

Preparation of Gallium Nitride Powders and Nanowires from a Gallium(III) Nitrate Salt in Flowing Ammonia

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Gallium nitride (GaN) powders were prepared by calcining a gallium(III) nitrate salt in flowing ammonia in the temperature ranging from 500 to 1050 °C. The process of conversion of the salt to GaN was monitored by X-ray diffraction and ^{71}Ga MAS (magic-angle spinning) NMR spectroscopy. The salt decomposed to $\gamma\text{-Ga}_2\text{O}_3$ and then converted to GaN without $\gamma\text{-}\beta\text{-Ga}_2\text{O}_3$ phase transition. It is most likely that the conversion of $\gamma\text{-Ga}_2\text{O}_3$ to GaN does not proceed through Ga_2O but stepwise via amorphous gallium oxynitride (GaO_xN_y) as intermediates. The GaN nanowires and microcrystals were obtained by calcining the pellet containing a mixture of $\gamma\text{-Ga}_2\text{O}_3$ and carbon in flowing ammonia at 900 °C for 15 h. The growth of the nanowire might be explained by the vapor-solid (VS) mechanism in a confined reactor. Room-temperature photoluminescence spectra of as-synthesized GaN powders obtained showed the emission peak at 363 nm.

Key Words : Gallium nitride, Powder, Nanowire, Confined reactor, ^{71}Ga MAS NMR

Introduction

One of Group III-V nitrides, gallium nitride (GaN) with a bandgap of 3.4 eV at room temperature is known to be a candidate material for highly effective blue light emitting diodes and short wavelength laser diodes for high optical storage.¹ Sapphire is the most widely used substrate for the thin-film growth of GaN. However, there exists severe mismatch both in lattice parameters and thermal expansion coefficients. Such a large mismatch induces stresses in the first few layers of GaN grown on sapphire. A trend for the future is, therefore, the development of GaN substrates for homoepitaxy by fabricating GaN bulk single crystals and wafers. Sublimation² and high-pressure solution methods³ are considered for crystal growth of GaN. The methods demand the availability of well-characterized GaN powder source with high purity and single phase. Balkas and Davis synthesized bulk GaN powders by reaction of ammonia with gallium metal or Ga_2O_3 as a Ga source.⁴

In this report we synthesize GaN powders, nanowires and microcrystals using a gallium(III) nitrate salt, which is one of readily available Ga sources. The process of conversion of the salt to GaN was monitored by XRD and ^{71}Ga magic-angle spinning (MAS) NMR spectroscopy. The results are compared with those obtained with other Ga sources.

Experimental Section

The precursor material $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Aldrich, 99.9%) was used without further purification. GaN powders were synthesized by calcining the salt powders in a crucible under a flow of ammonia (Showadenko Co., 99.999%) in the temperature range 500-1050 °C for 3 h. The flow rate of

ammonia was 50 mL min⁻¹. GaN nanowires and microcrystals were obtained by calcining pellets containing a mixture of $\gamma\text{-Ga}_2\text{O}_3$ and carbon at 900 °C for 15 h under a flow of ammonia. The pellets were prepared as follows: a gallium(III) nitrate salt was mixed with carbon (mole ratio of the salt to carbon = 1 : 2) in water and evaporated to dryness. The mixture powder was precalcined at 500 °C for 2 h under a flow of nitrogen and pressed into pellets. The sample was taken from the furnace after it was cooled to the room temperature under a flow of ammonia.

The conversion of the salt to GaN was monitored by XRD (Rigaku DMX-2500 diffractometer with Cu-K α radiation operating at 40 kV and 100 mA) and ^{71}Ga magic-angle spinning (MAS) NMR spectroscopy. High-resolution ^{71}Ga MAS NMR spectra were recorded at ambient temperature using a Varian Unity INOVA 600 spectrometer running at 183.0 MHz. The rotor used as sample chamber was spun at 14 kHz during data collection. Chemical shifts (δ) were referenced to 1 M aqueous gallium(III) nitrate solution. The morphology of GaN products was investigated by scanning electron microscopy (SEM, Hitachi S-4100). Room-temperature photoluminescence (PL) measurements of as-synthesized GaN powders obtained were carried out by using a He-Cd laser (excitation wavelength = 325 nm).

