Synthesis and Characterization of Gallium Nitride Powders and Nanowires Using Ga(S₂CNR₂)₃ (R = CH₃, C₂H₅) Complexes as New Precursors

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Gallium nitride (GaN) powders and nanowires were prepared by using tris(*N,N*-dimethyldithiocarbamato)gallium(III) (Ga(DmDTC)₃) and tris(*N,N*-diethyldithiocarbamato)gallium(III) (Ga(DeDTC)₃) as new precursors. The GaN powders were obtained by reaction of the complexes with ammonia in the temperature ranging from 500 to 1100 °C. The process of conversion of the complexes to GaN was monitored by their weight loss, XRD, and ^{71}Ga magic-angle spinning (MAS) NMR spectroscopy. Most likely the complexes decompose to γ-Ga₂S₃ and then turn into GaN via amorphous gallium thionitrides (GaS$_x$N$_y$). The reactivity of Ga(DmDTC)₃ with ammonia was a little higher than that of Ga(DeDTC)₃. Room-temperature photoluminescence spectra of as-prepared GaN powders exhibited the band-edge emission of GaN at 363 nm. GaN nanowires were obtained by nitridation of as-ground γ-Ga₂S₃ powders to GaN powders, followed by sublimation without using templates or catalysts.

Key Words : Gallium nitride, Powder, Nanowire, ^{71}Ga MAS NMR, Ga(III) complex

Introduction

Group 13 nitrides such as AlN, GaN, and InN have been attracting widespread interest for the last few years as suitable materials for various optoelectronic devices across the entire visible spectrum up to ultraviolet. Of the Group 13 nitrides, gallium nitride (GaN) has shown tremendous potentials in electronic applications due to its unusually large band gap.[1] Heteroepitaxial layers of GaN, commonly grown on sapphire, induce structural defects because a severe mismatch exists both in lattice parameters and thermal expansion coefficients. A trend for the future is, therefore, the development of GaN substrates for homoepitaxy by fabricating GaN bulk single crystals and wafers. Sublimation[2] and high-pressure solution methods[3] are considered for crystal growth of GaN. These methods demand the availability of a well-characterized GaN powder source with high purity and single phase. The GaN powders can be synthesized by the reaction of metal Ga,[4] gallium oxide (Ga₂O₃),[4] gallium oxyhydroxide,[5,6] α-Ga₂S₃[7] or gallium salts[8,9] with ammonia.

In the present study we use Ga(III) complexes with sulfur-donor ligands as new precursors of GaN and compared their reactivity with those of other precursors. We will also show that GaN nanowires are prepared by nitridation of the reaction intermediate γ-Ga₂S₃ to GaN powders, followed by sublimation without using templates or catalysts. In recent years GaN nanostructures such as nanowires and nanobelts have been synthesized by many different methods. Simple and inexpensive methods that do not use templates or catalysts were reported by Jian *et al.*[10] and Zhou *et al.*[11] To our knowledge, GaN powders or nanowires produced by using any air-insensitive Ga(III) complex have not been reported in the literature.

Experimental Section

Tris(*N,N*-dimethyldithiocarbamato)gallium(III) (Ga(DmDTC)₃) and tris(*N,N*-diethyldithiocarbamato)gallium(III) (Ga(DeDTC)₃) as precursors of GaN were prepared by dissolving Ga(NO₃)₃·xH₂O (x ~ 7.6) (Aldrich Chemical.) and sodium *N,N*-dimethyldithiocarbamate dihydrate (TCI) and sodium *N,N*-diethyldithiocarbamate trihydrate (Aldrich) (with a 1 : 3 mole ratio of the Ga salt to the ligand), respectively, in methanol and recrystallized from chloroform. The complexes were identified by ^{1}H NMR spectroscopy using a Bruker DPX-300 spectrometer. The alumina crucible containing powders of precursors was placed at the center of an alumina tube 1000 mm in length and 36 mm in diameter in a horizontal furnace and heated at a rate of 5 °C min⁻¹ to the calcination temperature (500-1100 °C) under an ammonia (Showadenko Co., 99.999%) flow of 50 mL min⁻¹. After the reaction, the product powder was cooled to room temperature under a flow of nitrogen and weighed. The samples were weighed before and after calcinations. To obtain GaN nanowires, Ga(DmDTC)₃ powders were converted to γ-Ga₂S₃ by calcining at 500 °C for 1 h in flowing N₂ and then ground in mortar with a pestle. As-ground γ-Ga₂S₃ powders were nitridated to GaN powders at 850 °C for 1 h and then sublimed at 1050 °C for 1 h under a flow of ammonia.

