Effect of high temperature annealing on strain and band gap of GaN nanoparticles*

Xiao Hong-Di(肖洪地)[a)†], Mao Hong-Zhi(毛宏志)[b)],
Lin Zhao-Jun(林兆军)[a)], and Ma Hong-Lei(马洪磊)[a)]

[a)] *School of Physics, Shandong University, Jinan* 250100, *China*
[b)] *School of Chemistry and Chemical Engineering, Shandong University, Jinan* 250100, *China*

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Black-coloured GaN nanoparticles with an average grain size of 50 nm have been obtained by annealing GaN nanoparticles under flowing nitrogen at 1200 °C for 30 min. XRD measurement result indicates an increase in the lattice parameter of the GaN nanoparticles annealed at 1200 °C, and HRTEM image shows that the increase cannot be ascribed to other ions in the interstitial positions. If the as-synthesised GaN nanoparticles at 950 °C are regarded as standard, the thermal expansion changes nonlinearly with temperature and is anisotropic; the expansion below 1000 °C is smaller than that above 1000 °C. This study provides an experimental demonstration for selecting the proper annealing temperature of GaN. In addition, a large blueshift in optical bandgap of the annealed GaN nanoparticles at 1200 °C is observed, which can be ascribed to the dominant transitions from the C(Γ_7) with the peak energy at 3.532 eV.

Keywords: GaN nanoparticles, thermal expansion, strain, blue shift, bandgap

PACC: 6170A, 7280E, 7855E, 6220F

1. Introduction

The family of group III nitrides has made the dream of realising high-efficiency blue/violet light emitting diodes (LEDs) and laser diodes (LDs). GaN and its related alloys have been used in a variety of light-emitting devices and electronic devices. Although heteroepitaxially grown devices have been commercialized, more technological innovations, such as ultraviolet (UV) light irradiation method,[1] hydrogenation method during growth,[2] laser annealing method,[3] isoelectronic in-doping method,[4] high-temperature rapid thermal annealing method,[5] etc., are needed to realize highly efficient, highly reliable, and low-cost devices. In general, the methods cited above can lead to some slight improvement in the GaN crystal quality.

The thermal annealing method among them has proved to be one of the simplest and most effective methods to improve the crystalline quality of GaN.[6−8] The studies in Refs. [6]–[8] revealed that thermal annealing below 900 °C hardly affected the crystalline quality of GaN, and that annealing at temperatures between 900 °C and 1100 °C resulted in the degradation of the crystalline quality of GaN. With increasing annealing temperature, there are some changes in the lattice stress and optical band gap of GaN,[9,10] which is very important for a better understanding of material properties and improving of nitride-based devices. For the lattice stress and optical band gap, however, more studies were focused on heteroepitaxial GaN layers,[9,11] and ion-implanted GaN.[12−14] In addition, the annealing above 1100 °C causes the decomposition of GaN,[7,15] so there are a few studies devoted to the investigation of annealing effect on the properties of GaN nanoparticles above 1100 °C, especially, on the deformation of GaN crystal lattice.

In the present work, we investigate the effects of high-annealing temperature on strain, thermal expansion, and band gap of GaN nanoparticles. The structural and optical properties of the GaN nanoparticles are subsequently investigated by x-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and low-temperature photoluminescence (PL).

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†Corresponding author. E-mail: hdxiao@sdu.edu.cn
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2. Experimental details

GaN nanoparticles prepared by ammonolysis of GaOOH powders at 950 °C were used as the stuff material.[16] The GaN-containing quartz boat was loaded into the centre of a horizontal quartz tube placed in a conventional tube furnace.[17,18] The GaN nanopowders were first annealed under flowing nitrogen with 300 ml·min^{-1} at 1200 °C for 30 min, and then the samples were cooled down to room temperature under flowing nitrogen. Lastly, black-coloured products were taken out for characterization.

The GaN powders and black-coloured products were characterized by D8 Advance x-ray diffraction with a Cu Kα radiation ($\lambda = 1.54178$ Å, 1 Å=0.1 nm). Angle accuracy of XRD is less than or equal to ±0.0001. HRTEM (JEM-2100, 200 kV) was applied to examine the structure and morphology. Energy dispersive x-ray fluorescence (EDX) attached to the JEM-2100 was used to analyse the amounts of constituent elements. Photoluminescence properties of the annealed GaN nanoparticles at 1200 °C were investigated with 325-nm line of He–Cd laser as an excitation source at 10 K.