Results and Discussion

The sample powders obtained by calcining gallium(III) nitrate were agglomerated in a form of lump and therefore lightly crushed by hand in an agate mortar and pestle for the analysis. Figure 1 shows XRD patterns of samples synthesized at different temperatures. Weak diffraction peaks of the sample obtained at 600 °C are assigned to $\gamma\text{-Ga}_2\text{O}_3$ ⁵ with low crystallinity. Decomposition of gallium(III) nitrate powders in air at 600 °C produced $\beta\text{-Ga}_2\text{O}_3$. This means that the rate of reaction between $\gamma\text{-Ga}_2\text{O}_3$ and ammonia is faster than that

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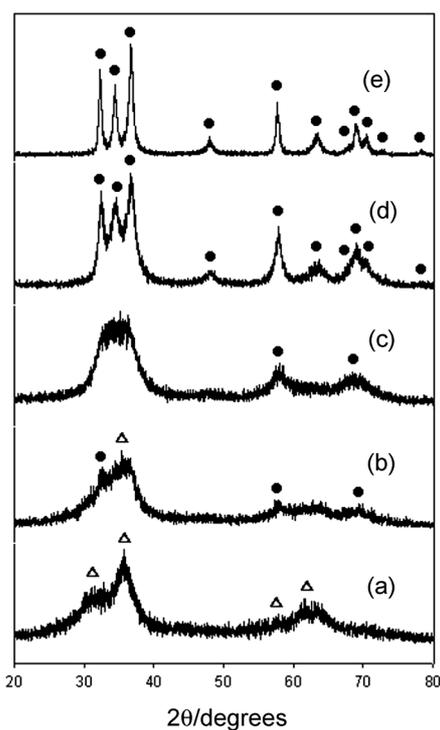


Figure 1. XRD patterns of powders obtained by calcination of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in flowing ammonia at various temperatures for 3 h: (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C, (e) 1000 °C. ●, GaN; Δ, $\gamma\text{-Ga}_2\text{O}_3$.

of phase transformation from γ to $\beta\text{-Ga}_2\text{O}_3$. The intensities of the peaks assigned to $\gamma\text{-Ga}_2\text{O}_3$ decrease and those of the peaks assigned to GaN^4 increase with the reaction temperature. The XRD pattern of the sample obtained at 800 °C has broad peaks of GaN, and is very similar to that of GaN nanocrystals in a silica xerogel matrix.⁶ The nanocrystals were prepared by calcination of gallium(III) nitrate incorporated into a silica xerogel, followed by nitridation of 900 °C for 48 h. In the case of the sample obtained at the temperatures above 900 °C, there are no detectable peaks other than the peaks assigned to GaN, as shown in Figure 1.

Each powder obtained was also characterized by ^{71}Ga MAS NMR spectroscopy. Solid-state NMR spectroscopy might be a more powerful probe than XRD in characterizing poorly crystalline materials because the latter provides little information about central-metal distribution owing to lack of long-range order. The NMR spectroscopy is also a useful tool for identification of defects in crystal structure.⁷ Up to now most investigators have employed the powder X-ray diffraction (XRD) to determine whether or not GaN powder synthesized is of high purity and single phase.⁴ But nitrogen deficiency in the GaN can be hardly revealed by the powder XRD, though GaN is expected to be nitrogen deficient in its synthetic process.

Figure 2 shows ^{71}Ga MAS NMR spectra of samples synthesized at different temperatures. The poorly resolved spectrum of $\gamma\text{-Ga}_2\text{O}_3$ obtained at 600 °C shows two broad peaks at 28 and 185 ppm. Each peak is assigned to six-coordinated (GaO_6) and four-coordinated (GaO_4) gallium,

