# The Preparation Methods of Gallium Nitride Powder

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**Abstract.** Gallium nitride (GaN) has attracted much attention for a long time as a promising material for semiconductor device application in the transistors, visible light-emitting sources and high powder diodes. Many investigations are paid to the synthesis method, the process of crystal growth, structure and optical properties of GaN powder and its film. In this article, the preparation methods of GaN powder using the different kinds of raw materials have been reviewed.

#### Introduction

Due to outstanding physical properties such as high thermal conductivity, wide and direct band gap, low compressibility, the Gallium nitride (GaN) has attracted considerable attentions in recent years for its application in optical devices [1]. Because its direct band gap energy is to be 3.4 eV, the research interesting is focus on the optical properties of GaN. Most studies of GaN have been made in synthesizing nanopowder [2], membranes [3], nanorods [4], and bulk single crystals [5].

In the present work, the synthesis methods of GaN powder through the different kinds of raw materials (Ga, Ga<sub>2</sub>O<sub>3</sub>, GaI<sub>3</sub>, and other Ga compounds) have been reviewed, and the characteristics of preparation methods have also been discussed.

#### Preparation Methods of Gallium Nitride Powder

#### Ga Metal as Raw Materials

Due to excellent characteristics like high efficient and contamination-free, plasma method was an important method to synthesize GaN nanopowder using Ga metal and  $NH_3/N_2$  as raw materials. Li et al [6, 7] had fabricated ultrafine hexagonal GaN powder with the size about 20-200nm using the dc arc plasma method. Their investigation demonstrated that the conversion of Ga metal to GaN nanopowder was determined by the mixture ration of  $NH_3$  and  $N_2$  in the mixture gas. Furthermore, Raman spectroscopy of nanocrystalline GaN was observed. The characteristics modes exhibited that the size and defected-related effects on the lattice vibrational properties of the GaN nanopowder [8]. In addition, GaN particles were synthesized by the reaction of molten Ga and ammonia using Bi as a catalyst. The Bi catalyst was effective at increasing the growth rate of GaN powder, and it was easily removed by evaporation to obtain the high purity powders [9].

Xiang et al reported that the single-crystalline GaN nanobelts were synthesized by gallium vapor and ammonia using Ni as a catalyst [10]. GaN nanobelts were grown on the Ni-deposited silicon substrate at 950 °C for 60 min with the flow of NH<sub>3</sub> (50ml/min). High purity GaN nanostructure with hexagonal wurtzite structure is belt-like, which the thickness and width is about 30 nm and 200 nm, respectively. The lengths of nanobelts are up to several tens of  $\mu$ m, which appear twist and waving shapes. The system investigations by Xu and coworkers [11] indicated that GaN particles were obtained by three different ways using the same Ga as a precursor. First of all, Ga metal (99.999% purity) and NH<sub>4</sub>I (99.9% purity) were used as raw material to synthesize GaN particle by ammonothermal method. The nanoparticle of cubic GaN with grain size 32 nm was obtained. And then, NH<sub>4</sub>I was replaced by NH<sub>4</sub>Cl (99.9% purity), and the molar ration of Ga to NH<sub>4</sub>Cl is 82:18. The high pure hexagonal GaN particle with 20 nm was also obtained by ammonothermal method. At last, a gas reaction route was used to obtain pure hexagonal GaN coarse-grain powder. NH<sub>3</sub> gas (200 ml/min for 4-6 h) was adopted as a nitrogen source. The study indicated that the crystal structure and grain size of GaN particle are significantly influenced by raw material and synthesis method.

Single crystal of GaN powder with  $1.5 \times 1 \times 0.1$  mm was also prepared from Ga vapours and ammonia (99.99%) at the temperature of 850-1150 °C [12]. The temperature in the zones of the reactor and the gas flow rate are the key factors on the shape and growth rate of GaN crystals. Both the X-ray diffraction and Raman spectroscopy demonstrated that the crystallographic structure of the crystals and powders was well pronounced. There was another way to obtain the monocrystalline GaN. Vodakov et al showed that the monocrystalline GaN epitaxial layers were deposited by the sublimation "sandwich method" (SSM) with growth rate as high as 1 mm/h at temperature from 1100 °C to 1250 °C in the flow of ammonia [13]. High-purity and high efficient are the advantages using Ga as raw materials. However, there are still are disadvantages. For examples, the particle size of GaN is difficult to control by ammonothermal method.

