Journal of Alloys and Compounds 499 (2010) 269–272

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Synthesis, thermal stability, and photocatalytic activity of nanocrystalline gallium nitride via the reaction of Ga_2O_3 and NH_4Cl at low temperature

Hong Zhang[a], Youjian Chen[a], Li Fu[a], Jianhua Ma[a,b,*]

[a] *College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325027, PR China*
[b] *Nanomaterials and Chemistry Key Laboratory, Advanced Materials Research Center of Wenzhou, Wenzhou University, Wenzhou, Zhejiang 325027, PR China*

ARTICLE INFO

Article history:
Received 28 January 2010
Received in revised form 19 March 2010
Accepted 21 March 2010
Available online 27 March 2010

Keywords:
Gallium nitride
Chemical synthesis
X-ray diffraction
Thermogravimetric analysis
Photocatalysis activity

ABSTRACT

Nanocrystalline gallium nitride (GaN) was prepared via one simple route by the reaction of metallic magnesium powders with gallium sesquioxide (Ga_2O_3) and ammonium chloride (NH_4Cl) in an autoclave at 650 °C. X-ray powder diffraction (XRD) pattern indicated that the product was hexagonal GaN, and the cell constant was ($a = 3.18962$ Å, $c = 5.18674$ Å). Scanning electron microscopy (SEM) images showed that the sample consisted of particles with an average size of about 30 nm in diameter. Raman spectroscopy study showed a frequency shift towards lower side due to the polycrystalline nature of the synthesized GaN. The hexagonal GaN powder exhibited good photocatalytic activity in degradation of Rhodamine-B (RhB) under 300 W mercury lamp light irradiation. The product was also studied by the thermogravimetric analysis (TGA). It had good thermal stability and oxidation resistance below 750 °C in air.

1. Introduction

Following the first generation of Ge, Si semiconductor materials, the second-generation GaAs, InP compound semiconductor materials, GaN with SiC, diamond and other wide bandgap compound semiconductor materials have been known as the third generation of semiconductor materials [1,2]. GaN, an important III–V semiconductor with a direct band gap of 3.39 eV at room temperature [3–5] and high optical transition probability, has a wide use in optoelectronic devices operating at blue-green light-emitting diode (LED) and laser diode (LD) and other material of choice [6–8]. At the same time, due to GaN-based material has a high electron drift saturation velocity, the small dielectric constant, good thermal conductivity, good chemical and thermal stability characteristics [9], it is also very suitable for the production of high-temperature, high-frequency and high-power electronic devices [10].

Traditionally, many approaches have been developed for the preparation of gallium nitride, such as metal organic vapor phase extension (MOVPE) [11–14], the molecular beam extension (MBE) [15,16], the hydride vapor phase extension (HVPE) [17] and alumina templates method [18,19]. Qian and co-workers [20] reported a benzene-thermal route to prepare nanocrystalline gallium nitride. Recently, some new methods have been used to synthesize gallium nitride. Li et al. [21] reported a facile solid-state reaction method to prepare GaN nanoparticles through using an organic reagent cyanamide (CN_2H_2) and Ga_2O_3 as precursors in a silica ampoule at 750 °C. Ogi et al. [22] reported that nanocrystalline GaN was also successfully synthesized from Ga_2O_3 nanoparticles derived from salt-assisted spray pyrolysis. Qiu et al. [23] reported the sol–gel method to synthesize nanocrystalline GaN. Kano et al. [24] reported mechanical alloying method to synthesize GaN powder by mechanochemical treatment of gallium oxide (Ga_2O_3) and lithium nitride (Li_3N) metal under NH_3 gas environment.

In this paper, we have developed a new convenient route to synthesize nanocrystalline gallium nitride at low temperature. Nanocrystalline GaN has been synthesized by the reaction of metallic magnesium powders with Ga_2O_3 and NH_4Cl in an autoclave at 650 °C. In this route, we use Ga_2O_3 as gallium source and NH_4Cl as nitrogen source, metallic magnesium powders as reductant, which are very safe and convenient in all manipulations.

2. Experimental

All of the manipulations were carried out in a dry glove box with flowing nitrogen gas. In a typical experiment, 0.0026 mol (about 0.4892 g) analytical grade Ga_2O_3, 0.0065 mol (about 0.3465 g) analytical grade NH_4Cl and 0.0143 mol (about 0.3470 g) analytical grade metallic magnesium powders (excessive) were put into a mortar, followed by mixing these powders thoroughly. Then the mixture was put into a stainless steel autoclave. After sealing under argon atmosphere, the autoclave was heated at 650 °C for 8 h, followed by cooling to room temperature in the furnace. The obtained product from the autoclave was washed several times with absolute ethanol, dilute HCl aqueous solution, distilled water to remove the impurities.

