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Synthesis and characterization of GaN powder by the cyanonitridation of gallium oxide powder

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Abstract

Gallium nitride (GaN) powder was synthesized by the cyanonitridation of β-gallium oxide (β-Ga_2O_3) powder and characterized by powder X-ray diffraction, ^{71}Ga magic-angle spinning nuclear magnetic resonance spectroscopy, Raman spectroscopy, and scanning electron microscopy. The cyano radical, which was formed by the thermal decomposition of organic compounds such as acetonitrile and melamine, was involved in the nitridation of β-Ga_2O_3. The formation of GaN *via* cyanonitridation commenced at slightly higher temperature than that *via* ammonolysis. The produced GaN powders showed five first-order phonon modes in Raman spectra. Particles' morphologies were maintained during cyanonitridation, indicating that the β-Ga_2O_3 did not convert to GaN through gaseous species such as Ga_2O.

Keywords: Gallium nitride; Gallium oxide; Acetonitrile; Melamine; Hydrogen cyanide

1. Introduction

Gallium nitride (GaN) is a promising semiconductor material for use in ultraviolet light-emitting diodes and laser diodes because of its wide-band gap (3.38 eV) and thermal and chemical stability [1]. GaN powder sintered into mechanically robust and machinable ceramics represents an economical alternative to GaN single-crystal supports for optoelectronics [2]. GaN powder is typically synthesized through the prolonged ammonolysis of ammonia (NH_3) with gallium oxide (Ga_2O_3) at elevated temperatures [3–6]:

$$Ga_2O_3(s) + 2NH_3(g) \rightarrow 2GaN(s) + 3H_2O(g) \tag{1}$$

Ga_2O_3 can alternatively be converted to GaN by routes which do not employ NH_3 as a nitridizing reagent. Zhao et al. synthesized GaN by heating a mixture of Ga_2O_3 and amorphous $C_3N_{3.69}$ or melamine, which was pressurized into a pellet and placed to a silica ampoule [7,8]. And they suggested that carbon nitrides such as CN_2 and NCNH, thermal decomposition products of melamine, are likely involved in the nitridation of Ga_2O_3 [8]. Buha et al. prepared GaN from γ-Ga_2O_3 nanopowders using cyanamide and urea as nitridizing reagents [9].

This work reports the preparation of GaN powder from β-Ga_2O_3 powder using organic compounds such as acetonitrile (CH_3CN) and melamine as nitridizing reagents. The thermal decomposition of CH_3CN and melamine yields hydrogen cyanide (HCN) [10,11]. Clément et al. prepared titanium nitride (TiN) by reacting titanium dioxide (TiO_2) with monomethylamine [12]. The reaction was termed the cyanonitridation because HCN formed by the decomposition of monomethylamine was involved in the nitridation of TiO_2 to TiN. Previous works have shown that the reaction of HCN with alumina (Al_2O_3) can give aluminum nitride (AlN) [10,11,13].

2. Experimental procedure

2.1. Synthesis of GaN from Ga_2O_3 under a flow of CH_3CN diluted in Ar

The precursor, β-Ga_2O_3 powder (99.99%, Wako Chemical Co.), in an alumina crucible was placed in an alumina tube with a 34 nm inner diameter. The furnace was heated to 600 °C under an argon (Ar) flow and then ramped at 5 °C/min to the reaction temperatures under a flow of CH_3CN diluted in Ar (hereafter referred to as CH_3CN/Ar). The duration time at the

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reaction temperature was 3 h. During cooling, the CH_3CN/Ar flow was switched to an Ar flow at 600 °C. After cooling to room temperature, the product was burned in air at 700 °C for 30 min to remove carbon. The flow rates of Ar and CH_3CN were 100 and 1.7–1.8 $\times 10^{-2}$ ml/min, respectively. The gas evolved during the reaction was bubbled through a solution of Fe^{2+} and Fe^{3+} ions to trap HCN gas.

2.2. Synthesis of GaN from Ga_2O_3 using melamine as a nitridizing reagent

Unlike the synthesis reported by Zhao et al. [8], melamine (99%, Sigma–Aldrich) was separated from β-Ga_2O_3 powder (99.99%, Wako Chemical Co.) in an alumina tube with a 34 mm inner diameter. The mole ratio of melamine to β-Ga_2O_3 was 9:1. The melamine sublimed upstream under a flow of Ar, before thermally decomposing and reacting with the Ga_2O_3 powder at the hot zone. The crucible containing melamine was at *ca*. 300 °C when the hot zone was at the reaction temperature. The duration time at the reaction temperature was 3 h. The Ar flow and ramping rates were 100 ml/min and 5 °C/min, respectively. After cooling to room temperature, the product was burned in air at 700 °C for 30 min to remove carbon.

