

Synthesis and Characterization of Gallium Nitride Powders from a Gallium(III) Sulfate Salt in Flowing Ammonia

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ABSTRACT

Gallium Nitride (GaN) powders were synthesized by calcining a gallium(III) sulfate salt in flowing ammonia in the temperature range 500–1100°C. The process of conversion of the salt to GaN was monitored by X-Ray Diffraction (XRD). The salt decomposed to γ -Ga₂O₃ and then converted to GaN without γ - β Ga₂O₃ phase transition. Variations in XRD patterns and weight loss of samples with temperature indicate that the conversion of γ -Ga₂O₃ to GaN does not proceed through Ga₂O but stepwise via amorphous gallium oxynitride (GaO_xN_y) as intermediates. Room-temperature photoluminescence spectra of GaN powders obtained showed the emission peak at 363 nm and no yellow band.

Key words : Gallium nitride, Gallium(III) sulfate, Powders, Gallium oxynitride, Photoluminescence

1. Introduction

Gallium Nitride (GaN) has a wide, direct band gap (3.4 eV at 300 K) and is potentially useful to blue and ultraviolet light emission and high-temperature, high powder electronic devices.¹⁾ The technology for growing high-quality GaN film on foreign substrates has been progressing in recent decades. 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. Bulk GaN powders were prepared by reaction of ammonia with gallium metal or Ga₂O₃⁴⁾ and gallium oxyhydroxide (GaOOH) as a Ga source.⁵⁾

In this report we synthesize GaN powders using a gallium(III) sulfate salt, which is one of readily available Ga sources. The process of conversion of the salt to GaN was monitored by X-Ray Diffraction (XRD) and GaN powders obtained were characterized. The results are compared with those obtained with a gallium(III) nitrate salt.⁶⁾

2. Experimental

The precursor material Ga₂(SO₄)₃·xH₂O (Kojundo Chemical Lab Co., 99.99%) was used without further purification. GaN powders were synthesized by calcining the salt powders in an alumina crucible under a flow of ammonia (Showadenko Co., 99.999%) in the temperature range 500–1100°C for 3 h. The flow rate of ammonia was 50 ml min⁻¹. The samples were weighed before and after calcination. 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). The morphology of GaN products was investigated by Scanning Electron Microscopy (SEM, Hitachi S-4100). Room-temperature photoluminescence (PL) measurements of GaN powders obtained were carried out by using a He-Cd laser (excitation wavelength = 325 nm).

3. Results and Discussion

Fig. 1 shows XRD patterns of samples synthesized by calcining a gallium(III) sulfate salt at different reaction temperatures for 3 h. The sample calcined at 600°C is identified as γ -Ga₂O₃.⁷⁾ In the sample calcined at 700°C weak diffraction peaks to assigned to GaN are detected together with those assigned to γ -Ga₂O₃. The temperature (700°C) at which the diffraction peaks of GaN is first observed is the same as that for the case of gallium(III) nitrate.⁶⁾ With increasing the reaction temperature the peaks assigned to γ -Ga₂O₃ decrease and the peaks assigned to GaN increase. In the case of the samples calcined above 800°C, there are no detectable peaks other than the peaks assigned to GaN. It is inferred from this observation that GaN is synthesized

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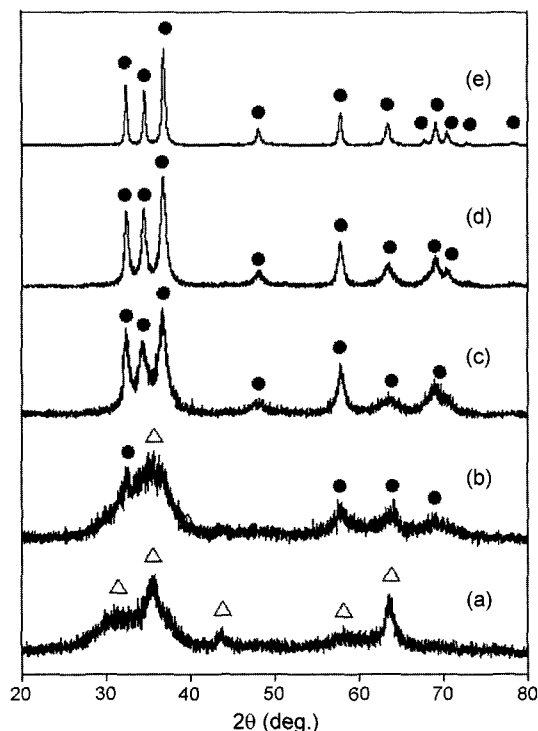


Fig. 1. XRD patterns of powders obtained by calcination of $\text{Ga}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ in flowing ammonia at various temperatures for 3 h: (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, and (e) 1000°C. ●, GaN; Δ, $\gamma\text{-Ga}_2\text{O}_3$.

