Novel Synthesis of Nanocrystalline Gallium Nitride Powder from Gallium(III)-Urea Complex

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A novel method is reported for the preparation of wurtzite gallium nitride (GaN) powder with a controlled particle size from nanometer to micron scale, using gallium(III)-urea complex as the precursor. The GaN powders as synthesized at various temperatures showed strong and distinct photoluminescence characteristics. The method developed here may provide a simple, potentially economical way to form other nitride materials with desired performances.

During last 10 years, gallium nitride (GaN) and related III-V semiconductors have emerged as leading materials for optoelectronic devices such as light emitting diodes and laser diodes in the blue/UV region.[1–6] They are almost exclusively used in thin films typically deposited by chemical vapor deposition or molecular beam epitaxy. Relatively little attention has been directed on nanocrystalline GaN powder material, which has potential uses in both mesoscopic research and future development of nanodevices.[7–9] GaN powder was traditionally synthesized by direct nitridation of Ga or Ga_2O_3 at high temperatures ($>850\,°C$) for an extended period. Several methods have been developed recently,[10–14] typically using expensive and air-sensitive molecular precursors which tend to limit large-scale materials development and increase application costs.

In the present work, we report an alternative route to produce nanocrystalline wurtzite GaN powder from cheaper gallium(III)-urea complex at lower temperatures (500–600 °C) for 1 h. This novel route is an attractive method for producing GaN powder in a tube furnace, while it is possible to control over particle size from nanometers to microns, and the photoluminescence characteristics.

10.25 g of gallium (99.9999%) was dissolved in hydrochloric acid (36–38%), and was heated to be concentrated. After some ethanol was added in, the solution was dried at 100 °C to get a gelatin and then reacted with 52.98 g of urea (>99%) under stirring in ethanol. Ga(III)-urea complex was obtained after being dried at 110 °C.

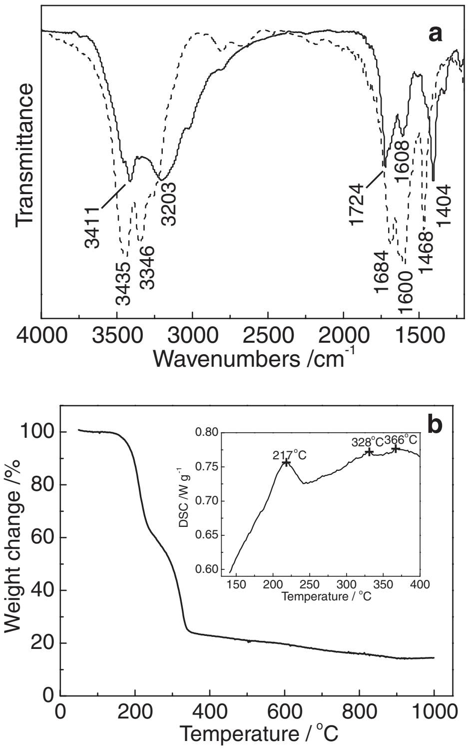

Figure 1. (a) Infrared spectra of (- - -) urea and (—) Ga(III)-urea complex. (b) Thermogravimetrical curve of Ga(III)-urea complex under argon atmosphere. Inset: differential scanning caloric curve.

IR characteristics of the complex are shown in Figure 1a, compared with those of urea. The presence of a carbonyl vibration at $1724\,cm^{-1}$ and the shift of CN absorption peaks from 1468 to $1404\,cm^{-1}$ indicate the formation of a nitrogen-to-gallium coordinate bond between urea molecules and Ga^{3+} ion.[15] Other bands of the complex are assigned as the coordinated N-H stretching vibration at $3203\,cm^{-1}$, and the free NH_2 vibration at 3411 and $1608\,cm^{-1}$, respectively. For comparison, the bands of urea are assigned as followed; peaks at 3435 and $3346\,cm^{-1}$ to NH_2 group, a peak at $1600\,cm^{-1}$ to a combined carbonyl stretching vibration and bending vibration of NH_2, and a shoulder at $1684\,cm^{-1}$ to carbonyl vibration. Since both the free and coordinated N–H frequencies are observed, it is concluded that only one nitrogen atom of each urea molecule coordinates to Ga^{3+} ion.[15] The molecular formula may be written as $Ga(NH_2CONH_2)_6Cl_3$, where the coordination number 6 is calculated from the original urea/Ga ratio, because no excessive urea is detected under the detectability of IR (ca. 5%). TG curve of the complex under argon atmosphere (Figure 1b) exhibits a two-stage weight loss between 120–380 °C. Correspondingly, DSC shows a strong endothermic peak around 217 °C, and two minors between 300–380 °C (inset of Figure 1b). Our previous studies suggest that these endothermic processes involve the dissociation of the coordinated urea.[16,17] The weight-loss curve is near flat above 400 °C. Considering the high vapour pressure of $GaCl_3$, the final solid remaining should be GaCl, which is stable at temperatures above 600 °C. The total weight loss at 600 °C is 80.4%, equal to the calculated value on the assumption of GaCl.