2.3. Product characterization

The sample powders were characterized by powder X-ray diffraction (XRD) using a PANalytical X'Pert PRO MPD X-ray diffractometer with Cu Kα radiation operating at 40 kV and 30 mA and by high-resolution ^{71}Ga magic-angle spinning (MAS) NMR spectroscopy. The NMR spectra were recorded using a radio frequency of 183.0 MHz (Unity INOVA 600 spectrometer). The samples in a rotor were spun at 23 kHz. Chemical shifts (δ) were referenced to 1 M aqueous gallium(III) nitrate solution. Raman spectra were measured at room temperature using the 514.5 nm line of an Ar^+ laser with a 200 mW output power (Jobin-Yvon LabRam HR spectrophotometer). The morphologies and chemical compositions of the sample powders were investigated by scanning electron microscope (SEM, Hitachi S-4200) equipped with an energy dispersive X-ray spectrometer (EDS).

3. Results and discussion

3.1. Synthesis of GaN from Ga_2O_3 under a flow of CH_3CN diluted in Ar

Fig. 1 shows XRD patterns of samples obtained by calcining β-Ga_2O_3 powder at various temperatures under a flow of CH_3CN/Ar. The sample obtained at 800 °C exhibited only peaks assigned to β-Ga_2O_3 (ICDD-PDF #00-43-1012). In the sample calcined at 850 °C, intense peaks corresponding to GaN (ICDD-PDF #00-50-0792) were detected together with the peaks attributable to unreacted β-Ga_2O_3. Samples calcined at 900 and 950 °C exhibited only diffraction peaks assigned to GaN; calcination at 900 °C resulted in wider peaks than calcination at 950 °C due to lower crystallinity.

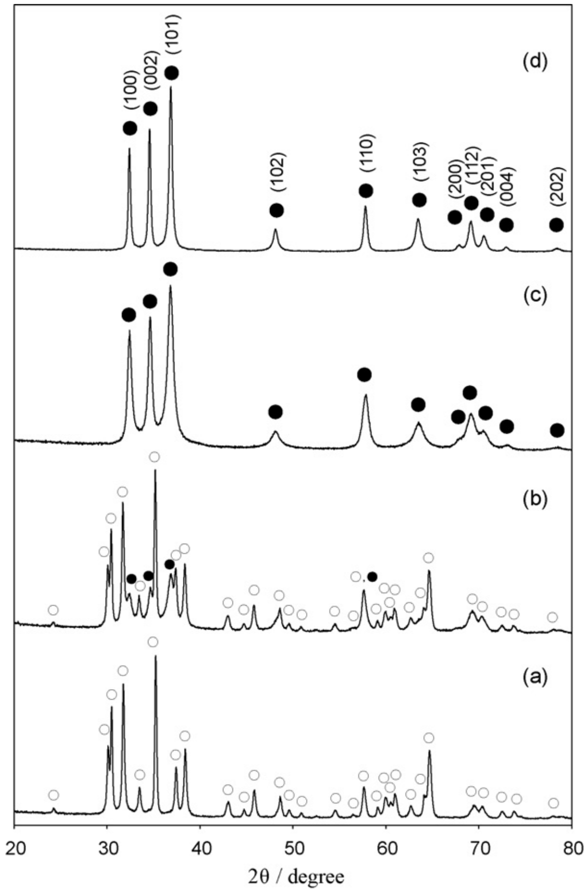

Fig. 1. XRD patterns of samples obtained by calcination of β-Ga_2O_3 at (a) 800 °C, (b) 850 °C, (c) 900 °C, and (d) 950 °C for 3 h under a flow of CH_3CN diluted in Ar. (○) β-Ga_2O_3, (●) GaN.