The process of conversion of the complexes to GaN was investigated by XRD (Rigaku DMX-2500 diffractometer with Cu-Kα 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 zirconia rotor used as a sample chamber was spun at 14 kHz during data collection. Chemical shifts were referenced to 1 M aqueous gallium(III) nitrate solution.

The morphology and structure of the products were examined using a scanning electron microscopy (SEM, Hitachi S-4100), transmission electron microscopy (TEM, Philips CM 200 STEM, working at 200 kV) and selected-area electron diffraction (SAED). PL measurements were carried out with a He-Cd laser (excitation wavelength = 325 nm) at room temperature.

Results and Discussion

The complexes Ga(DmDTC)$_3$) and Ga(DeDTC)$_3$ were identified by ^{1}H NMR spectra. The spectrum of the former complex in CDCl$_3$ showed one singlet peak at 3.38 ppm, whereas the spectrum of the latter complex showed one quartet peak (3H, J = 7.2 Hz) at 3.76 ppm and one triplet peak (2H, J = 7.2 Hz) at 1.28 ppm.[12] Figure 1 shows X-ray diffraction (XRD) patterns of samples obtained by calcining the complex Ga(DmDTC)$_3$ at different calcination temperatures for 1 h. The complex decomposed to γ-Ga$_2$S$_3$[13] with a defect zinc-blende structure, as shown in Figure 1(a) and then turned into GaN with increasing temperature. Diffraction peaks assigned to GaN[4] were very poorly resolved for the sample calcined at 700 °C because of its low crystallinity and they became more resolved with increasing temperature.
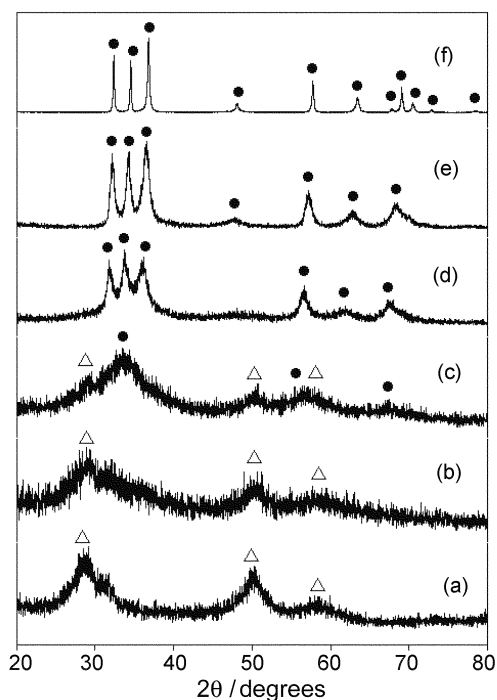

Figure 1. XRD patterns of powders obtained by calcination of Ga(DmDTC)$_3$ in flowing ammonia at various temperatures for 1 h: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 750 °C, (e) 900 °C, (f) 1100 °C. $\triangle$, γ-Ga$_2$S$_3$; ● , GaN.
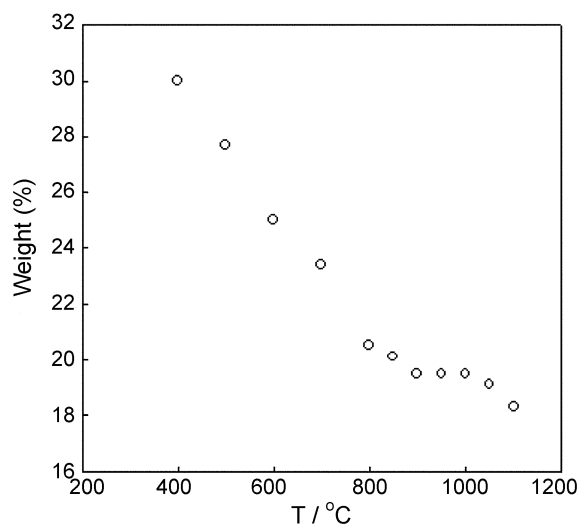

Figure 2. Variation in weight % of Ga(DmDTC)$_3$ as a function of calcination temperature.

Detectable peaks other than the peaks assigned to GaN were absent in the samples calcined above 750 °C.