The pyrolysis of the complex powders at 500–900 °C for 1 h under flowing ammonia (0.5 L/min) resulted in the formation of GaN, via the reaction

$$GaCl + NH_3 \rightarrow GaN + HCl + H_2.$$

In conventional vapour phase epitaxy of GaN, GaCl was formed

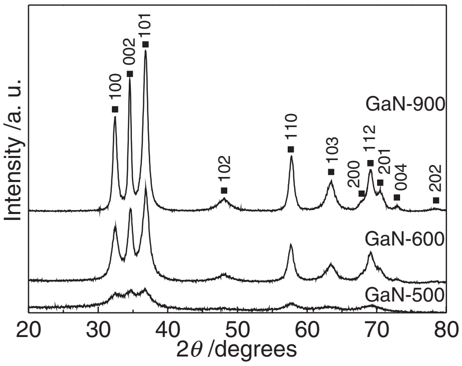

Figure 2. XRD patterns of GaN powders with the wurtzite structure (■).

by the reation of liquid Ga and highly corrosive HCl in a two-zone furnace at high temperatures (>800 °C).[6] In this work, GaCl was produced in situ as the Ga source after the decomposition, thus the reactor structure can be simplified and the production cost will be lowered. The GaN powder prepared at 500, 600, and 900 °C are denoted as GaN-500, GaN-600 and GaN-900, respectively.

The X-ray powder diffraction (XRD, Cu $K\alpha$ $\lambda = 1.5418$) patterns of GaN-500 and GaN-600 in Figure 2 show broadened diffraction peaks, indexed as wurtzite GaN, corresponding to the characteristic of nanocrystallites, while peaks for GaN-900 are stronger and sharper, indicating a higher crystallization degree and a larger particle size. TEM micrographs demonstrate clearly that particles of GaN-500 and GaN-600 are in the nanometer scale (Figure 3). These powders have an average particle size of 13 and 24 nm, respectively, by measuring the maximum diameter of 500 particles. For GaN-900, flaky particles of 0.1–1 µm are obtained.

PL measurements of GaN powders were carried out using a fluorescence spectrometer with a Xe lamp (excited at 347 nm) at room temperature. All samples show a strong and narrow band-edge emission peak at 362 nm (Figure 4).[13,18] GaN-500 exhibits the strongest band-edge emission. However, its PL spectrum consists of a typical yellow luminescence at 400–620 nm[19,20] and an impurity-related shoulder at 470 nm.[21] A peak at 394 nm is not firmly identified. Increasing the synthesis temperature, and therefore at the same time increasing the particle sizes, resulted in a dramatic decrease of the impurity-related emission and a minor decrease of the band-edge emission. The yellow band is absent in GaN-600 and GaN-900. The present results show that a small particle size obtained at a lower temperature facilitates the band-edge emission, and 600 °C should be an appropriate synthesis temperature for both a small particle size and good optical performance.

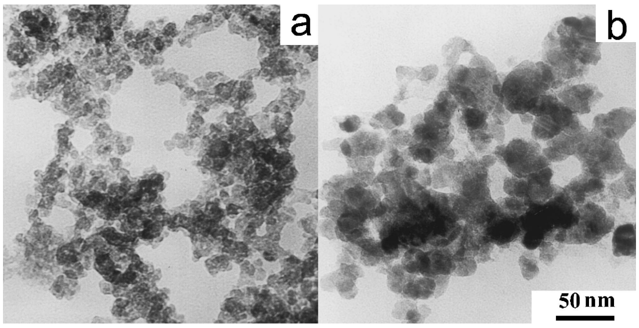

Figure 3. Transmission electron micrographes of (a) GaN-500 and (b) GaN-600. The same scale is used in both images.

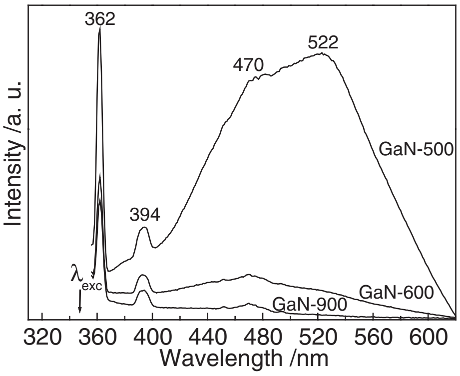

Figure 4. PL spectra of GaN powders measured at room temperature.

In summary, nanocrystalline wurtzite GaN powder with intense photoluminescence was synthesized at 500–600 °C from Ga(III)-urea complex. The synthesis provide a simple, potentially economical method with control over the GaN particle size and its photoluminescence characteristics, and may also be extended to form other nitride and III-V semiconductor materials. Further efforts are underway to perform extended investigation of the photoluminescence, thus to clarify the underlying mechanism, and to produce size-controlled GaN powder with strong emission by optimizing the synthetic parameters.

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