The conversion of β-Ga_2O_3 to GaN under a flow of CH_3CN/Ar was also monitored by ^{71}Ga MAS NMR spectroscopy, as shown in Fig. 2. The ^{71}Ga MAS NMR spectra of the sample obtained at 800 °C exhibited two powder patterns resulting from the second-order broadening of the central transition. The quadrupole coupling constants of GaO_6 and GaO_4 sites in β-Ga_2O_3 were determined to be 11.0 and 8.3 MHz, respectively [14]. Their high values hindered the recording of spectra of polycrystalline samples without severe intensity distortions of the broad powder pattern. Calcination at 850 °C resulted in an intense peak (at δ 327 ppm) assigned to GaN [15] and weaker peaks assigned to β-Ga_2O_3. The peaks attributable to β-Ga_2O_3 were not observed for the samples obtained at 900 and 950 °C.

3.2. Synthesis of GaN from Ga_2O_3 using melamine as a nitridizing reagent

Fig. 3 shows XRD patterns of samples obtained by calcination of β-Ga_2O_3 powder at various temperatures using melamine. Calcination at 700 °C resulted in only diffraction peaks assigned to β-Ga_2O_3. The sample calcined at 750 °C showed intense peaks corresponding to GaN and also peaks attributable to unreacted β-Ga_2O_3. Samples calcined at temperatures ≥800 °C did not exhibit any detectable peaks other than those assigned to GaN.

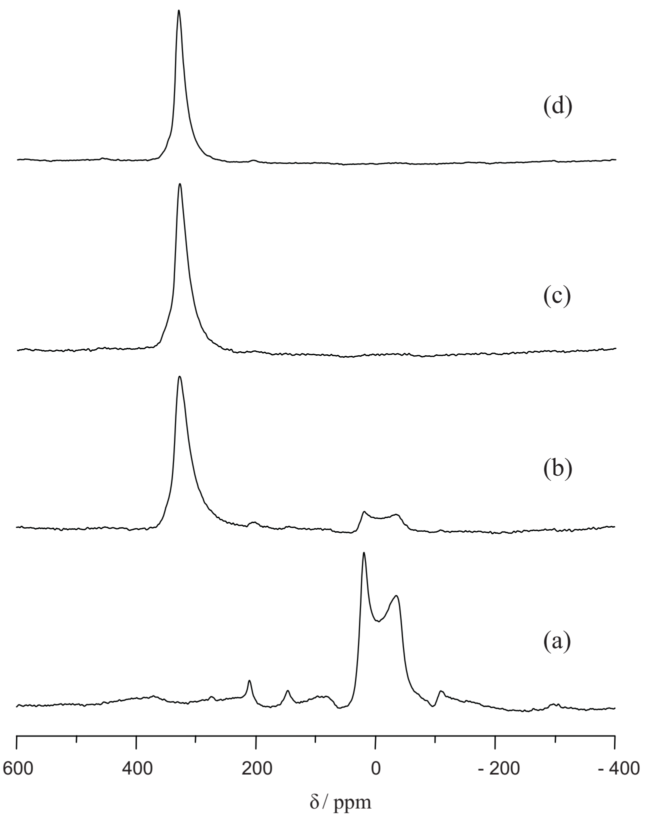

Fig. 2. ^{71}Ga MAS NMR spectra of samples obtained by calcination of β-Ga_2O_3 at (a) 800 °C, (b) 850 °C, (c) 900 °C, and (d) 950 °C for 3 h under a flow of CH_3CN diluted in Ar.

