

Preparation and Performance of Gallium Nitride Powders with Preferred Orientation

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Abstract. The paper prepared the III-V semiconductor, hexagonal wurtzite Gallium nitride powders by calcining a gallium oxide in flowing ammonia above 900 °C (1173K). Because of the solid-state reaction process that the gallium oxide transformed to GaN through solid-state gallium oxynitrides (GaO_xN_y) as inter-mediate, the Gallium nitride powders which are agglomerates of tens nanometers flake crystallites retain the rod shape and grain size of raw gallium oxide and have slight (002) plane preferred orientation. The near-edge emission of Gallium nitride at 346 nm has a blue shift of 187 meV attributed to a decrease in disorder of the material that is decided by the (002) plane preferred orientation. The preferred orientation and a blue shift have some kind of reference significance to single crystal growth.

1 Introduction

As a representative of the third generation of semiconductor, Gallium nitride (GaN) has a wide direct gap of 3.39 eV at room temperature, high luminescent efficiency and low temperature-quenching effect, promising application prospects in blue and UV lighting, Ultraviolet Detecting and other areas. Sapphire, Silicon chip and SiC are all the widely used substrates for the thin-film growth of GaN. However, there exists severe mismatch both in lattice parameters and thermal expansion coefficients between GaN and the substrates, which introduce stresses in the first few layers of the grown GaN. Therefore the development of high-purity GaN crystalline for homoepitaxy by wafers is a trend in the future.

The most popular methods to grow single-crystal bulk GaN demand high purity and single phase GaN powder as precursor source, thus one of current significance research topic is the synthesis GaN powder directly. In this research, we took an easy method to synthesize GaN powders, which is based on the reduction reaction of gallium oxides (Ga₂O₃) in ammonia gas.

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2 Experiments

The starting materials include β -Ga₂O₃ (99.999%) and liquid ammonia (NH₃, 99.999%). 0.25 g Ga₂O₃ powders were placed in a quartz tube which was fixed in a furnace. After the air in the tube was expelled by argon (Ar, 99.999%) gas flow for 5 minutes, the furnace was heated to 600 °C at the rate of 10 °C /min with an Ar flow. Then the flow was changed into NH₃ mixing in Ar (NH₃/Ar, NH₃:Ar =1:2) and the temperature was increased continuously with a rate of 5 °C/min (K/min) until it reached the reaction temperatures of 850 °C (1123 K), 875 °C (1148 K), 900 °C (1173 K) and 925 °C, (1198 K) respectively. The reaction time under high-temperature condition was 30 minutes. In the cooling process, the NH₃/Ar flow were kept until the temperature reached 600 °C (873 K) and then it was switched to a pure Ar flow.

The as-synthesized GaN samples were characterized by powder X-ray diffraction (XRD) using a Bruker D8 Advanced X-ray diffract-meter with Cu K α radiation operating at 60 kV and 80 mA. The morphologies of the powders were investigated by JSM-6490LV scanning electron microscope (SEM). The high-resolution transmission electron microscope (HRTEM) lattice images and the corresponding selected-area electron diffraction (SAED) of an individual grain were from JEM-2100 (UHR) HRTEM. The luminous property of GaN was performed by a Horiba FL3 photoluminescence (PL) spectroscopy.

3 Results and discussion

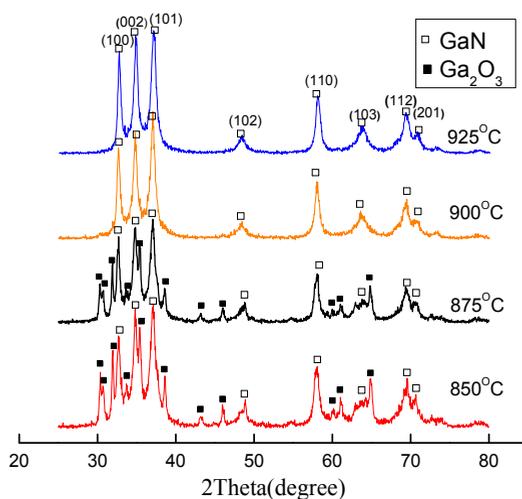


Fig. 1. X-ray diffraction patterns of GaN powders synthesized at different temperatures.