The conversion of the complexes to GaN was accompanied by a weight loss. Therefore, the weight loss can be used as a measure of the degree of completion of the reaction. Figure 2 shows the change in the weight % (which is defined by $100 \times$ weight of the product/weight of the Ga(DmDTC)$_3$ complex used) against the reaction temperature. The weight % (27.7%) measured at 500 °C was close to that (27.4%) obtained if Ga(DmDTC)$_3$ is completely to converted to γ-Ga$_2$S$_3$. The weight % almost linearly decreased with increasing temperature up to 900 °C. The weight % was nearly constant (19.5%) in the temperature range from 900 to 1000 °C, where GaN powders synthesized become more crystalline and denser.[8] The value of 19.5% will be obtained if there is no loss of Ga species from the reaction system during reaction and the complex is completely converted to GaN. Above 1000 °C the weight % decreases again with increasing temperature because GaN powders sublime and/ or decompose. As mentioned above, the XRD patterns of the samples obtained between 750 and 850 °C shows that they are a single phase of GaN, though their weight % values were quite higher than 19.5%. We inferred from this finding that a small amount of the reaction intermediates such as amorphous gallium thionitrides (GaS$_x$N$_y$) were involved in the samples. As the nitridation proceeds, the sulfur content in the intermediates gradually decreases, leading to a complete conversion to GaN. The analogous intermediates, gallium oxynitrides (GaO$_x$N$_y$), were suggested in conversion of β-Ga$_2$O$_3$ to GaN in flowing ammonia.[14]

Solid-state NMR spectroscopy might be a more powerful probe than XRD in characterizing less crystallined materials because the latter provides little information about the central-metal distribution owing to a lack of long-range order. Figure 3 shows [71]Ga MAS NMR spectra of samples obtained by calcining the complex Ga(DmDTC)$_3$ at different calcination temperatures for 1 h. The spectrum of the sample
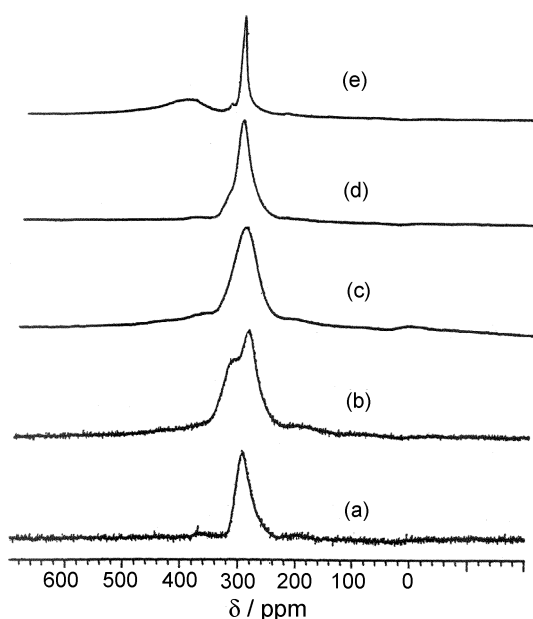
Figure 3. ^{71}Ga MAS NMR spectra of powders obtained by calcination of Ga(DmDTC)$_3$ in flowing ammonia at various temperatures for 1 h: (a) 500 °C, (b) 700 °C, (c) 750 °C, (d) 900 °C, (e) 1100 °C.

obtained at 500 °C shows one peak at 299 ppm, which is assigned to four-coordinated gallium atoms (GaS$_4$) in γ-Ga$_2$S$_3$. In the spectrum (Figure 3(b)) of the sample obtained at 700 °C, the shoulder peak on the downfield side of the peak of γ-Ga$_2$S$_3$ is assigned to GaN.[15] The spectrum (Figure 3(c)) of the sample obtained at 750 °C shows a very broad peak at 310 ppm, which is a superposition of GaN and γ-Ga$_2$S$_3$ peaks of almost equal intensity. As the reaction temperature increased with increasing the degree of crystallinity of GaN, the peak assigned to GaN became more narrow and somewhat downfield shifted. The spectrum (Figure 3(d)) of the sample at 900 °C exhibited an asymmetrical resonance with a shoulder on the downfield side. The shoulder peak became more distinct at 345 ppm for samples obtained above 1000 °C and is tentatively assigned to the Ga atom in GaN, in which one Ga-N bond is different from the other three bonds in bond length. In the spectrum (Figure 3(e)) of the sample obtained at 1100 °C, the GaN peak at 330 ppm appears along with a very broad peak at 425 ppm, the latter being due to nitrogen-deficient GaN.[7] The failure to detect any intermediates such as GaS$_x$N$_y$ in the NMR spectra may be due to the fact that their relative amounts were very small and/or their signals were broadened beyond detection because of their poor symmetry.