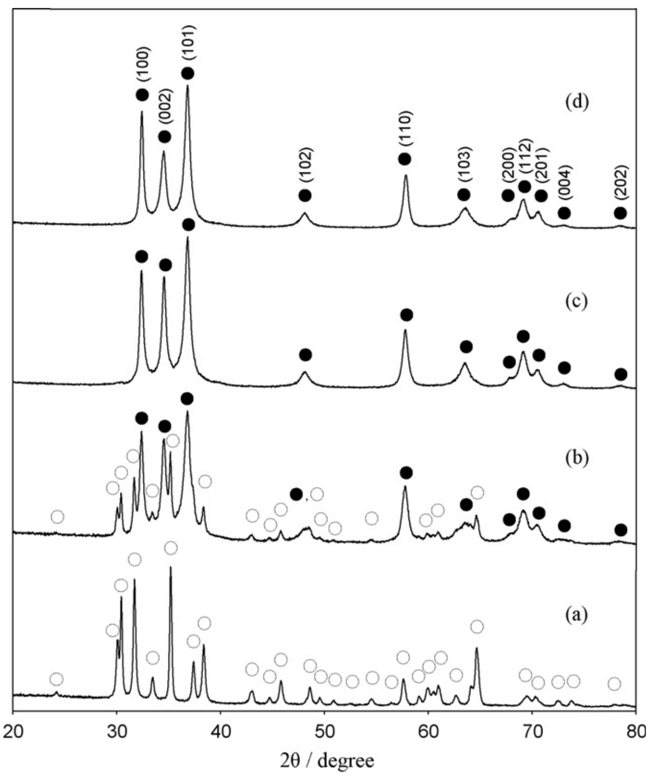

Fig. 3. XRD patterns of samples obtained by calcination of β-Ga_2O_3 at (a) 700 °C, (b) 750 °C, (c) 800 °C, and (d) 900 °C for 3 h using melamine. (○) β-Ga_2O_3, (●) GaN.

^{71}Ga MAS NMR spectra were also measured after calcining β-Ga_2O_3 powders at various temperatures (Fig. 4). Calcination at 700 °C resulted in a very weak peak assigned to GaN and peaks assigned to unreacted β-Ga_2O_3, despite XRD pattern (Fig. 3(a)) showing the sample be single-phase β-Ga_2O_3. The NMR peak assigned to GaN became more intense with increasing reaction temperatures. The spectrum of the sample obtained at 900 °C showed a broad peak at δ 410 ppm and a peak assigned to GaN. The origin of the broad peak, which was not shown by the samples obtained at 900 °C under a flow of CH_3CN/Ar or NH_3 [4], is not fully understood. The peak can be explained in terms of the nitrogen deficiency in GaN [5,16,17] or a Knight shift due to the presence of conduction electrons [6,18].

3.3. Mechanism of cyanonitridation

The thermal decomposition of CH_3CN and melamine yields HCN [10,11]. If the HCN is involved in the nitridation of Ga_2O_3, the cyanonitridation reaction of Ga_2O_3 with HCN may be expressed as:

$$Ga_2O_3(s) + 3HCN(g) \rightarrow 2GaN(s) + 3CO(g) + 3/2H_2(g) + 1/2N_2(g) \qquad (2)$$

It is worthwhile to determine whether or not the CN radical reacts with Ga_2O_3 to give GaN. A 4:1 mole ratio mixture of

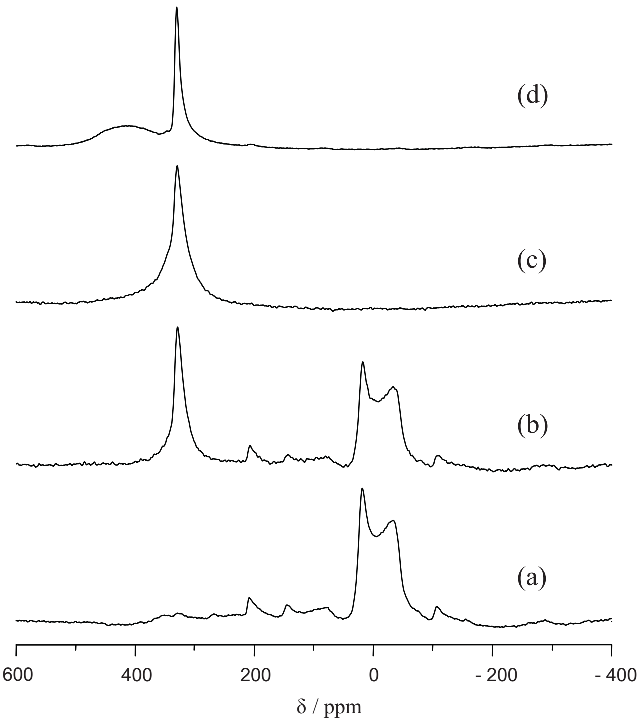

Fig. 4. ^{71}Ga MAS NMR spectra of samples obtained by calcination of β-Ga_2O_3 at (a) 700 °C, (b) 750 °C, (c) 800 °C, and (d) 900 °C for 3 h using melamine.