3. Results and discussion

Figure 1(a) and 1(b) show the XRD patterns of the as-synthesized and annealed GaN nanoparticles at 1200 °C, respectively. The patterns display diffraction lines that could be ascribed to the formation of hexagonal GaN with a wurtzite type structure (JCPDS card no. 2-1078). In our experiment, the annealed GaN nanoparticles at 1200 °C are black-coloured instead of khaki-coloured, because the GaN surface decomposes to liquid metallic Ga and N_2 above 1100 °C.[7,15] Namely, the GaN surface is terminated by an equilibrium Ga adlayer that is stable.[19,20] For clarity, in the inset in Fig. 1, a comparison of the (110) peak in the diffractograms of the as-synthesized and annealed samples is shown on a magnified scale.

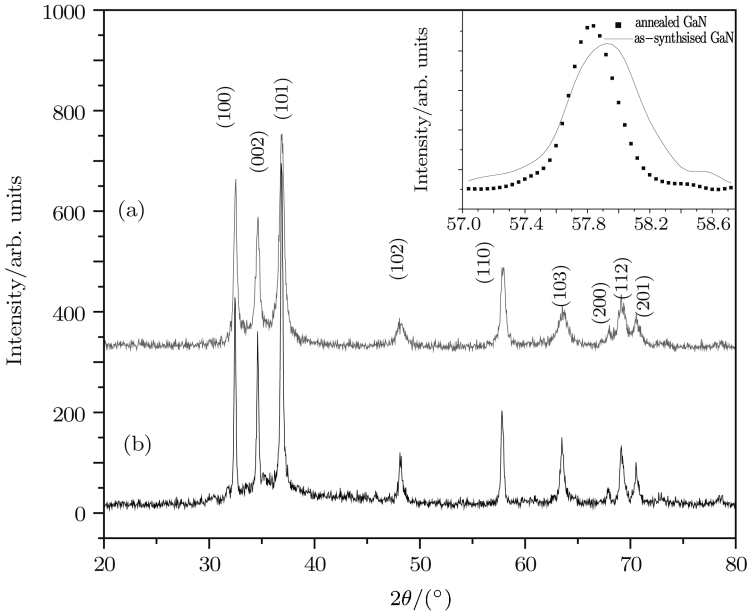


Fig. 1. The XRD patterns obtained from the as-synthesized (a) and annealed GaN nanoparticles (b) at 1200 °C. The inset shows the direct comparison of the (110) diffraction peak.

The peaks of the annealed GaN nanoparticles shift to the smaller angle side, indicating an increase in the lattice parameters $a = 0.3192 \pm 0.0001$ nm and $c = 0.5191 \pm 0.0001$ nm obtained from the weighted nonlinear least-squares fit of $1/(d_{hkl})^2$ to the following equation:

$$\left(\frac{1}{d_{hkl}}\right)^2 = \frac{4}{3}\left(\frac{h^2 + k^2 + hk}{a^2}\right) + \frac{l^2}{c^2},$$

where d_{hkl} is the lattice plane spacing of a hexagonal crystal. To clarify the strain relaxation in the annealed GaN crystal, the biaxial strain ($\varepsilon_{xx} = \varepsilon_{yy} \neq \varepsilon_{zz}$) along the a and c axes is estimated by $\varepsilon_{xx} = (a - a_0)/a_0$ and $\varepsilon_{zz} = (c - c_0)/c_0$ where a_0 and c_0 are, respectively, the lattice constants in the unstrained crystal and taken to be $a_0 = 0.3186$ nm and $c_0 = 0.5178$ nm from the literature (JCPDS card no. 2-1078). According to the strain formula, ε_{xx} and ε_{zz} are equal to 0.19% and 2.51%, respectively, indicating that the thermal expansion of the annealed GaN nanocrystal at 1200 °C is anisotropic. The corresponding increase in the unit-cell volume is 0.48%.