3.1 Structure

Fig. 1 shows the XRD patterns of GaN powder obtained at different temperatures. The XRD patterns show that the samples synthesized at 850 °C and 875 °C are mixtures of hexagonal wurtzite GaN and monoclinic β -Ga₂O₃ (PDF card no. 43-1012 with lattice constants of $a = 1.223$ nm, $b = 0.304$ nm, $c = 0.58$ nm and angles of 90, 103.7, 90 degrees respectively). However, the GaN powders obtained at 900 °C and 925 °C have the typical wurtzite structure. According to PDF card no. 65-3410, the main peaks of the wurtzite structured GaN are indexed to refined lattice constants of $a = 0.3173$ nm and $c = 0.5158$ nm.

Even though no other diffraction peak were observed, it was possible that oxygen element existed in GaN samples grown at 900 degree and above because the starting materials were oxides. At the same time, an uncommon phenomenon is seen in the XRD patterns that the diffraction from (002) plans is extra strong compared with the other peaks. This result indicates that the present samples exist preferred (002) crystal plane orientation, like in the thin films [1].

After removing background of curves and fitting peaks processes, the average size of the sub-grains is rough calculated by the full width at half maximum using the Scherrer formula ($t = \lambda/B\cos\theta$), as shown in Table 1; the number in parenthesis is error range. The sizes of GaN crystallite only from GaN diffraction peaks increase with synthesize temperature. The average sizes of powders obtained at 850 °C and 875 °C from the whole spectra are very large because the two samples are mixtures of GaN and large size Ga₂O₃ particles.

Table 1. The crystallite size of samples obtained at different temperatures

Nitride temperature [degree]	850	875	900	925
Average size of powder samples [nm]	310(12)	275(21)	118(2)	126(2)
Average size of GaN crystallite [nm]	69(4)	118(3)	118(2)	126(2)

3.2 Morphology

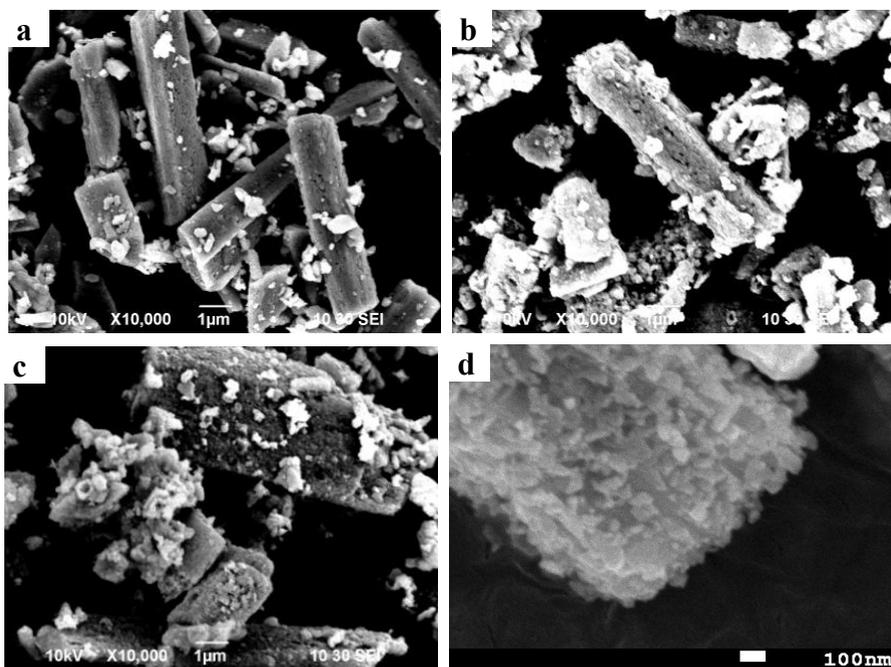


Fig. 2. SEM pictures of Ga₂O₃ (a), GaN samples annealed at 900 °C (b and d), at 875 °C (c).

SEM images of raw material Ga₂O₃ and GaN powders obtained at 900 °C and 875 °C are shown in Fig.2 (a), (b) and (c), respectively. The magnification times are all 10,000. The distribution of the powder size is wide spread from tens of nanometers to several

micrometers. GaN samples grown at 900 °C and 875 °C were of rod morphology with a small quantity of GaN nanograins enclosed on its surface. The micrometer rod is consisting of particles about 100 nanometer, as show in Fig.3 (d) GaN at 900 °C details image. The estimated average size is in a good agreement with calculated numbers of XRD. By the comparison of Ga₂O₃ and GaN, we see that both of the shape and size of GaN powders are similar to those of raw material of Ga₂O₃. From this result it can be proved that the GaN powders retain the rod shape and grain size of Ga₂O₃. Thus, a conclusion of the conversion of gallium oxide to GaN don't go through the gaseous species of Ga₂O but solid-state gallium oxynitrides (GaO_xN_y) as inter-mediate is obtained [2].

