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Research Article

Synthesis of GaN Nanorods by a Solid-State Reaction

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An atom-economical and eco-friendly chemical synthetic route was developed to synthesize wurtzite GaN nanorods by the reaction of $NaNH_2$ and the as-synthesized orthorhombic GaOOH nanorods in a stainless steel autoclave at 600°C. The lengths of the GaN nanorods are in the range of 400–600 nm and the diameters are about 80–150 nm. The process of orthorhombic GaOOH nanorods transformation into wurtzite GaN nanorods was investigated by powder X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM), indicating that the GaN product retained essentially the same basic topological morphology in contrast to that of the GaOOH precursor. It was found that rhombohedral Ga_2O_3 was the intermediate between the starting orthorhombic GaOOH precursor and the final wurtzite GaN product. The photoluminescence measurements reveal that the as-prepared wurtzite GaN nanorods showed strong blue emission.

1. Introduction

GaN, an important III–V semiconductor with a direct band gap of 3.39 eV at room temperature, has a wide use in optical devices operating at blue and ultraviolet wavelengths and in high-temperature electronic devices [1]. The recent development of commercial blue-light emitters based on GaN has propelled these materials into the mainstream of interest. Up to now, many structures of GaN such as nanowires [2–6], nanorods [7–11], nanobelts [12], and tubes [13–17] have been successfully synthesized. Many reports showed that these one-dimensional (1D) structures of GaN have been grown by many methods, such as chemical vapor deposition [18], metal-organic chemical vapor deposition [19], molecular beam epitaxy [20], halide vapor-phase epitaxy [21], arc discharge [22], magnetron sputtering [23], chemical thermal-evaporation process [24], etching [25], and ammonolysis [26–29]. For example, GaN nanowires were fabricated on Si substrates coated with $NiCl_2$ thin films using chemical vapor deposition method by evaporating Ga_2O_3 powder at 1100°C in ammonia gas flow [30]. Wurtzite GaN nanowires were synthesized via sublimation sandwich method using Ga and NH_3 as starting reagents [31]. However, among most of these methods, an atmosphere of superfluous NH_3 is obligatory, which caused air pollution and waste.

In this paper, we reported an economical and eco-friendly chemical synthetic method for synthesis wurtzite GaN nanorods. In detail, the preparation of wurtzite GaN nanorods involved two steps: first, hydrothermal synthesis of orthorhombic GaOOH nanorods at 180°C for 12 hours, and second, preparation of GaN nanorods using $NaNH_2$ and the as-prepared orthorhombic GaOOH nanorods as reactants in a stainless steel autoclave at 600°C for 5 hours.

2. Experimental Section

2.1. Synthesis of GaOOH Nanorods. In a typical synthesis, under continually stirring, 0.88 g of $GaCl_3$ (5 mmol) was dissolved into a mixture of 40 mL of deionized water. After 5 minutes, 5 mL of sodium hypochlorite solution was introduced to the above solution. Then the solution was transferred to a 50 mL Teflon-lined autoclave. The autoclave was sealed, maintained at 180°C for 12 hours, and then allowed to cool to room temperature naturally. The product

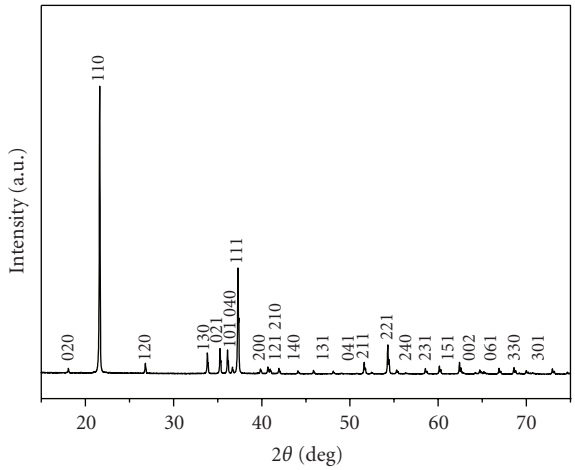

Figure 1: XRD pattern of the as-prepared GaOOH product.

was retrieved by filtration, washed several times with distilled water, and absolute ethanol, and dried under vacuum at 60°C for 6 hours.

2.2. Preparation of GaN Nanorods. 1.03 g (10 mmol) of the as-prepared GaOOH nanorods and 0.63 g (16 mmol) of $NaNH_2$ were mixed and then put into a stainless steel autoclave. The autoclave was maintained at 600°C for 5 hours and then cooled to room temperature naturally. A yellow powder was retrieved by centrifugation, washed several times with dilute hydrochloric acid, distilled water and absolute alcohol, and finally dried in a vacuum oven at 60°C for 6 hours.