Figure 2(a) shows a typical TEM image of the annealed GaN nanoparticles and corresponding selected area electron diffraction (SAED) pattern. The single-crystal GaN nanoparticles with an average size of about 50 nm can be identified from the SAED pattern shown in the inset in Fig. 2(a), which can be indexed to the reflection of hexagonal wurtzite GaN single crystal. In order to further explain the thermal expansion of GaN nanocrystal, a high-resolution of microscopic (HRTEM) image of a typical nanoparticle is shown in Fig. 2(b). The wavelength of the modulation in the HRTEM image is about 0.265 nm. Due to the increase in crystal lattice of the annealed GaN nanoparticles at 1200 °C, the wavelength corresponds to the interplanar distances of (002) lattice plane. Due to the interplanar distances of (002) lattice plane of a standard GaN powders being 0.259 nm from the literature (JCPDS card no. 2-1078), the strain along the [002] direction is equal to 2.41% which is in agreement with the c axial strain. The crystal lattice shown in Fig. 2(b) is very perfect, however, the molecular ratio of Ga/N of the nanopaticle calculated from the EDX data (data not shown) is about 1:0.945 instead of 1:1. It indicates that a large number of N vacancies exist in the GaN crystal lattice. Obviously, the expansion of GaN crystal lattice does not ascribed to N vacancies and other ions which are not observed in the interstitial position.

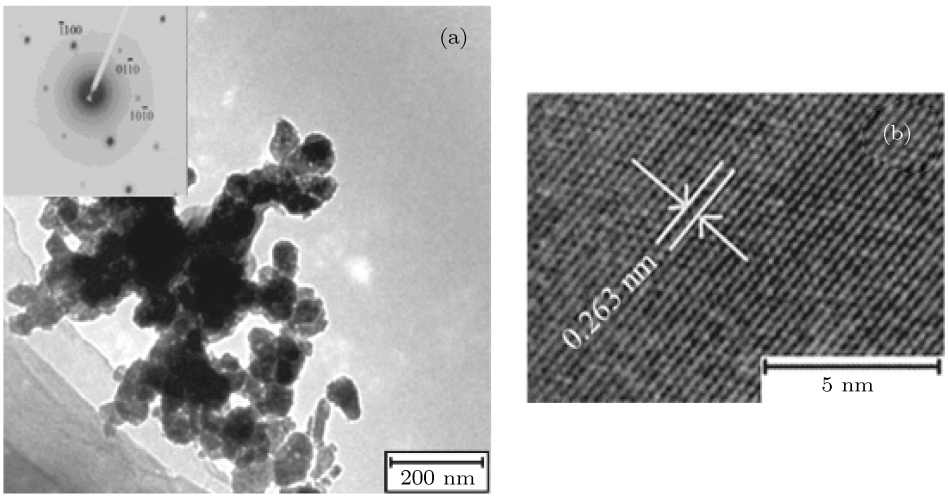


Fig. 2. (a) A TEM image of the annealed GaN nanoparticles at 1200 °C. The inset is the corresponding SAED pattern of the nanoparticle. (b) The HRTEM image of a selected GaN nanoparticle.

In order to study the temperature dependence of the deformation of GaN crystal lattice, figures 3(a)–3(d) show the temperature dependence of the interplanar distances of (100), (002), (101), and (110) lattice planes, respectively. If the as-synthesized GaN nanopowders at 950 °C are regarded as standard, the interplanar distances of all lattice planes of the as-synthesized GaN nanparticles are smaller than those of the annealed GaN nanoparticles (XRD data not shown). As shown in Fig. 3, it should be noted that in every growth direction, the increasing rate of interplanar distance is slow at lower annealing temperatures, indicating that the thermal expansion changes nonlinearly with temperature. The expansion along the [101] direction is larger than that along others, which indicates that GaN crystals are anisotropic. In general, the thermal expansion of a crystal reflects the anharmonicity of the crystal lattice, and the anisotropy of the anharmonicity is related to the distortion of the tetrahedral bonding.[21] Thus, the anisotropic thermal expansion of the GaN crystals is associated with the anisotropies of both elasticity and anharmonicity.

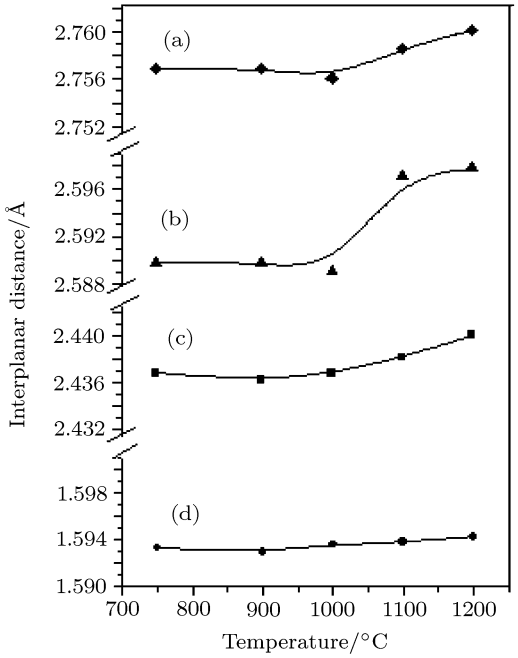


Fig. 3. Temperature dependence of the different interplanar distances of (a) (100), (b) (002), (c) (101), and (d) (110).