TEM image, HRTEM image and selected area electron diffraction (SAED) pattern (inset) of the GaN powders at 925 °C are shown in Fig. 3(a) and (b). TEM image shows the presence of irregular agglomerates of tens nanometers of tabular GaN crystallites, being consistent with the calculated results of table 1. The d-spacing between the two adjacent lattice fringes is 0.2586 nm from (002) plane. The calibrated SAED pattern was depicted in the Fig. 2(c). Comparing to those of standard GaN powders and their d-spacing, all the diffraction rings could be attributed to hexagonal wurtzite GaN. The discontinuous diffraction rings demonstrate that the samples exists preferred orientation; this result keeps in line with our XRD measurement.

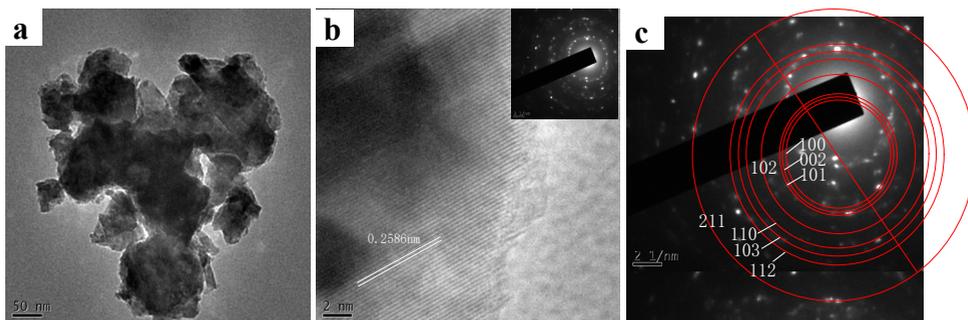


Fig. 3. TEM image (a), HRTEM image (b) and SAED pattern (c) of GaN at 925 °C.

Basing on anionic coordination polyhedron growth units theory model [3], the strong polarity faces grow faster and appear in smaller areas, whereas the weak polarity faces grow slower and appear in large areas [4]. In hexagonal wurtzite GaN, the tetrahedron [Ga-N₄]⁸⁻ growing from GaO₄ tetrahedral is considered as the basic unit. Because the vertexes of [Ga-N₄]⁸⁻ appear on the (110) faces, the (110) faces show higher surface energy and stronger polarity. On the contrary, the planes of [Ga-N₄]⁸⁻ are parallel to (002) faces, so the (002) faces of GaN particles have low surface energy and weak polarity. Therefore (002) faces appear in large areas in the GaN particles growing process. As mentioned earlier, gallium oxide transforms to GaN via gallium oxynitrides (GaO_xN_y) as inter-mediate. As the nitridation proceeds, the oxygen content in the intermediates gradually decreases, leading to complete conversion to GaN and this conversion completed from outside to inside of the rod gradually. The before-mentioned factors result in that there are some GaN plates which are corresponding to the (002) plane attaching on the rod surface. Therefore, the GaN materials obtained have slight (002) plane preferred orientation.

3.3 Luminescence

The luminescent properties of the GaN powders synthesized at 925 °C, 900 °C and 875 °C were examined by photoluminescence (PL) spectroscopy at room temperature, and the PL spectra are shown in Fig. 4a. The exciting source is 294 nm UV.

The dominant emission of the obtained GaN powders is a broad emission from 320 nm to 400 nm centered near 360nm. This broad UV emission band of the GaN powders sample synthesized at 925 °C is fitted with four Gaussians and the peaks are located at 346 nm (3.584 eV), 364 nm (3.407 eV), 365 nm (3.397 eV) and 398 nm (3.116 eV), as shown in the Fig. 4b. The raw data (red hollow square symbols), separated peaks (blue solid line) and the fitted curve (black dotted line) are all provided. The curve fitting result of the GaN powders sample synthesized at 900 °C is similar to that of the GaN powders sample synthesized at 925 °C within the margin of error, and the graph isn't given there.