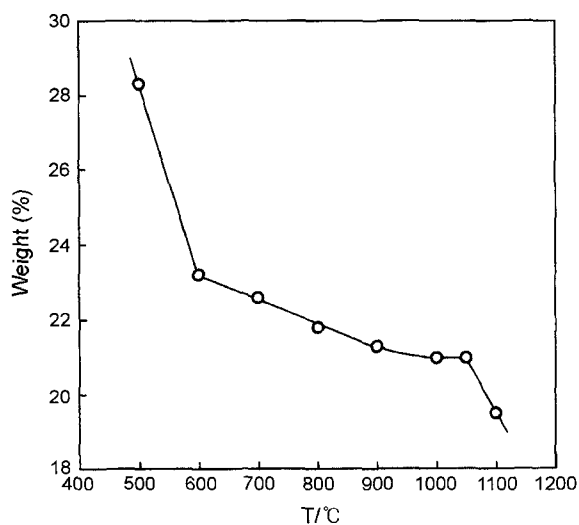


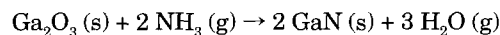
Fig. 2. Variation in weight % of $\text{Ga}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ as a function of calcination temperature for 3 h.

directly from $\gamma\text{-Ga}_2\text{O}_3$ without phase transition from γ - to $\beta\text{-Ga}_2\text{O}_3$, as in the case of synthesis of GaN from a gallium(III) nitrate salt.⁶⁾ It is noted that gallium(III) sulfate converted to the most stable form of Ga_2O_3 , *i.e.*, $\beta\text{-Ga}_2\text{O}_3$ above 700°C under a flow of nitrogen.⁸⁾ The diffraction peaks of GaN powders have more narrow for gallium(III) sulfate than for gallium(III) nitrate, suggesting that GaN powders are higher in crystallinity for gallium(III) sulfate than for gallium(III) nitrate.

The conversion of a gallium(III) sulfate salt to GaN in flowing ammonia is accompanied by weight loss. Fig. 2 shows the change in sample weight against reaction temperature. As in the case of gallium(III) nitrate,⁶⁾ variation in the weight % (which is defined by 100 x weight of the product/weight of gallium(III) sulfate used) 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 second one is between 600 and 950°C, where $\gamma\text{-Ga}_2\text{O}_3$ converts to GaN. The third one between 950 and 1050°C is almost a plateau, where GaN powders become crystalline and denser. The last one is above 1050°C, where GaN powders sublime and/or decompose. The color of GaN powders changed from yellow to yellowish-gray on their decomposition. The value of *x* in $\text{Ga}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ used in this study was determined to be *ca.* 20 from the weight % of the sample obtained at 1000°C, assuming that the sample is a single phase of GaN.

Crystals of $\text{Ga}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ lose water in stages, yielding $\text{Ga}_2(\text{SO}_4)_3$ above 165°C.⁹⁾ The latter anhydrous salt decomposed to Ga_2O_3 at *ca.* 700°C under a flow of nitrogen. The fact that the weight % below 700°C was much lower in flowing ammonia than that in flowing nitrogen (for example, 23.2% vs. 52.3% at 600°C and 22.6% vs. 23.8% at 700°C) indicates that the sulfate ions in the anhydrous salt react with ammonia. The product of the reaction was found at outlet of alumina tube and was identified as $(\text{NH}_4)_2\text{SO}_4$ by XRD.

The reaction between Ga_2O_3 and ammonia is expressed as follows:



Despite the apparent simplicity of the reaction, its detailed reaction mechanism is still unknown. Balkas and Davis showed that on the basis of the thermodynamic calculations, the reaction will not occur at temperatures where GaN production is feasible and suggested that the reaction intermediate is likely to be gallium(I) suboxide (Ga_2O).⁴⁾ It is supposed, however, in a previous paper¹⁰⁾ that the conversion of $\beta\text{-Ga}_2\text{O}_3$ to GaN does not proceed through Ga_2O but stepwise via amorphous gallium oxynitrides (GaO_xN_y) intermediates. 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 also valid for this reaction system. Fig. 1 shows that the samples obtained above 800°C are a single phase of GaN, whereas Fig. 2 shows that the samples obtained between 600 and 950°C are not a single phase of GaN. This discrepancy is well explained by existence of the amorphous GaO_xN_y intermediates in the samples between 600 and 950°C. The intermediates will not be detected by XRD because of their lack of crystallinity and turn into GaN with decrease in weight %. The mechanism involving GaO_xN_y intermediates in conversion of Ga_2O_3 to GaN is very similar with that involving AlO_xN_y intermediates in the carbothermal reduction and nitridation of Al_2O_3 to AlN.¹¹⁾