The process of conversion of Ga(DeDTC)$_3$ to GaN was very similar to that of Ga(DmDTC)$_3$, but its reactivity with ammonia was a little lower than that of Ga(DmDTC)$_3$, in view of the fact that the temperature at which Ga(DeDTC)$_3$ was completely converted to GaN was about 100 °C higher than it was for Ga(DmDTC)$_3$.

The reactivity of γ-Ga$_2$S$_3$ with ammonia is higher than that of α-Ga$_2$S$_3$, considering that the latter was completely nitrided to GaN at 1000 °C for 3 h.[7] The GaN powders

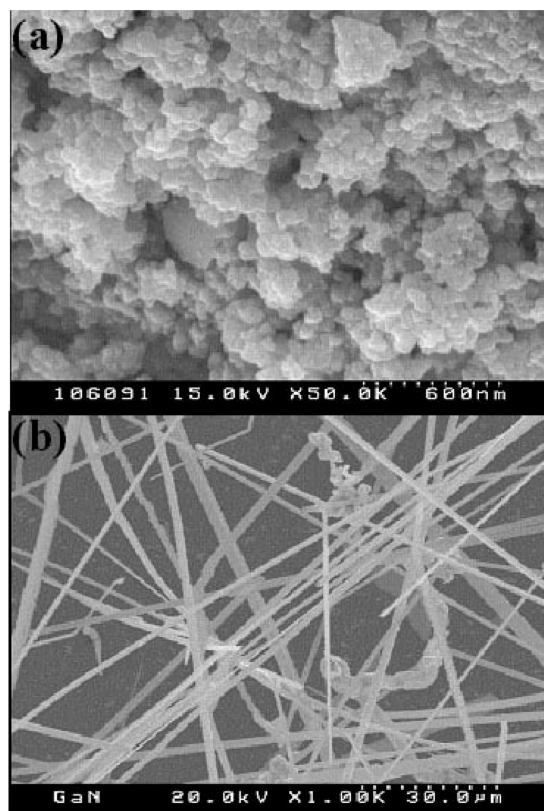**Figure 4**. SEM images of (a) GaN powders obtained by calcination of Ga(DmDTC)$_3$ at 900 °C for 1 h in flowing ammonia and (b) GaN nanostructures obtained by nitridation of as-ground γ-Ga$_2$S$_3$ powders to GaN powders, followed by sublimation at 1050 °C for 1 h in flowing ammonia.

obtained from α-Ga$_2$S$_3$ above 900 °C showed high nitrogen-deficiency because of its low reactivity, as revealed by their ^{71}Ga MAS NMR spectra.[7] The reactivity of γ-Ga$_2$S$_3$ with ammonia is similar to that of γ-Ga$_2$O$_3$.[8,9]

The morphology of GaN powders obtained at 900 °C was observed by SEM. Figure 4 (a) shows that the powders are

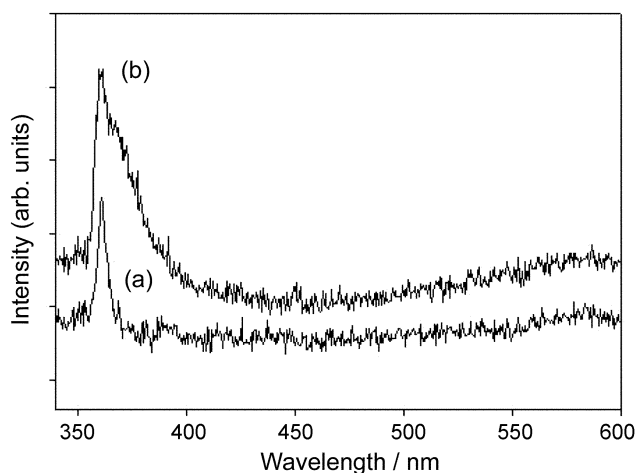**Figure 5**. Room-temperature PL spectra of GaN powders obtained by calcination of Ga(DmDTC)$_3$ at (a) 900 and (b) 1100 °C for 1 h in flowing ammonia.