---

* Corresponding author at: College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325027, PR China. Tel.: +86 577 86669317; fax: +86 577 86689508.
E-mail address: mjh820@ustc.edu (J. Ma).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.03.185

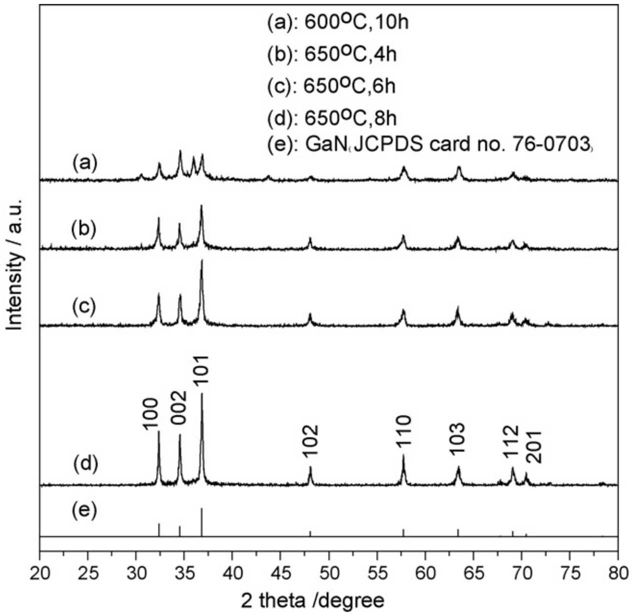

Fig. 1. XRD patterns of the as-prepared samples and standard pattern.

Finally the product was washed three times with absolute ethanol to remove water. The final product was vacuum-dried at 60 °C for 12 h. Gray powders were obtained.

The obtained sample was analyzed by powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray powder diffractometer using Cu K-α radiation (wavelength λ = 1.54178 Å). The morphology of the sample was examined on a JEOL JSM-6700F scanning electron microscope. Raman spectra were measured on a Raman spectrophotometer (model Jobin Yvon T64000). The 514.5 nm laser was used as an excitation light source. The optical diffuse reflectance spectra were recorded on a UV2501PC (Shimadzu) using $BaSO_4$ as reference to study its photocatalysis. The thermogravimetric analysis was performed on a thermal analyzer (Model: Q600) below 1000 °C in air at a rate of 10 °C min^{-1} to study its thermal stability and oxidation behavior.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of the as-prepared samples under different reaction conditions. Pattern (d) shows the sample prepared under the condition of 650 °C and 8 h. There are eight obvious diffraction peaks in this pattern. And all these diffraction peaks ((1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), and (2 0 1)) at different *d*-space can be indexed as hexagonal gallium nitride (GaN). The refinement gives the cell constants (a = 3.18962 Å, c = 5.18674 Å), which is consistent with the value reported in the literature (a = 3.190 Å, c = 5.189 Å) (JCPDS card no. 76-0703). No evidences of impurities such as Ga, gallium oxide, other gallium nitrides, can be found in this XRD pattern.

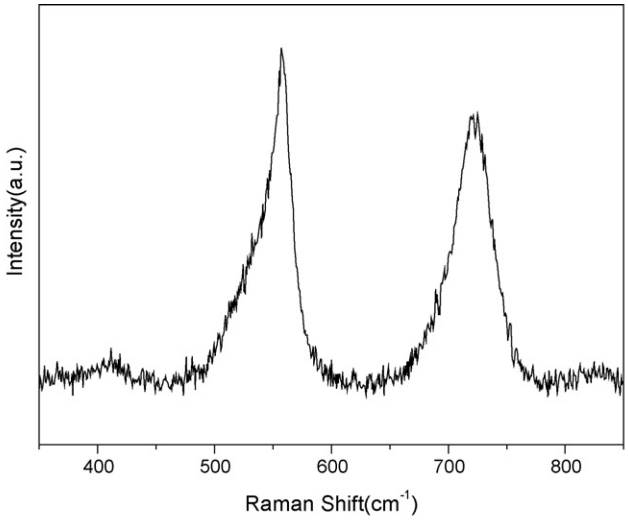

Fig. 3. Raman spectrum of the GaN powders deposited on Si substrate.

3.2. Scanning electron microscopy

The morphology of the prepared GaN sample was investigated by field emission scanning electron microscopy. The SEM images of the as-prepared GaN samples prepared under different reaction conditions are shown in Fig. 2. Fig. 2(c) shows the sample prepared under 650 °C and 8 h. In this figure, the sample shows that it consists of particles with an average diameter of 30 nm. These particles exhibit slightly agglomerated particle morphology due to the ultrafine size of the sample.