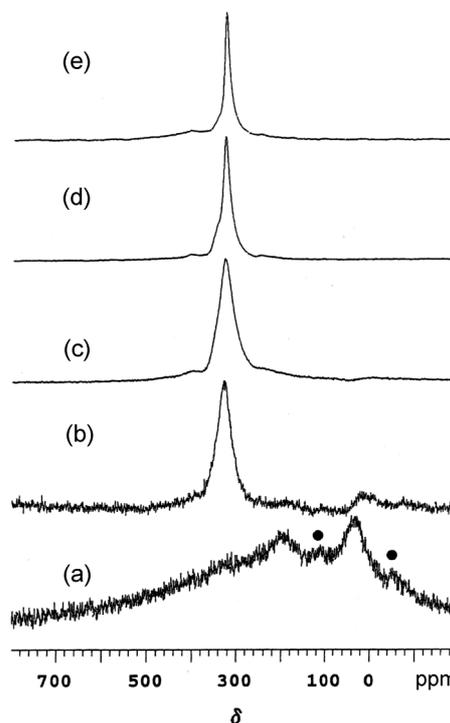


Figure 2. ^{71}Ga MAS NMR spectra of powders obtained by calcination of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in flowing ammonia at various temperatures for 3 h: (a) 600 °C, (b) 700 °C, (c) 800 °C, (d) 900 °C, (e) 1000 °C. The peaks marked by closed circles are the spinning sidebands.

respectively. The peak pattern is similar to that of $\gamma\text{-Al}_2\text{O}_3$ ⁸ because $\gamma\text{-Ga}_2\text{O}_3$ has a (defective) spinel-type structure similar to that of $\gamma\text{-Al}_2\text{O}_3$. In the sample obtained at 700 °C the peak (at 330 ppm) assigned to GaN⁹ is observed along with the very weak peaks assigned to $\gamma\text{-Ga}_2\text{O}_3$. With increasing reaction temperature, the former peak becomes more narrow because of increase in crystallinity. The GaN peak for samples obtained at 900 °C has a small shoulder on its low-field side. The shoulder may be due to some point defects in crystalline GaN. The peak at 425 ppm,⁷ which is assigned to nitrogen-deficient GaN (GaN_{1-x} where $0 < x < 1$), was not observed for samples in this study.

The conversion of a gallium(III) nitrate salt to GaN in flowing ammonia is accompanied by weight loss, as shown in Figure 3. Variation in the weight loss % with increasing temperature is divided into four segments. The first one is below 600 °C, where the salt decomposes to $\gamma\text{-Ga}_2\text{O}_3$. The dissociation of ammonia seems to be very difficult below 600 °C, in view of the fact that the weight loss % of the sample obtained at 500 °C for 20 h was almost the same as that of the sample at 600 °C for 3 h within experimental errors. The second one is between 600 and 900 °C, where $\gamma\text{-Ga}_2\text{O}_3$ converts to GaN. The third one between 900 and 1000 °C is almost a plateau, where GaN powders become crystalline and denser. The last one is above 1000 °C, where GaN powders sublime and/or decompose. The discrepancy between experimental and theoretical yields for the product obtained at 1050 °C for 5 h, which has been reported by

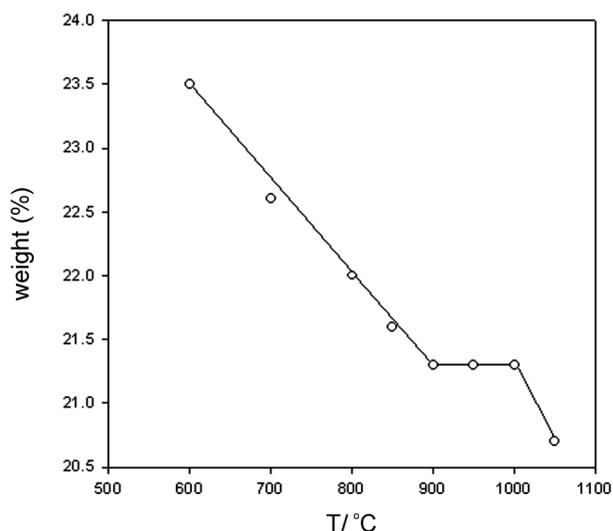


Figure 3. Variation in weight % of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ as a function of calcination temperature for 3 h.

Wood *et al.*,¹⁰ may be attributed to the sublimation and/or decomposition of GaN. The value of x in $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ used in this study was determined to be 7.6 from the weight loss % of the sample obtained at 950 °C, assuming that the sample is a single phase of GaN.