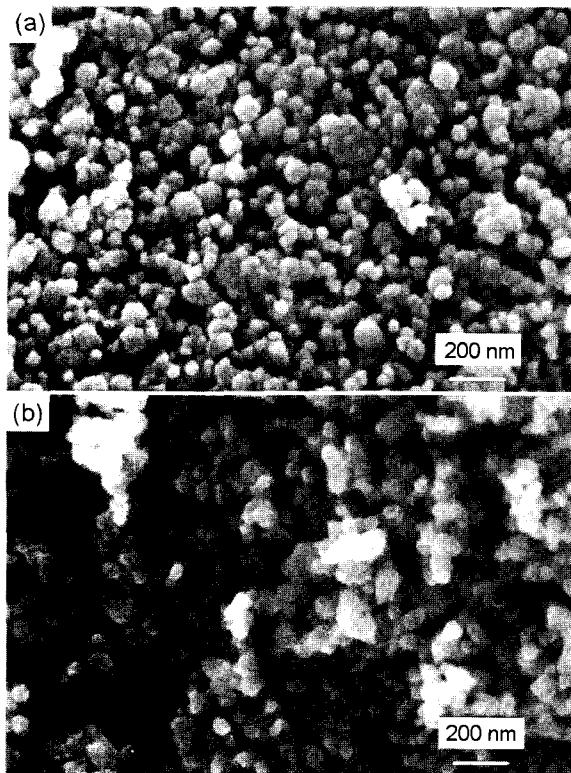


Fig. 3. SEM micrographs of powders obtained by calcining $\text{Ga}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ at 600 (a) and 1000°C (b) for 3 h in flowing ammonia.

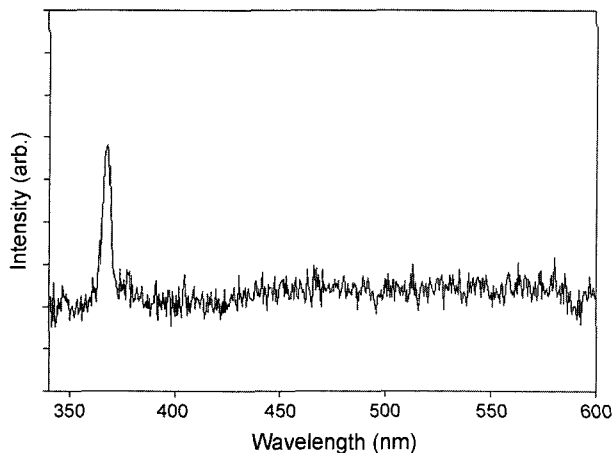


Fig. 4. Room-temperature PL spectrum of the powder obtained by calcination of $\text{Ga}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ at 1000°C for 3 h in flowing ammonia.

The morphology of powders ($\gamma\text{-Ga}_2\text{O}_3$ and GaN) obtained at 600 and 1000°C was observed by SEM. The former powders (Fig. 3(a)) are agglomerated with homogeneous primary particles, the diameter of which is *ca.* 50 nm. The morphology of the latter powders (Fig. 3(b)) is very similar with that of the former powder. This retention in morphology indicates that $\gamma\text{-Ga}_2\text{O}_3$ converts to GaN stepwise via GaO_xN_y intermediates, as mentioned above.

The PL spectrum of GaN powders obtained at 1000°C is

shown in Fig. 4. The band edge of GaN with the wurtzite structure is observed at 363 nm, but the yellow band around 580 nm is not observed. GaN is apt to be nitrogen deficient in its high-temperature synthetic process, leading to occurrence of the yellow band. Using gallium(III) nitrate⁶⁾ and $\alpha\text{-Ga}_2\text{S}_3$ ¹²⁾ as a precursor, the nitrogen deficiency in GaN was found for samples calcined above 900 and 1000°C, respectively. No observation of the yellow band for GaN powders obtained in this study may be ascribed to their high crystallinity.

4. Conclusions

One of readily available Ga sources, gallium(III) sulfate is proved to a candidate precursor for GaN powders with high purity and single phase. The process of conversion of the salt to GaN in flowing ammonia was monitored by XRD. 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. A close examination of XRD patterns, weight loss, and SEM suggests that the conversion of $\gamma\text{-Ga}_2\text{O}_3$ to GaN does not proceed through Ga_2O but stepwise via amorphous GaO_xN_y as intermediates. Room-temperature PL spectra show that high-crystalline GaN powders obtained have the emission band at 363 nm and are not nitrogen deficient on calcination at high temperature of 1000°C.

Acknowledgements

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