2.3. Characterization. Powder X-ray diffraction (XRD) measurements were carried out with a Philips X'Pert diffractmeter (Cu Kα λ = 1.541874 Å; Nickel filter; 40 kV, 40 mA). Field emission scanning electron microscope (FESEM) images were taken on a JEOL JSM-6300F SEM. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images, and selected area electron diffraction (SAED) patterns were performed on JEOL JEM-2010 microscope operating at 200 kV. The Raman spectrum was obtained on the JY LABRAM-HR laser micro-Raman spectrometer with 514.5 nm emission lines. Photoluminescence (PL) measurements were carried out on a Perkin-Elmer LS-55 luminescence spectrometer using a pulsed Xe lamp.

3. Results and Discussion

3.1. Characterization of GaOOH Nanorods. Figure 1 shows the X-ray diffraction (XRD) pattern of the GaOOH nanorods. It can be observed that orthorhombic phase of GaOOH formed in our synthesis. All the reflection peaks can be indexed as orthorhombic phase of GaOOH (JCPDS PDF No. 26-0674, a = 4.5 Å, b = 9.75 Å, c = 2.97 Å). No peaks of impurities were detected.

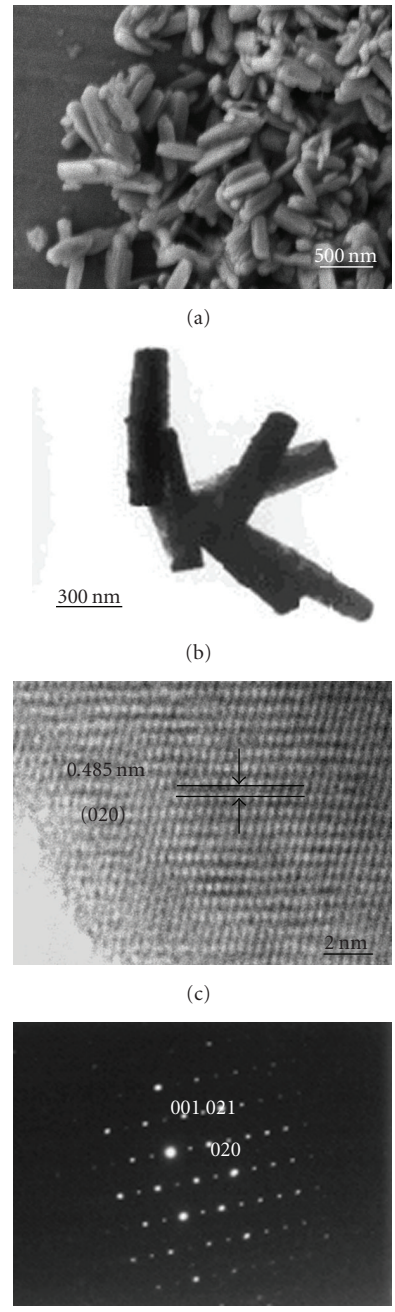

Figure 2: (a) FESEM image, (b) TEM image, (c) HRTEM image, and (d) corresponding SAED pattern of the as-synthesized orthorhombic GaOOH nanorods.

Figure 2(a) shows a typical the field-emission scanning electron microscopy (FESEM) image of the as-prepared orthorhombic GaOOH, which clearly exhibits that the product consists of uniform nanorods with lengths in the range of 400–600 nm and diameters of about 80–120 nm. Figure 2(b) is a representative transmission electron microscopy (TEM) image of the GaOOH product, indicating that the nanorods are solid structure, about 500 nm in length. A high-resolution transmission electron microscopy

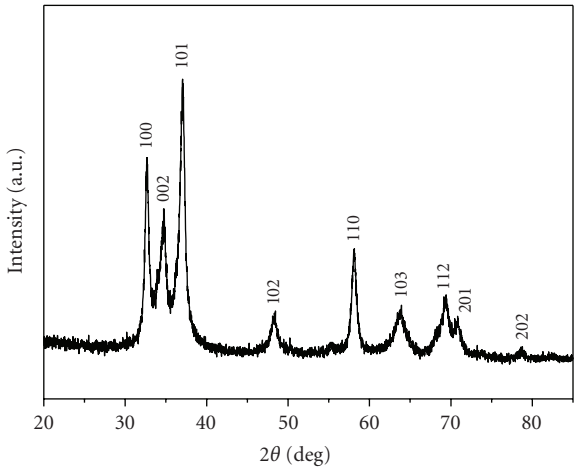

Figure 3: XRD pattern of the as-prepared GaN nanorods.