3.3. Raman spectroscopy

Further evidence for the formation of GaN can be obtained through Raman. Fig. 3 shows the room temperature Raman spectra of GaN sample. Two wide bands at around 557 cm^{-1} and 724 cm^{-1} can be clearly observed, which are the characteristic of hexagonal phase of GaN [25]. In our result, there is a frequency shift of about 11 cm^{-1} observed in the powder GaN data. This may be due to the polycrystalline nature of the synthesized GaN, which may have several grain boundaries and defects.

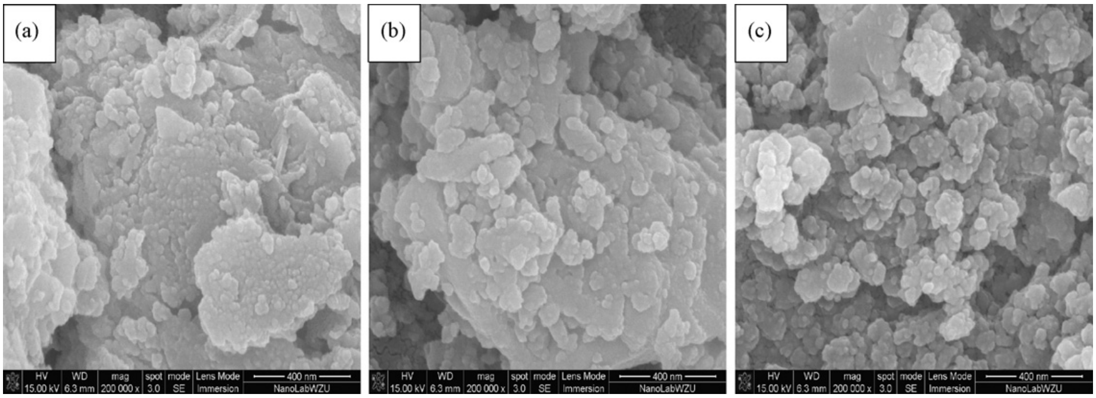

Fig. 2. SEM images of the as-prepared samples prepared under different reaction conditions (a) 650 °C, 4 h; (b) 650 °C, 6 h; and (c) 650 °C, 8 h.

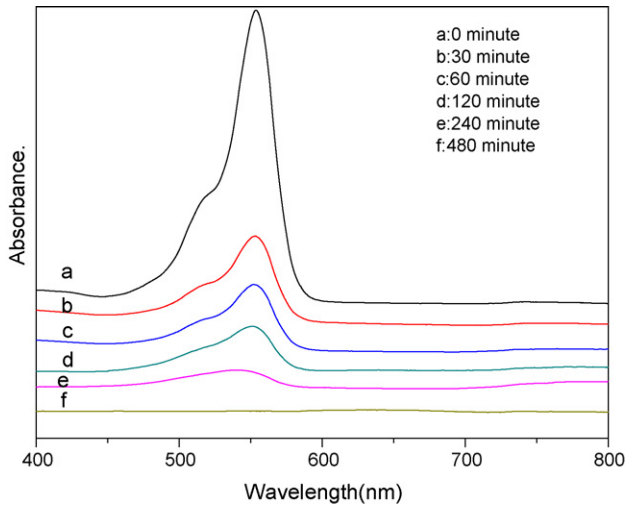

Fig. 4. The temporal evolution of the absorption spectrum of the RhB solution (10^{-5} mol/L) in the presence of 100 mg of GaN under mercury lamp light irradiation.

3.4. Photocatalysis

Photocatalytic activity of nanocrystalline GaN was evaluated by degradation of RhB under mercury lamp light. In every experiment, 0.1 g of the photocatalyst was added to 100 mL of RhB solution (10^{-5} mol/L). Before illumination, the suspensions were magnetically stirred in the dark for 12 h to ensure the establishment of an adsorption–desorption equilibrium between the photocatalysts and RhB. After that, the solution was exposed to 300 W mercury lamp light irradiation under magnetic stirring. At given time intervals, 3 mL aliquots were sampled and centrifuged to remove the photocatalyst particles. Then, the filtrates were analyzed by recording variations of the absorption band maximum (553 nm) in the UV–vis spectra of RhB by using a Shimadzu UV2501PC spectrophotometer [26].