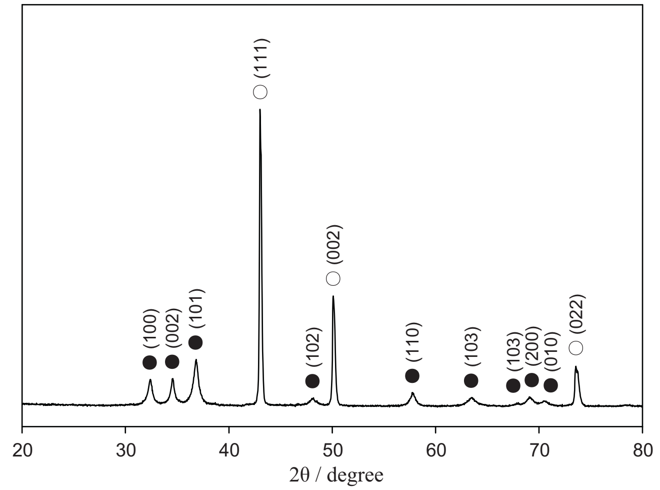

Fig. 5. XRD pattern of the sample obtained by calcination of a mixture of CuCN and β-Ga_2O_3 at 900 °C for 3 h under a flow of Ar. (●) GaN, (○) $Cu_{0.917}Ga_{0.183}$.

copper cyanide (CuCN) and β-Ga_2O_3 was pressurized into a pellet and heated at 900 °C for 3 h under a flow of Ar. The XRD pattern (Fig. 5) of the resulting sample showed to be a mixture of GaN and $Cu_{0.917}Ga_{0.183}$ (ICDD-PDF #98-007-2649). The complete conversion of β-Ga_2O_3 to GaN indicated that the CN radical rather than HCN was involved in the cyanonitridation of Ga_2O_3. Therefore, reaction (2) may be expressed as follows:

$$HCN(g) \rightarrow H(g) + CN(g) \tag{3}$$

$$Ga_2O_3(s) + 3CN(g) \rightarrow 2GaN(s) + 3CO(g) + 1/2N_2(g) \tag{4}$$

At elevated temperatures, the CN radical is expected to dissociate into atomic carbon and nitrogen as the dissociation energies of its excited-state electronic structures are smaller than that of its ground-state electronic structure [19]. The thermal dissociation of the CN radical into atomic carbon and nitrogen is evidenced by the reaction of In_2O_3 with melamine giving $In_{2.24}(NCN)_3$ [8], in which cyanoamide is assumed to form by the reaction of CN radical with atomic nitrogen.

Reaction (4) is similar to reaction (1) in that Ga_2O_3 is deoxygenated and nitridated. Both reaction mechanisms are thereby expected to be similar. In reaction (4), the temperature at which the formation of GaN commenced was slightly higher than the 700 °C at which it commenced in reaction (1) [4]. This difference may be due to the difference in the dissociation energies of the CN radical and NH_3. The deoxygenation and nitridation of Ga_2O_3 will be either successive or concurrent reactions. In the mechanism of the successive reaction the reaction intermediates such as gaseous Ga_2O may be assumed to form [20], resulting in the change in morphology during conversion of Ga_2O_3 to GaN. The morphology was preserved in this study (see below). It is, therefore, reasonable to assume that reaction (4) is a concurrent reaction.

3.4. Characterization of GaN powders

Fig. 6 shows Raman spectra of samples obtained at 900 and 950 °C under a flow of CH_3CN/Ar. The spectra were similar to those of sub-micrometer GaN tubes made of textured GaN nanoparticles [21]. Five first-order phonon modes corresponding to wurtzite GaN were observed at 250, ~310, 418, 564, and 730 cm^{-1} in the sample obtained at 950 °C. The bands at 564 and 730 cm^{-1} corresponded to E_2(high) and A_1(LO) modes, respectively. The low intensity ratio of $I(E_2)/I(A_1)$ was contrary to the high intensity ratios of >1 usually observed [22]. The A_1(TO) and E_1(TO) modes appeared as unresolved shoulders on the lower frequency side of the E_2(high) mode. Two bands at ~310 and 418 cm^{-1} were assigned to acoustic overtones, and the band at 250 cm^{-1} was ascribed to the zone boundary phonon activated by surface disorders and finite size effects [22]. As shown in Fig. 6(a), each phonon mode for the sample obtained at 900 °C was slightly red-shifted relative to the spectrum of the sample obtained at 950 °C because of lower crystallinity [23].