Figure 4(a) shows the PL spectrum taken at 10 K of the GaN nanopowders annealed at 1200 °C. From Fig. 4(a), a PL peak at around 3.52 eV is observed. By means of the Varshni formula,[22] the energy of the band-edge emissions for bulk GaN materials at 10 K has been determined to be 3.489 eV. Comparing the annealed GaN with bulk GaN, the PL peak at 3.52 eV is evidently blueshifted. Due to the size of annealed GaN nanoparticles over 11 nm (Bohr exciton radius of GaN), the PL peak at 3.52 eV could not be explained by the quantum confinement effect.

In order to explain the above phenomenon, a schematic diagram of crystal field splitting is shown in Fig. 4(b). The degeneracy of the valence band is lifted due to crystal field and spin–orbit coupling. The valence band splits into three bands designated as A, B, and C bands. The symmetry of the A band is Γ_9 and that of the B and C bands is Γ_7.[23,24] Gaussian fitting analysis on the PL spectrum of the GaN nanoparticles annealed at 1200 °C exhibits three emission bands located at 3.436, 3.465, and 3.532 eV, which correspond to A(Γ_9), B(Γ_7), and C(Γ_7) levels, respectively. Compared with the calculated values of the band energy,[25] these values exist an obvious red-shift. This is because the distance between the conduction band and these bands decreases under tension. Still, a distinct blueshift of the PL peak could be ascribed to the dominant transitions from the C(Γ_7) with the peak energy at 3.532 eV as shown in Fig. 4(a).

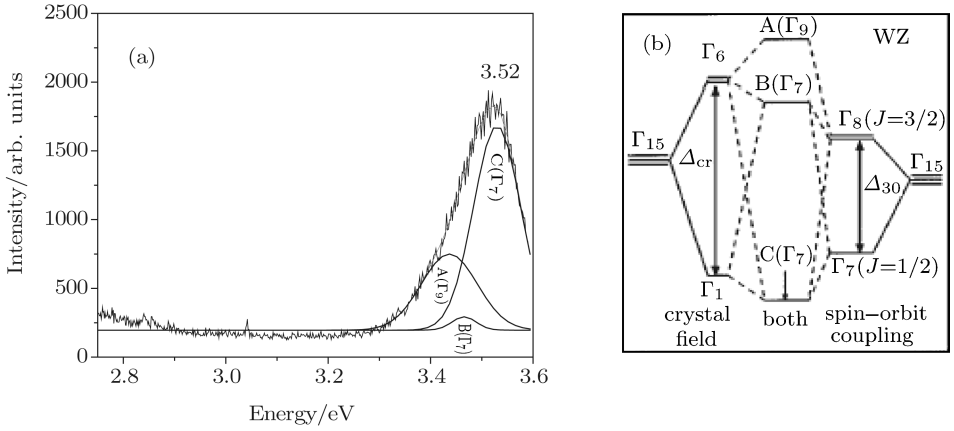


Fig. 4. (a) Low-temperature PL spectra at 10 K obtained from the annealed GaN nanoparticles. (b) Effect of crystal field splitting and spin–orbit coupling on the valence band (near the Γ point) of wurtzite GaN.[23,24]

4. Conclusions

Black-coloured nanopowders synthesized by using thermal annealing of GaN nanoparticles at 1200 °C under flowing nitrogen were identified to be hexagonal wurtzite GaN nanoparticles by x-ray diffraction and TEM image. We found that the thermal expansion generally increases with increasing temperature. If the GaN nanoparticles synthesized at 950 °C regarded as a standard, the expansion below 1000 °C is smaller than that above 1000 °C. In PL spectrum, an obvious blue-shift could be ascribed to the dominant transitions from the C(Γ_7), instead of quantum confinement effect.

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