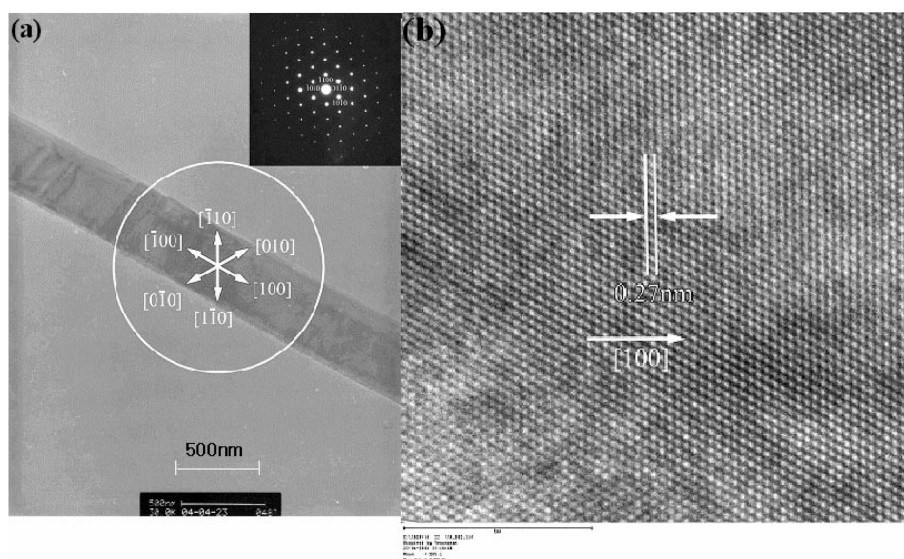**Figure 6**. TEM images of the GaN nanowire obtained by nitridation of as-ground γ-Ga$_2$S$_3$ powders to GaN powders, followed by sublimation at 1050 $^{\circ}$C for 1 h in flowing ammonia: (a) Bright-field image, with the direction of the long axis being [100]. The inset is the corresponding SAED pattern, with the zone axis being [001]. (b) HRTEM image of a single GaN nanowire with a diameter of about 45 nm. The image was recorded along [001] zone axis. The direction of the long axis is [100].

fused with homogeneous primary particles, the diameter of which is about 60 nm. Room-temperature photoluminescence (PL) spectra of as-synthesized GaN powders were measured using a He-Cd laser excitation source. Figure 5 shows the PL spectra of GaN powders obtained at 900 and 1100 $^{\circ}$C. In Figure 5(a) the band edge of GaN with the wurtzite structure is observed at 363 nm along with negligible yellow emission band, whereas in Figure 5(b) a very broad and weak yellow emission band around 580 nm is observed besides a broad band edge of GaN. The occurrence of the yellow band and the broadening of the band edge are due to the nitrogen deficiency in GaN.[7]

To obtain GaN nanowires, as-ground γ-Ga$_2$S$_3$ powders were nitridated to GaN powders, followed by sublimation at 1050 $^{\circ}$C for 1 h in flowing ammonia without using templates or catalysts. A large quantity of wool-like products (Figure 4(b)), which involved a variety of GaN nanostructures (such as nanowires, nanobelts, and nanosaws), were found on the inner wall of the alumina tube about 30 cm away from the center of the alumina crucible. The energy dispersive X-ray spectroscopy (EDX) analyses indicated that all the nanostructures were composed only of elements Ga and N. Of the GaN nanostructures synthesized, the GaN nanowires were characterized by TEM. As can be seen from the TEM image in Figure 6(a), the long axis of GaN nanowires is parallel to [100] direction. The inset of Figure 6(a) shows a selected-area electron diffraction (SAED) pattern taken along the [100] direction, which is consistent with that of a wurtzite structure. As shown in Figure 6(b), a lattice spacing of 0.27 nm for (100) planes of the wurtzite structure can be readily resolved in a high-resolution TEM image of a single GaN nanowire with a diameter of about 45 nm. Considering that no metal catalyst was used in this study and no Ga droplets on the tip of the nanowires were detected by TEM, the nanowires are likely grown by the vapor-solid (VS) mechanism.

Conclusion

Gallium(III) complexes with sulfur-donor ligands, Ga(DmDTC)$_3$ and Ga(DeDTC)$_3$ were used as new precursors of GaN. GaN powders were easily obtained by reaction of the complexes with ammonia. Measurements of the weight loss, XRD, and ^{71}Ga MAS NMR spectra indicated that the complexes may decompose to γ-Ga$_2$S$_3$ and then turn into GaN via amorphous gallium thionitrides (GaS$_x$N$_y$). ^{71}Ga MAS NMR and PL spectra revealed that there is nitrogen deficiency in GaN powders obtained at temperatures above 900 $^{\circ}$C. To obtain high-quality GaN powders, therefore, the calcination temperature must be maintained below 900 $^{\circ}$C. GaN nanowires were obtained by nitridation of as-ground γ-Ga$_2$S$_3$ powders to GaN powders, followed by sublimation without using templates or catalysts and characterized by means of SEM, TEM, and SAED. Further work is in progress for controlling growth of GaN nanomaterials with various morphologies.

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