and GaN powders (>99.99%, KOJUNDO CHEMICAL LABORATORY CO., LTD.) were purchased and utilized in this study. These powders are displayed in scanning electron microscopy (SEM) photomicrographs in Fig. 1. The β -Ga₂O₃ powder contains columnar-shaped particles about 4–5 μ m long, comprising aggregates of primary particles about 0.1 μ m long with interparticle voids [Fig. 1(a)]. The GaN powder particles show resemble those of β -Ga₂O₃ [Fig. 1(b)]. The powders were mixed in a container by shaking, taking care to preserve their microstructures. About 0.02–0.1 g of the mixed powders were placed in alumina crucibles and heated at 700–1,000 °C for 1 h using an electric tube furnace. The atmosphere was NH₃ balanced by Ar, with the total flow rate fixed at 50 mL min^{−1}. The samples were then characterized by powder X-ray diffraction (XRD, Rigaku,

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Fig. 1. SEM images of the as-received (a) β -Ga₂O₃ and (b) GaN powders. Both are similar to each other and are consisted primary particles about 0.1 μ m long with interparticle voids.

Rint-TTR3), SEM (JEOL, JSM-7400F), and transmission electron microscopy (TEM, JEOL, JEM-2100).

3. Results and discussion

3.1 Effect of adding GaN powder to the β -Ga₂O₃ powder

An SEM photomicrograph after heating a β -Ga₂O₃ sample at 900 °C for 1 h in an NH₃ atmosphere is shown in **Fig. 2(a)**. The size and shape of the sample is similar to the original sample [Fig. 1(a)], but the interparticle voids are smaller. Only peaks corresponding to GaN¹⁶⁾ are observed in the XRD pattern. In a previous study, we demonstrated that Ga₂O₃ is converted to GaN in an NH₃ atmosphere above 700 °C,¹⁷⁾ which is consistent with other studies.^{18),19)}

The SEM photomicrograph of the mixed GaN and β -Ga₂O₃ powders at a weight ratio of 1:1 heated under the same condition as Fig. 2(a) is shown in Fig. 2(b). Contrasting dark and bright particles are evident, with the dark particles exhibiting shapes almost identical to those of the sample in Fig. 2(a), but the particles are slightly denser. The white particles are also found to be aggregates of fine particles, and since only peaks corresponding to GaN are present in the XRD pattern for the sample, both particle types are considered as GaN.

Fig. 2. SEM images of the samples heated at 900 °C in an NH₃ atmosphere for 1 h. The starting samples are (a) β -Ga₂O₃ and (b) mixed powders of β -Ga₂O₃ and GaN. The white particles are found to be aggregates of fine particles in the mixed powder (b).

Fig. 3. XRD patterns of samples heated at (a) 700 °C, (b) 900 °C, and (c) 1,000 °C under a 100 kPa NH₃ atmosphere.

3.2 Impact of reaction temperature and ammonia partial pressure

The XRD patterns for mixed β -Ga₂O₃ and GaN powders at a weight ratio of 1:1 and heated at 700, 900, and 1,000 °C in an NH₃ atmosphere for 1 h are displayed in **Fig. 3**. Because only peaks corresponding to GaN are observed in the XRD patterns, complete conversion of the β -Ga₂O₃ powder in the starting powders to GaN is inferred. The SEM photomicrographs of particles in the samples in

Fig. 4. SEM images of samples heated at (a) 700 °C, (b) 900 °C, and (c) 1,000 °C in a 100 kPa NH_3 atmosphere.

Fig. 3 are exhibited in **Fig. 4**. In the sample heated at 700 °C, fine particles and severely aggregated particles are observed in the lower left part of Fig. 4(a). For the sample heated at 900 °C, fine particles are observed in the bright part of Fig. 4(b), whereas for the sample heated at 1,000 °C, an aggregate of fine particles about 100 nm long is observed in Fig. 4(c). Therefore, heating in NH_3 produces fine particle aggregates and dense particles between 700–1,000 °C, with the size of the fine particles increasing with temperature.

The TEM photomicrographs of the NPs aggregates are shown in **Fig. 5**, with the sample from heating at 700 °C displaying particles with diameters ranging from 20 to 70 nm. Observation at higher magnification depicts the

Fig. 5. TEM images of samples heated at (a) 700 °C and (b) 900 °C in a 100 kPa NH_3 atmosphere. A higher magnification image of (b) is shown in (c).

lattice structure and confirms crystallization of particles [Fig. 5(c)]. In the sample heated at 900 °C, the particle diameters show lower variation with values from 30 to 50 nm. Also, the shapes of the particles are clearer compared with the heated sample at 700 °C.

Fig. 6. XRD patterns of samples heated at 900 °C for 1 h in (a) 10 and (b) 50 kPa NH_3 atmosphere balanced by Ar. The presence of residual $\beta\text{-Ga}_2\text{O}_3$ phase in (a) suggest that the nitridation did not proceed completely.