There was little difference in reactivity of ammonia between γ and β - Ga_2O_3 ,¹¹ though the latter is thermodynamically more stable than the former. It is supposed in a previous paper¹¹ that the conversion of β - Ga_2O_3 to GaN does not proceed through gallium(I) suboxide (Ga_2O) but stepwise *via* amorphous gallium oxynitrides (GaO_xN_y) intermediates. It is speculated that the gallium oxynitride is formed by the dissociation of ammonia adsorbed on the surface of Ga_2O_3 . As the nitridation proceeds, the oxygen content in the intermediates gradually decreases, leading to the complete conversion to GaN. The mechanism involving GaO_xN_y intermediates is supported by the following findings. First, the sample obtained at 800 °C turned into a mixture of GaN and β - Ga_2O_3 by its calcinations at 700 °C in air for 1 h. This derives from the conversion of a small amount of GaO_xN_y intermediates to β - Ga_2O_3 because the oxidation of GaN to Ga_2O_3 is very slow below 900 °C.¹² Second, the morphology of γ - Ga_2O_3 is retained on its conversion to GaN. If the mechanism involving a Ga_2O intermediate is valid, the retention is expected to be impossible for the mechanism.

In order to prevent the product powder from being agglomerate, a mixture of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and charcoal (mole ratio = 1 : 20) in aqueous solution was evaporated to dryness and then calcined in flowing ammonia at 950 °C for 1 h, followed by burning up the charcoal at 700 °C in air. The powder was much unagglomerated than powders obtained without using charcoal. As shown in Figure 4(a), the morphology is very similar to that of powders synthesized by the aerosol-assisted vapor phase synthesis method using aqueous gallium(III) salt solution,¹⁰ particularly in that agglomerates are composed of faceted particles.

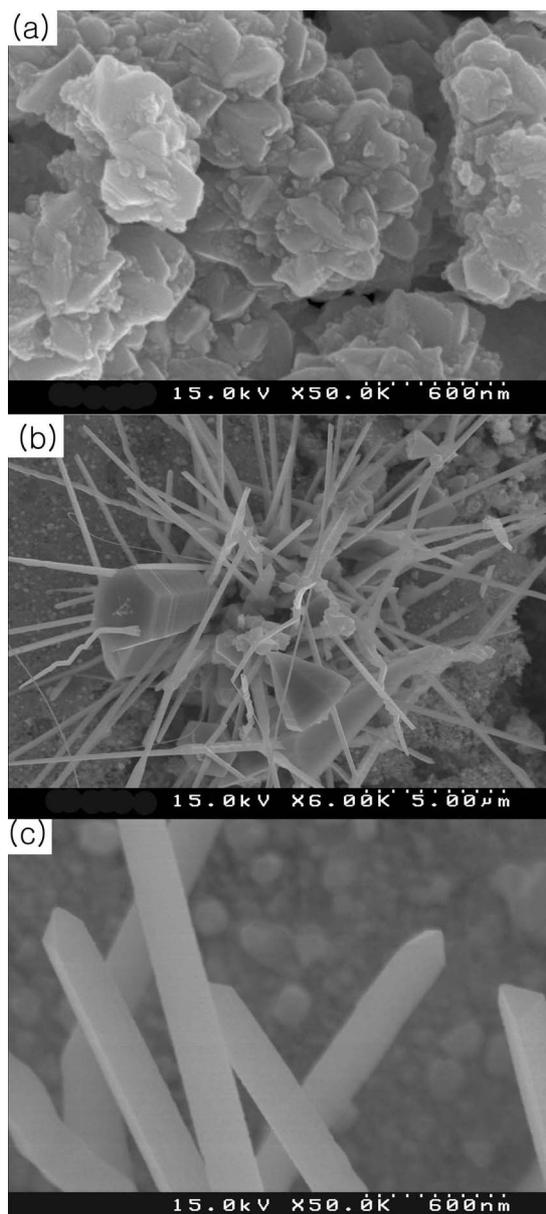


Figure 4. SEM micrographs of (a) the GaN powders (a) obtained by calcining a mixture of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and carbon (mole ratio = 1 : 20) at 950 °C for 1 h and of (b, c) GaN nanowires and microcrystals obtained by calcining the pellet containing a mixture of γ - Ga_2O_3 and carbon at 900 °C for 15 h in flowing ammonia.