Fig. 4 displays the temporal evolution of the spectra during the photodegradation of RhB. RhB has strong absorption at 553 nm. As the exposure time was extended, the strength of the absorption peak was reduced. Under 300 W mercury lamp illumination, RhB was de-ethylated in a stepwise manner and followed a destruction of the conjugated structure, which had previously been reported in the literature [27]. After 8 h, the absorption peak completely disappeared and the intense pink color of the starting RhB solution faded.

3.5. Thermogravimetric analysis

To investigate the thermal stability and the oxidation resistance of the as-prepared nanocrystalline GaN, the thermogravimetric analysis (TGA) was carried out at temperatures below 1000 °C under nitrogen gases or flowing air. Fig. 5 shows the TGA curves of the sample. The TGA curve (a) is carried out under flowing nitrogen gases. We can find that the weight of the product has not changed significantly below 1000 °C except a slight water weight loss on the surface. From the TGA curve (b), heated under flowing air, we can find that the weight of the product has not changed significantly below 750 °C. A slight weight loss indicates that the sample might adsorb a little water on the surface. But the quantity of the adsorbed water is very small. As the temperature keeps on rising from 750 °C to 1000 °C, there is an obvious weight gain during the process, indicating that the GaN sample is oxidized into Ga_2O_3 and nitrogen oxides. Theoretically, the whole weight increment is about 11.93% according to the calculation when GaN is thoroughly oxidized to the corresponding oxides (Ga_2O_3 and NO_2). The experimental result is within 8.722%. So we can conclude that the sample is not oxidized thoroughly. These indicate that the prepared GaN has good thermal stability and anti-oxidation property under 750 °C that will make it particularly useful for high-temperature applications.

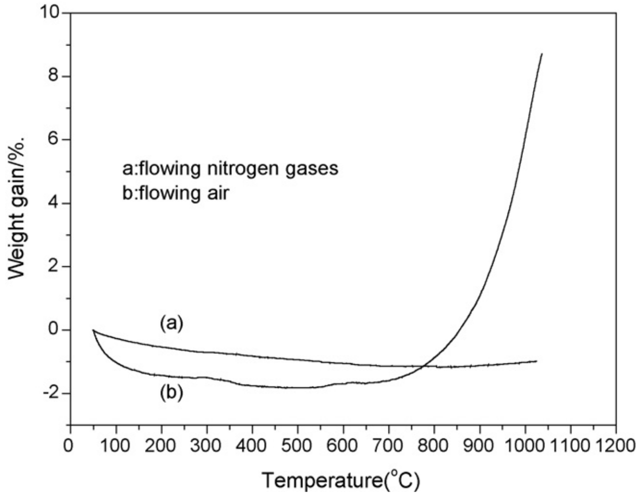

Fig. 5. TGA curves of the as-prepared GaN sample.

It was found that both reaction temperature and time had significant influence on the formation of GaN. Nanocrystalline GaN can be prepared if the reaction temperature reaches a certain temperature. Fig. 1 shows the XRD patterns of the as-prepared samples synthesized under different temperature and time conditions. Heating at 600 °C could produce GaN, but the crystallinity is not very good, impurity such as Ga_2O_3 can be found in XRD pattern (a). When the temperature is 650 °C, the crystallinity of the sample is very good. An optimum temperature for the formation of nanocrystalline GaN is about 650 °C. If the reaction time is shorter than 4 h, the reaction is incomplete and the crystallinity of GaN is lower. So an optimum reaction condition for the formation of nanocrystalline GaN is 650 °C for 8 h. The SEM images of these samples are shown in Fig. 2. According to this, we can know that varying the reaction time in the range of 4–8 h at 650 °C did not significantly affect the particle size of the as-prepared GaN. And the XRD patterns of the as-prepared samples show that each product is hexagonal GaN, different reaction conditions in this research do not affect the lattice structure of the as-prepared GaN.

In our experiments, as the temperature rose, NH_4Cl could decompose generating NH_3 and HCl gases above 338 °C [28]. So the pressure in the autoclave may be very high. At the reaction temperature, Ga_2O_3, NH_3 and metallic magnesium powders could react with each other to produce GaN. The high pressure in the autoclave would be helpful for reducing the reaction temperature and enhancing the reaction speed. The produced HCl gas was strongly absorbed by the metallic magnesium powders to form $MgCl_2$ and H_2. Therefore, the thermal reaction might be expressed as follows:

$$NH_4Cl \rightarrow NH_3 + HCl$$

$$Ga_2O_3 + 2NH_3 + 3Mg \rightarrow 2GaN + 3MgO + 3H_2$$

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

And the total reaction process can be represented as the following:

$$Ga_2O_3 + 2NH_4Cl + 4Mg = 2GaN + 3MgO + MgCl_2 + 4H_2$$

4. Conclusion

In summary, nanocrystalline GaN has been prepared via a simple thermal route by the reaction of metallic magnesium powders with gallium sesquioxide (Ga_2O_3) and ammonium chloride (NH_4Cl) in an autoclave at 650 °C for 8 h. The product has the nanocrystalline GaN structure. It consists of particles with an average size of 30 nm. And it exhibits good photocatalytic activity in degradation of Rhodamine-B (RhB) under 300 W mercury lamp light irradiation. The product has good thermal stability and oxidation resistance below 750 °C.