EDS analysis of GaN powder prepared at 900 °C under a flow of CH_3CN/Ar revealed that the atomic ratio of Ga to N was 1:0.94 and that the oxygen content was 2.2 wt%. The oxygen content is not attributable only to the residual oxygen incorporated in GaN powder but also to O_2 and H_2O molecules adsorbed on the powder surface [7,17]. The oxygen content attributable to the adsorbed molecules was determined to be 0.81 wt% by an elemental analyzer (Flash 1112, Thermo

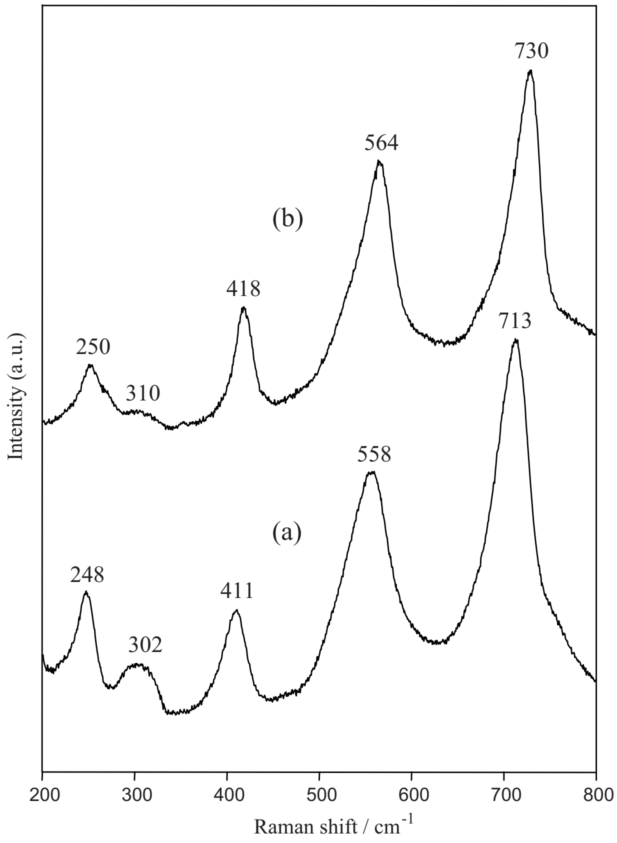

Fig. 6. Room-temperature Raman spectra of β-Ga_2O_3 calcined at (a) 900 and (b) 950 °C for 3 h under a flow of CH_3CN diluted in Ar.

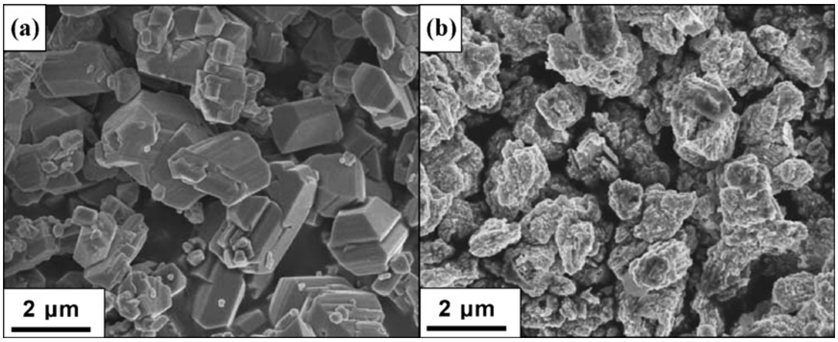

Fig. 7. SEM images of samples (a) before and (b) after calcination of β-Ga_2O_3 at 900 °C for 3 h under a flow of CH_3CN diluted in Ar.

Fischer Scientific). Therefore, the residual oxygen content in GaN powder was 1.4 wt%.

The morphologies of GaN particles obtained at 900 °C under a flow of CH_3CN/Ar were observed by SEM (Fig. 7). The morphologies of block-shaped β-Ga_2O_3 particles were almost maintained during the cyanonitridation except that its smooth faces were coarsened. Brendt et al. explained this change in terms of stress in the Ga_2O_3 bulk induced by the formation of the inner GaN phase [24].

4. Conclusions

Organic compounds such as CH_3CN and melamine were demonstrated to be useful nitridizing reagents for the preparation of GaN powder from Ga_2O_3 powder, similar to their use in the preparation of AlN powder from Al_2O_3 powder. The cyanide radical, which was produced by thermal decomposition of the organic compounds, was shown to react with Ga_2O_3 to form GaN. The conversion rate of Ga_2O_3 to GaN *via* the cyanonitridation was slightly lower than that *via* the ammonolysis. The conserved morphology during cyanonitridation indicated that the β-Ga_2O_3 did not convert to GaN through gaseous species such as Ga_2O.

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