The Preparation Methods of Gallium Nitride Powder

Wen-Zhi YANG¹, a, *, Wei HUANG¹, 2, b, Ya-Feng LI³, c, Wei-Ming HUANG¹, d, Fu-Jun SHANG¹, e, Zi-Ming CHEN¹, f

¹Ningbo Branch of China Academy of Ordnance Science, Ningbo, 315103, China
²College of Mechanical Engineering and Mechanics, Ningbo University, Ningbo, 315103, China
³Zhejiang Business Technology Institute, Ningbo, 315103, China
a email: yangwenzhith@163.com, b email: hw315@126.com, c email: lyf1128@126.com,
d email: diinm11@163.com, e email: sfjnb@126.com, f email: czmwm@163.com
*Corresponding author

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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 power 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, Ga₂O₃, Ga₃, 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 NH₃/N₂ 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 NH₃ and N₂ 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 NH₃ (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 μm, 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 NH₄I (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, NH₄I was replaced by NH₄Cl (99.9% purity), and the molar ration of Ga to NH₄Cl 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. NH₃ 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 1.5x1x0.1 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 1mm/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.

**Ga₂O₃ as Raw Materials**

Using Ga₂O₃ 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 LaAlO₃ substrate by milling Ga₂O₃ under NH₃ 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) \( \text{Ga}_2\text{O}_3(s) + 2\text{H}_2(g) \rightarrow \text{Ga}_2\text{O}(s) + 2\text{H}_2\text{O}(g) \); (2) \( \text{Ga}_2\text{O}(g) + 2\text{NH}_3(g) \rightarrow 2\text{GaN}(s) + \text{H}_2\text{O}(g) + 2\text{H}_2(g) \). H₂ is generated from NH₃ 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 Ga₂O₃ and Li₃N 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 Li₂O, LiOH, H₂O, Li₅GaO₄ 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, Ga₂O₃ and HNO₃ were put into vessel to obtain the solution. The solution was dried by microwave reactor, which could stimulate and accelerate the conversion of Ga₂O₃ into Ga(NO₃)₃. And then, Ga(NO₃)₃ placed in an alumina crucible were calcinated at 600 °C for 6 h in the air to obtain Ga₂O₃. Finally, Ga₂O₃ powder was heated at 1050 °C under NH₃ 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 Ga₂O₃/NH₃ system, the other is from Ga₂O₃/3C/NH₃ reaction system. The X-ray diffraction results demonstrated that both GaN and unreacted Ga₂O₃ powder existed in Ga₂O₃/NH₃ system. The high quality GaN powder can be obtained by optimizing the quality of carbon source, the Ga₂O₃/C ratio and reactions parameters using the Ga₂O₃/3C/NH₃ reaction system.

Wang et al [18] reported that single-crystal GaN nanowires were fabricated on Si substrates through evaporating Ga₂O₃ powder at 1100 °C in ammonia gas flow by chemical vapor deposition (CVD) method. Their experiments demonstrated that appropriate temperature, ammonia, NiCl₂ layer, and Ga₂O₃ 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 Ga₂O₃ 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.

**GaI₃ 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 GaI₃ as a precursor. They synthesized 50 nm GaN powder with rocksalt structure by the reaction of GaI₃ and NaNH₂ at 210 °C under 3 MPa pressure, employing I₂ acted as the transporting agent. The entire process could be described by the following equation: (1) 3NaNH₂ → Na₃N + NH₃; (2) GaI₃ + Na₃N → 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 GaI₃, NH₄Cl and NaNH₂ at 500 °C for 6 h [20]. The GaN microspindles were composed of many single-crytalline 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 Ga₂O₃, GaI₃ is not extensively used in industry production as chemistry material. The method using GaI₃ 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 Li₃N and GaCl₃. 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 NaNH₂ 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, GaCl₃ 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