Acknowledgments

This work was supported by the Department of Education of Zhejiang Province of China under Grant No. 20070546. Thanks are due to Dr. Dekun Ma for his useful technical help and discussions.

References

[1] C.J. Youn, T.S. Jeong, M.S. Han, et al., J. Cryst. Growth 250 (2003) 331–338.
[2] S. Nakamura, M. Senoh, N. Iwasa, et al., Appl. Phys. Lett. 67 (1995) 1868–1870.
[3] H.P. Maruska, J.J. Tietjen, Appl. Phys. Lett. 15 (1969) 327–329.
[4] J.I. Pankove, J.E. Berkeyheiser, H.P. Maruska, et al., J. Solid State Commun. 8 (1970) 1051–1053.
[5] S. Bloom, J. Phys. Chem. Sol. 32 (1971) 2027–2032.
[6] C.-R Lee, K.-W. Seol, J.-M. Yeon, et al., J. Cryst. Growth 222 (2001) 459–464.
[7] B. Gil, Group (III) Nitride Semiconductors Compounds: Physics and Applications, Oxford University Press, 1998.
[8] S. Nakamura, S. Pearton, G. Fasol, The Blue Laser Diode, Springer-Verlag, 1997.
[9] H.D. Xiao, H.L. Ma, C.S. Xue, et al., Mater. Chem. Phys. 88 (2004) 180–184.
[10] S.N. Mahammad, A.A. Salvador, H. Morkoc, Proc. IEEE 83 (1995) 1306–1355.
[11] P. Chen, S.Y. Xie, Z.Z. Chen, et al., J. Cryst. Growth 213 (2000) 27–32.
[12] Sugianto, R.A. Sani, P. Arifin, et al., J. Cryst. Growth 221 (2000) 311–315.
[13] R.D. Vispute, V. Talyansky, Z. Trajanovic, et al., Appl. Phys. Lett. 70 (1997) 2735–2737.
[14] S. Nakamura, M. Senoh, S. Nagahama, et al., Jpn. J. Appl. Phys. 36 (1997) L1568–L1571.
[15] K. Lorenz, R. Vianden, R. Birkhahn, et al., Nucl. Instrum. Methods Phys. Res. Sect. B 161–163 (2000) 946–951.
[16] T.D. Moustakas, E. Iliopoulos, A.V. Sampath, et al., J. Cryst. Growth 227–228 (2001) 13–20.
[17] J.W. Lee, H.S. Paek, J.B. Yoo, et al., J. Mater. Sci. Eng. B 59 (1999) 12–15.
[18] G.S. Cheng, S.H. Chen, X.G. Zhu, et al., J. Mater. Sci. Eng. A 286 (2000) 165–168.
[19] P. Sanguino, M. Niehus, L.V. Melo, et al., J. Solid-State Electron. 47 (2003) 559–563.
[20] Y. Xie, Y.T. Qian, S.Y. Zhang, et al., Appl. Phys. Lett. 69 (1996) 334–336.
[21] P.G. Li, M. Lei, Y.X. Du, et al., J. Appl. Surf. Sci. 255 (2009) 3843–3847.
[22] T. Ogi, Y. Kaihatsu, K. Okuyama, et al., J. Adv. Powder Technol. 20 (2009) 29–34.
[23] H.L. Qiu, C.B. Cao, H.S. Zhu, J. Mater. Sci. Eng. B 136 (2007) 33–36.
[24] J. Kano, E. Kobayashi, W. Tongamp, et al., J. Alloy. Compd. 464 (2008) 337–339.
[25] G. Bentoumi, A. Deneuville, B. Beaumont, J. Mater. Sci. Eng. B 50 (1997) 142–147.
[26] D.K. Ma, S.M. Huang, W.X. Chen, et al., J. Phys. Chem. C 113 (2009) 4369–4374.
[27] W. Zhao, C. Chen, J. Zhao, et al., J. Phys. Chem. B 106 (2002) 5022–5028.
[28] http://www.sciencelab.com/xMSDS-Ammonium_chloride-9927431.