#### Ga<sub>2</sub>O<sub>3</sub> as Raw Materials

Using Ga<sub>2</sub>O<sub>3</sub> as a raw material to synthesize was fully investigated by many methods. Zhao et al [14] reported that GaN nanobelts with wurtzite structure were grown on Ni-coated LaAlO<sub>3</sub> substrate by milling Ga<sub>2</sub>O<sub>3</sub> under NH<sub>3</sub> atmosphere. The growth direction of GaN nanobelts is parallel to [210]. The formation process could be a two-step chemical reaction as the following: (1) Ga<sub>2</sub>O<sub>3</sub>(s)+2H<sub>2</sub>(g) $\rightarrow$ Ga<sub>2</sub>O(s)+2H<sub>2</sub>O(g); (2) Ga<sub>2</sub>O<sub>3</sub>(g)+2NH<sub>3</sub>(g) $\rightarrow$ 2GaN(s)+H<sub>2</sub>O(g)+2H<sub>2</sub>(g). H<sub>2</sub> is generated from NH<sub>3</sub> at the high temperature in the reactions. Photoluminescence (PL) spectrum demonstrated that GaN nanobelts showed a broad strong emission peak at 2.65 eV in the blue range. In addition, GaN particles were synthesized by milling Ga<sub>2</sub>O<sub>3</sub> and Li<sub>3</sub>N at a molar ratio of 1:2 under ammonia atmosphere with the speed of 300rpm for 2 h [15]. However, this method to obtain GaN particles had a fatal drawback. There were many by-products such as Li<sub>2</sub>O, LiOHH<sub>2</sub>O, Li<sub>5</sub>GaO<sub>4</sub> and so on. The removal process was a time-consuming, complicated and expensive process.

GaN nanopowder with the particles size from 10 to 30 nm had been prepared by combustion method [16]. Firstly,  $Ga_2O_3$  and  $HNO_3$  were put into vessel to obtain the solution. The solution was dried by microwave reactor, which could stimulate and accelerate the conversion of  $Ga_2O_3$  into  $Ga(NO_3)_3$ . And then,  $Ga(NO_3)_3$  placed in an alumina crucible were calcinated at 600 °C for 6 h in the air to obtain  $Ga_2O_3$  again. Finally,  $Ga_2O_3$  powder was heated at 1050 °C under NH<sub>3</sub> atmosphere for 5 h to get high pure GaN with a wurtzite type structure. The optical properties of GaN nanopowder were related closely to the grain size of particles. The emission peak of GaN band gap disappeared as grain size was less than 10 nm. This was attributed to the surface-to-volume ratio.

Di Lello et al synthesized the GaN powder by two routes [17]. One is gas-solid reaction from  $Ga_2O_3/NH_3$  system, the other is from  $Ga_2O_3/3C/NH_3$  reaction system. The X-ray diffraction results demonstrated that both GaN and unreacted  $Ga_2O_3$  powder existed in  $Ga_2O_3/NH_3$  system. The high quality GaN powder can be obtained by optimizing the quality of carbon source, the  $Ga_2O_3/C$  ratio and reactions parameters using the  $Ga_2O_3/3C/NH_3$  reaction system.

Wang et al [18] reported that single-crystal GaN nanowires were fabricated on Si substrates through evaporating  $Ga_2O_3$  powder at 1100 °C in ammonia gas flow by chemical vapor deposition (CVD) method. Their experiments demonstrated that appropriate temperature, ammonia, NiCl<sub>2</sub> layer, and  $Ga_2O_3$  have a crucial influence on the growth process of GaN nanowires. Furthermore, they indicated that the liquid droplets exist at the tips of the nanowires, which demonstrated that the growth mechanism of GaN nanowires is VLS mechanism. There is a common way to obtain GaN powder using  $Ga_2O_3$  as raw materials. But it has many weaknesses such as lower purity, complex process. For example, the distribution of particle size of GaN nanopowder is uncontrollable and low purity by combustion method. The CVD method is a time consuming process.

# GaI<sub>3</sub> as Raw Materials

Spherical GaN nano particles with hexagonal structure were prepared from sodium azide using iodine as a heat sink and diluents [19]. X-ray photoelectron spectra (XPS) of the as-prepared GaN powder with an average size of 30 nm demonstrated that the surface element molar ration of Ga to N is 1:0.94. Photoluminescence (PL) spectrum at room temperature exhibited that GaN nanoparticles had one broad weak emission peak at 365 nm.