When a mixture of γ - Ga_2O_3 and carbon was pressed into a pellet and then calcined at 900 °C for 15 h under a flow of ammonia, the confinement effect was observed on morphology of GaN. As shown in Figures 4(b) and 4(c), a lot of GaN nanowires and some hexagonal microcrystals soared up out of surface of the pellet. Most of the nanowires are as thick as 200 nm and some nanowires are about 50 nm in diameter. No droplets were observed at tips (Figure 4(c)), indicating that the nanowires do not grow by the vapor-liquid-solid (VLS) mechanism. Peng *et al.*¹³ proposed the reaction mechanism on growth of GaN nanowires during conversion of a mixture of Ga_2O_3 and carbon to GaN. According to the mechanism, Ga_2O_3 should be reduced to gaseous Ga_2O by

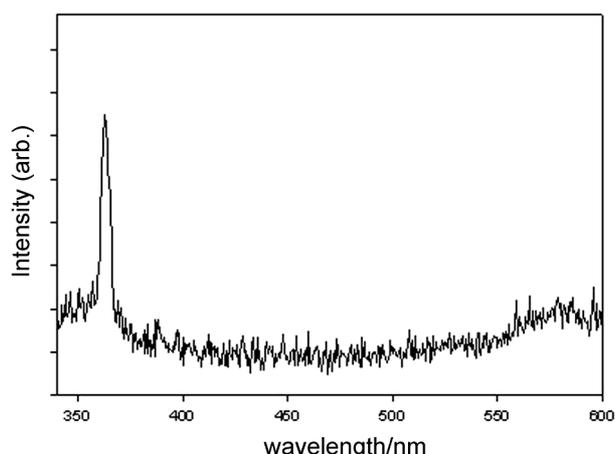


Figure 5. Room-temperature PL spectrum of the powders obtained by calcination of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ at 900 °C for 3 h in flowing ammonia.

carbon and then the reaction of Ga_2O with ammonia result in formation of GaN. If such a gaseous intermediate is involved during reaction, some weight loss of the intermediate must take place in flowing ammonia. But the amount of $\beta\text{-Ga}_2\text{O}_3$ was quantitatively obtained by calcination of a $(\text{NH}_4)[\text{Ga}(\text{edta})] \cdot 2\text{H}_2\text{O}$ complex¹⁴ at 1100 °C for 3 h under a flow of nitrogen, followed by burning out the carbon at 700 °C in air. The formation of gaseous Ga_2O should be, if Ga_2O_3 is reduced to gaseous Ga_2O by carbon, much more feasible because the pyrolysis of the complex gives an intimate mixture of Ga_2O_3 and carbon at the molecular level. We propose that GaN nanowires and microcrystals might grow by the vapor-solid (VS) mechanism, *i.e.*, by sublimation-condensation of GaN formed through the intermediates GaO_xN_y . The growth process of GaN nanowires in this study is thought to be similar to that in a reaction using nanometer confined reactors such carbon nanotubes¹⁵ and anodic alumina membranes.¹⁶ Calcination of a mixture of $\gamma\text{-Ga}_2\text{O}_3$ and carbon, if it was not pressed into pellets, gave neither GaN nanowires nor microcrystals. Thus, the confinement of GaN in voids among pressurized carbon particles might be responsible for the growth of nanowires and microcrystals of GaN because the confinement is expected to be very favorable for supersaturation of GaN vapor. It is well known that the degree of supersaturation determines the prevailing

growth morphology. A low supersaturation is required for whisker (or nanowire) growth whereas a medium supersaturation support bulk crystal growth.¹⁷ Further work is in progress for obtaining homogeneous GaN nanowires.

The PL spectrum of GaN powder obtained at 900 °C is shown in Figure 5. The strong emission peak at 363 nm is the band edge of GaN with the wurtzite structure, and the weak and broad peak around 580 nm corresponds to the well-known yellow band observed in GaN.¹⁸ The latter band became more intense for the powders obtained at higher temperatures.

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