The emission peak at 346 nm is considered belongs to a blue shift of the near band edge emission at 365 nm (3.39 eV) of the bulk GaN. The blue shift of 19 nm (187 meV) is attributed to a decrease on disorder of the material that is decided by the (002) plane preferred orientation. Considering the separation of the peaks is 174 meV and 10 meV, the 364 nm and 365 nm peaks are possible the electron transition radiation between the shallow donor levels and the valence band [5]. The donor is believed to be a residual oxygen impurity from raw material [5]. The broad violet band centered at 398 nm is relating to defect levels. The well-known yellow band emissions from Carbon impurity deep acceptor defect energy are not observed.

However, the curve of the GaN powders sample synthesized at 875 °C was fitted only with two Gaussians and the peaks were located at 360 nm (3.444 eV), 445 nm (2.787 eV), as shown in the Fig. 4c. The recombination radiation between the shallow donor levels and the valence band will have a red shift and broaden because of the high oxygen content of sample at 875 °C and below [6], then merge with the peak relating to defect levels.

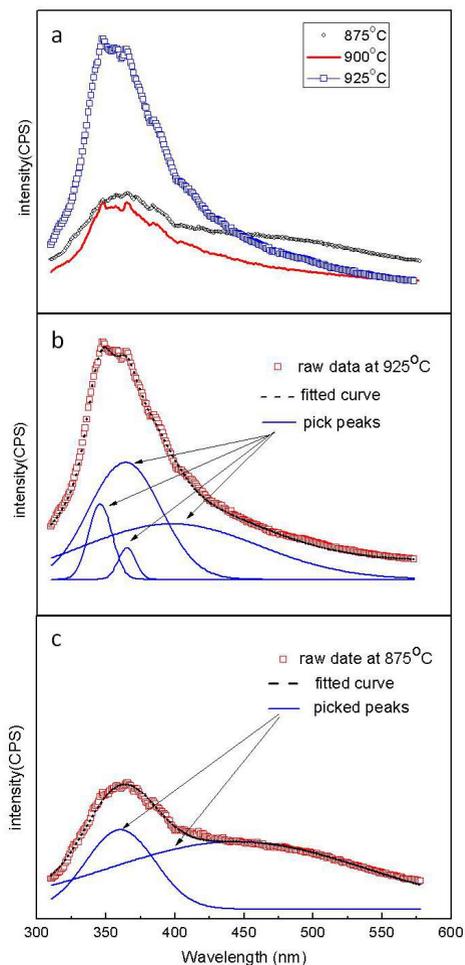


Fig. 4. Room-temperature PL spectra (a) of the powders at 925°C (blue square symbols line), 900°C (red solid line), and 875 °C (black circle symbols), fitted curve graphs of the powders at 925 °C (b), and

4 Conclusions

In summary, GaN powders with hexagonal wurtzite structure are synthesized using a simple and economical method that gallium oxide is nitrided under flow of ammonia at quartz tube furnace. From the XRD and TEM result the present GaN powders have clear

preferred orientation of $\langle 002 \rangle$. The similar shape and size of Ga_2O_3 and GaN provide explanation to the growth mechanism of the GaN, i.e. the conversion of gallium oxide to GaN don't go through the gaseous species of Ga_2O but solid-state gallium oxynitrides (GaO_xN_y) as intermediates, and that is the very reason of preferred orientation. The PL spectra show that the near band edge emission of the present GaN is 346 nm (3.584 eV) at room temperature, which exhibits an obvious blue shift of 19 nm (187 meV) because of a decrease in disorder of the material that is decided by the (002) plane preferred orientation. It accounts for the GaN powder with preferred orientation prepared in this method can be used as UV luminescence material.

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References

1. C. B. Han, C. He, X. J. Li, *Adv. Mater.*, **23** 4811-4814 (2011)
2. W. J. Jung, *Mater. Lett.*, **60** 2954-2957 (2006)
3. W. Z. Zhong, H. S. Luo, S. K. Hua, G. S. Xu, *J. Synth. Cryst.*, **33(4)** 475-478 (2004)
4. Z. Y. Zhao, X. G. Li, S. R. Wang, Y. Xiao, *J. Synth. Cryst.*, **43(7)** 1611-1619 (2014)
5. R. Garcia., G. A. Hirata, A. C. Thomas, F. A. Ponce, *Opt. Mater.*, **29** 19-23 (2006)
6. H. S. Guder, B Abay ., H. Efeoglu, Y. K. Yogurtcu, *Bulg. J. Phys.*, **27(2)** 72-75 (2000)