Xu and coworkers [20, 21] had completed many interesting researches about synthesizing single-crytalline GaN at low temperature using GaI<sub>3</sub> as a precursor. They synthesized 50 nm GaN powder with rocksalt structure by the reaction of GaI<sub>3</sub> and NaNH<sub>2</sub> at 210 °C under 3 MPa pressure, employing I<sub>2</sub> acted as the transporting agent. The entire process could be described by the following equation: (1)  $3NaNH_2 \rightarrow Na_3N + NH_3$ ; (2)  $GaI_3 + Na_3N \rightarrow GaN + 3NaI$ . The X-ray photoelectron spectra (XPS) analysis demonstrated that the average composition of Ga: N is 1.14: 1. Furthermore, they synthesized GaN microspindles using a solid state reaction of GaI<sub>3</sub>, NH<sub>4</sub>Cl and NaNH<sub>2</sub> at 500 °C for 6 h [20]. The GaN microspindles were composed of many single-crystalline platelets, which were observed by high-resolution transmission electron microscopy (HRTEM). The shape of GaN microspindles had significantly influenced on optical properties. These works suggested that it may be possible to synthesize high pure GaN nanopowder at low temperature. Compared with Ga and Ga<sub>2</sub>O<sub>3</sub>, GaI<sub>3</sub> is not extensively used in industry production as chemistry material. The method using GaI<sub>3</sub> as raw materials are some problem such as time consuming, low purity and toxic by-products.

# Other Ga Compounds as Raw Materials

Xie et al [22] firstly reported that the GaN nanoparticles were prepared by the thermal reaction of  $Li_3N$  and  $GaCl_3$ . The reaction was under the benzene solvent at 280 °C, and the yield of hexagonal GaN with particle size of 30 nm reached 80%. In addition, wurtzite GaN nanorods were synthesized by solid-state reaction through the reaction of NaNH<sub>2</sub> and GaOOH nanorods at 600 °C. This method was regards as an atom-economical and eco-friendly chemical synthetic route. The GaN nanorods with the length of 400-600 nm and the diameters 80-150 nm showed strong blue emission by photoluminescence tests [23]. However, GaCl<sub>3</sub> is hypertoxic and not suitable for industrial production.

# Conclusion

GaN is one of the most promising materials for application in optical and high powder electronic devices. GaN powders are synthesized by many methods such as dc arc plasma, milling, and combustion method and so on. However, there are still some drawbacks. Most methods are time consuming process, and not suitable for industrial production. Some preparation processes are complicated and miscellaneous. Due to the lack of a simple, efficient, and inexpensive synthesis approach, the industrial production of high purity GaN powders have been hampered in a certain extent. It is important to explore a simple process having the ability of producing GaN powders with high purity and efficient.

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# References

[1] H.Q. Wu, P. Konkapaka, Y. Makarov, M.G. Spencer, Bulk GaN growth by gallium vapor transport technique, Phys. Stat. Sol. (c) 2 (2005) 2032-2035.

[2] H.D. Xiao, H.L. Ma, C.S. Xue, J. Ma, F.J. Zong, X.J. Zhang, F. Ji, W.R. Hu, Synthesis and structural properties of GaN powders, Mater. Chem. Phys. 88 (2004) 180-184.

[3] T. Maruyama, H. Miyake. Gallium nitride thin films deposited by radio-frequency magnetron sputtering, J.Vacuum Sci. Technol. A 2006 (24) 1096-1099.

[4]Y.J. Ai, C.S. Xue, C.W. Sun, L.L.Sun, H.Z. Zhuang, F.X. Wang, H. Li, J.H. Chen, Synthesis of GaN nanowires through Ga<sub>2</sub>O<sub>3</sub> film' reaction with ammonia, Mater. Lett. 61 (2007) 2833-2836.

[5]S.Y. Zhang, H.Z. Zhuang, C.S. Xue, B.L. Li, D.X. Wang, J.B. Shen, Synthesis and optical properties of single-crystalline GaN nanorods, Vacuum, 82 (2008) 539-542.