The XRD pattern of the sample heated at 900 °C for 1 h under P_{NH_3} of 10 and 50 kPa are displayed in **Fig. 6**. In the pattern for P_{NH_3} of 10 kPa, peaks corresponding to $\beta\text{-Ga}_2\text{O}_3$ ²⁰⁾ and GaN are observed, whereas for the pattern at P_{NH_3} of 50 kPa, only GaN peaks are present. This suggests that a P_{NH_3} of 10 kPa is insufficient for complete $\beta\text{-Ga}_2\text{O}_3$ nitridation, while a P_{NH_3} of 50 kPa is sufficient.

The SEM photomicrograph for the sample heated at 900 °C for 1 h under P_{NH_3} of 10 and 50 kPa are shown in **Figs. 7(a)** and **7(b)**, respectively. The sample heated under P_{NH_3} of 10 kPa exhibits particles with surface pores and high density, without NPs [Fig. 7(a)]. Conversely, the sample heated at P_{NH_3} of 50 kPa displays aggregated fine particles in the center of the photomicrograph, albeit in low numbers [Fig. 7(b)].

In addition to the experiment previously described, other experiments were performed under different conditions to confirm the crystalline phases by the XRD, with the size of the NPs presented in **Table 1**. The results demonstrate that the NPs formed at 700–1,000 °C under P_{NH_3} of 100 kPa, and the temperature range narrowed with decreasing P_{NH_3} .

3.3 Formation mechanism of the NPs

A proposed mechanism for the formation of the NPs is shown in **Fig. 8**. This mechanism involves a reaction between $\beta\text{-Ga}_2\text{O}_3$ and NH_3 that proceeds via Ga_2O gas species.^{17),21),22)} Firstly, H_2 or other gas species formed by thermal decomposition of NH_3 (represented as NH_x) reacts with $\beta\text{-Ga}_2\text{O}_3$ and the Ga_2O gas formed (Fig. 8, Stage 1). High vapor pressures ranging from 0.3–1.3 kPa are reported for Ga_2O at 800–1,000 °C.²³⁾ This favors the reaction of the Ga_2O gas with NH_3 to produce GaN. The produced GaN rapidly deposits on existing GaN particles surfaces (heterogeneous nucleation). Generally, the heterogeneous nucleation process is energetically advantageous compared with homogeneous nucleation, because of its lower activation energy. In this process, the preliminarily added GaN absorbs $\beta\text{-Ga}_2\text{O}_3$, and as the process progresses (Stage 2), $\beta\text{-Ga}_2\text{O}_3$ is consumed, causing decrease in the $\beta\text{-Ga}_2\text{O}_3$

Fig. 7. SEM images of samples heated at 900 °C in (a) 10 and (b) 50 kPa NH_3 atmosphere. The aggregates of fine particles are found in the center of the photograph of (b).

Table 1. Crystalline phases and particle size of the NPs observed in samples obtained under different conditions

Temperature (°C)	P_{NH_3} = 10 kPa		50 kPa		100 kPa	
	Phase	Size (nm)	Phase	Size (nm)	Phase	Size (nm)
700	—		—		GaN	20–70
750	—		—		GaN	20–70
800	Ga_2O_3 GaN	N/A	Ga_2O_3 GaN	N/A	GaN	30–50
850	—		Ga_2O_3 GaN	N/A	GaN	30–50
900	Ga_2O_3 GaN	N/A	GaN	50	GaN	30–50
950	Ga_2O_3 GaN	N/A	GaN	N/A	GaN	60–100
1,000	GaN	N/A	GaN	N/A	GaN	80–110

*The — sign indicates no experiment was conducted, while N/A means nano-sized particles were not obtained.

primary particles. In Stage 3, as the $\beta\text{-Ga}_2\text{O}_3$ primary particles decrease, conversion to GaN NPs occurs. The reason for conversion of the low amount of $\beta\text{-Ga}_2\text{O}_3$ to GaN at this stage is presently unclear, but without this conversion, explaining the formation of the GaN NPs agglomerates is difficult. Finally, the mixture of GaN NPs and GaN particles are produced.

Fig. 8. Proposed reaction mechanism for formation of the GaN NPs.

However, this method involves two problems that must be overcome. The first is that most of the $\beta\text{-Ga}_2\text{O}_3$ particles are converted to non-nano-sized GaN particles, while the other is that the obtained samples are mixtures of nano- and micro-sized GaN particles. Since this method is simple and involves no expensive precursor, overall, it is a cost-effective method. Also, the method produces a mixture of fine and coarse particles. Efficiently separating the GaN NPs from other particles is envisaged in future studies. In the proposed mechanism, the GaN powder in the starting material adsorbs the produced GaN, but other materials may be used for adsorbing the produced GaN.

4. Summary

In this study, GaN NPs were synthesized by a simple nitridation method. Mixed powders of commercially available Ga_2O_3 and GaN of about $5\text{ }\mu\text{m}$ particle size were heated for 1 h under an NH_3 atmosphere to produce NPs. The NPs characterized by XRD, SEM, and TEM revealed a mixture of GaN NPs and GaN micro-sized particles formed after heating. The GaN NPs were obtained at 700–1,000 °C under P_{NH_3} of 50–100 kPa, with NPs of 30–50 nm produced at optimal conditions of heating at 900 °C for 1 h under P_{NH_3} of 100 kPa. The size of the NPs increased with increasing temperature.

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