[6] H.D. Li, H.B. Yang, S. Yu, G.T. Zou, Y.D. Li, S.Y. Liu, S.R. Yang, Synthesis of ultrafine gallium nitride powder by the direct current arc plasma method, Appl. Phys. Lett. 69 (1996) 1285-1287.

[7] H.D. Li, H.B. Yang, G.T. Zou, S. Yu, J.S. Lu, S.C. Qu, Y. Wu, Formation and photoluminescence spectrum of w-GaN powder, J. Cryst. Growth 171 (1997) 307-310.

[8] H.D. Li, S.L. Zhang, H.B. Yang, G.T. Zou, Y.Y. Yang, K.T. Yue, X.H. Wu, Y. Yan, Raman spectroscopy of nanocrystalline GaN synthesized by arc plasma, J. Appl. Phys. 91 (2002) 4562-4567.

[9] H.Q. Wu, J. Hunting, K. Uheda, L. Lepak, P. Konkapaka, F.J. DiSalvo, M.G. Spencer, Rapid synthesis of gallium nitride powder, J. Cryst. Growth 279 (2005) 303-310.

[10] X. Xiang, C.B. Cao, H.S. Zhu, Catalytic synthesis of single-crystalline gallium nitride nanobelts, Solid State Comm. 126 (2003) 315-318.

[11] Y.P. Xu, W.Y. Yang, D.F. Zhang, X.L. Chen, Dielectric properties of GaN nanoparticles, J. Mater. Sci. 36 (2001) 4401-4403.

[12] G. Kamler, J. Zachara, S. Podsiadlo, L. Adamowicz, W. Gebicki, Bulk GaN single-crystals growth, J. Cryst. Growth 212 (2000) 39-48.

[13] Y.A. Vodakov, E.N. Mokhov, A.D. Roenkov, M.E. Boiko, P.G. Baranov, High rate GaN epitaxial growth by sublimation sandwich method, J. Cryst. Growth 183 (1998) 10-14.

[14] M. Zhao, X.L. Chen, J.K. Jian, X.N. Zhang, H.Z. Zhao, Y.P. Xu, Growth and optical characterization of high-quality GaN nanobelts, J. Cryst. Growth 283 (2005) 418-424.

[15] J. Kano, E. Kobayashi, W. Tongamp, F. Saito, Preparation of GaN powder by mechanochemical reaction between  $Ga_2O_3$  and  $Li_3N$ , J. Alloy. Compd. 464 (2008) 337–339.

[16] R. Kudrawiec, M. Nyk, M. Syperek, A. Podhorodecki, J. Misiewicz, W. Strek, Photoluminescence from GaN nanopowder: The size effect associated with the surface-to-volume ratio, Appl. Phys. Lett. 88 (2006) 181916.

[17] B.C. Di Lello, F.J. Moura, I.G. Solorzano, Synthesis and characterization of GaN using gas-solid reactions, Mater. Sci. Eng. B93 (2002) 219-223.

[18] Y. Wang, C.S. Xue, H.Z. Zhuang, Z.P. Wang, D.D. Zhang, Y.L. Huang, W.J. Liu, Synthesis and characterization of GaN nanowires, Appl. Surf. Sci. 255 (2009) 7719-7722.

[19] J. Q. Hu, B. Deng, W.X. Zhang, K.B. Tang, Y.T. Qian, Gallium nitride synthesis from sodium azide using iodine as a heat sink and diluents, Chem. Phys. Lett. 351 (2002) 229-234.

[20] F. Xu, Y. Xie, X. Zhang, S.Y. Zhang, L. Shi, A benzene-thermal metathesis route to pure metastable rocksalt GaN, New J. Chem. 27 (2003) 565 - 567.

[21] F. Xu, Y. Xie, X. Zhang, S.Y. Zhang, X.M. Liu, W. Xi, X.B. Tian, Single-crystalline gallium nitride microspindles: synthesis, characterization, and thermal stability, Adv. Funct. Mater. 14 (2004) 464-470.

[22] Y. Xie, Y.T. Qian, W.Z. Wang, S.Y. Zhang, Y.H. Zhang, A Benzene-Thermal Synthetic Route to Nanocrystalline GaN, Science, 272 (1996) 1926-1927.

[23] K.Y. Bao, L. Shi, X.D. Liu, C.Z. Chen, W.T. Mao, L.L. Zhu, J. Cao, Synthesis of GaN Nanorods by a Solid-State Reaction. J. Nanomater. 2010.