(HRTEM) image of a single GaOOH nanorod is shown in Figure 2(c). As can be seen from the image, this nanorod is structurally uniform single crystal. The observed interplanar spacing is about 0.485 nm, which corresponds to the separation between (020) lattice planes of orthorhombic GaOOH. The corresponding SAED pattern (Figure 2(d)) also indicates that the as-prepared GaOOH is single crystal and the SAED spots can be indexed as orthorhombic GaOOH (001), (021) and (020) planes.

3.2. Characterization of GaN Nanorods. The GaN nanorods were prepared via a solid-state reaction using $NaNH_2$ and the as-prepared orthorhombic GaOOH nanorods as reactants in a stainless steel autoclave. Figure 3 indicates the XRD pattern of the as-prepared product. All the reflection peaks can be indexed as wurtzite GaN, which is in good agreement with the standard data (JCPDS PDF No. 74-0243, $a = 3.195$ Å, $c = 5.182$ Å). No peaks of impurities such as Ga_2O_3 and Ga were detected, revealing that the orthorhombic GaOOH precursor was completely converted into wurtzite GaN under the experimental conditions.

FESEM, TEM, and HRTEM analyses were used to explore the morphologies and crystal structures of the as-synthesized wurtzite GaN nanorods. Figure 4(a) presents a panoramic FESEM image of the GaN product, indicating that the nanorods have rough surfaces which consist of densely packed GaN nanoparticles about 100–200 nm. Figure 4(b) is a representative TEM image of the GaN nanorods, displaying that the product is solid structure, about 500 nm in length and 100 nm in diameter. Figure 4(c) is the HRTEM image, showing that the crystal planes have lattice spacing of about 0.275 nm corresponding to (100) plane of wurtzite GaN. The corresponding SAED pattern (Figure 4(d)) also confirmed its wurtzite structure.

Further study shows that reaction temperature has a dramatic effect on the formation of GaN nanorods. When the reaction temperature was lower than 300°C, the obtained sample was still orthorhombic phase of GaOOH. If increases the reaction temperature to 500°C, the product

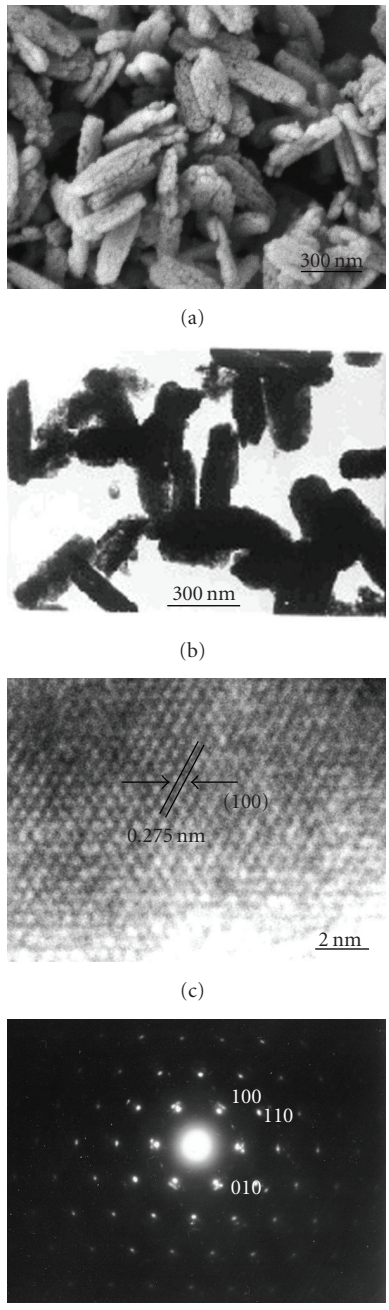

Figure 4: (a) FESEM image, (b) TEM image, (c) HRTEM image, and (d) corresponding SAED pattern of the as-synthesized wurtzite GaN nanorods.

was rhombohedral Ga_2O_3 instead of orthorhombic GaOOH. This is to say at 500°C rhombohedral Ga_2O_3 could not react with $NaNH_2$ and no wurtzite GaN was obtained. Pure wurtzite GaN could be obtained when the reaction temperature was higher than 600°C. Further study suggests that varying reaction temperature in the range of 600–700°C led to obvious change in the morphologies of wurtzite GaN products. When the temperature was moderated at 600°C, the product was GaN nanorods, while at 700°C the product

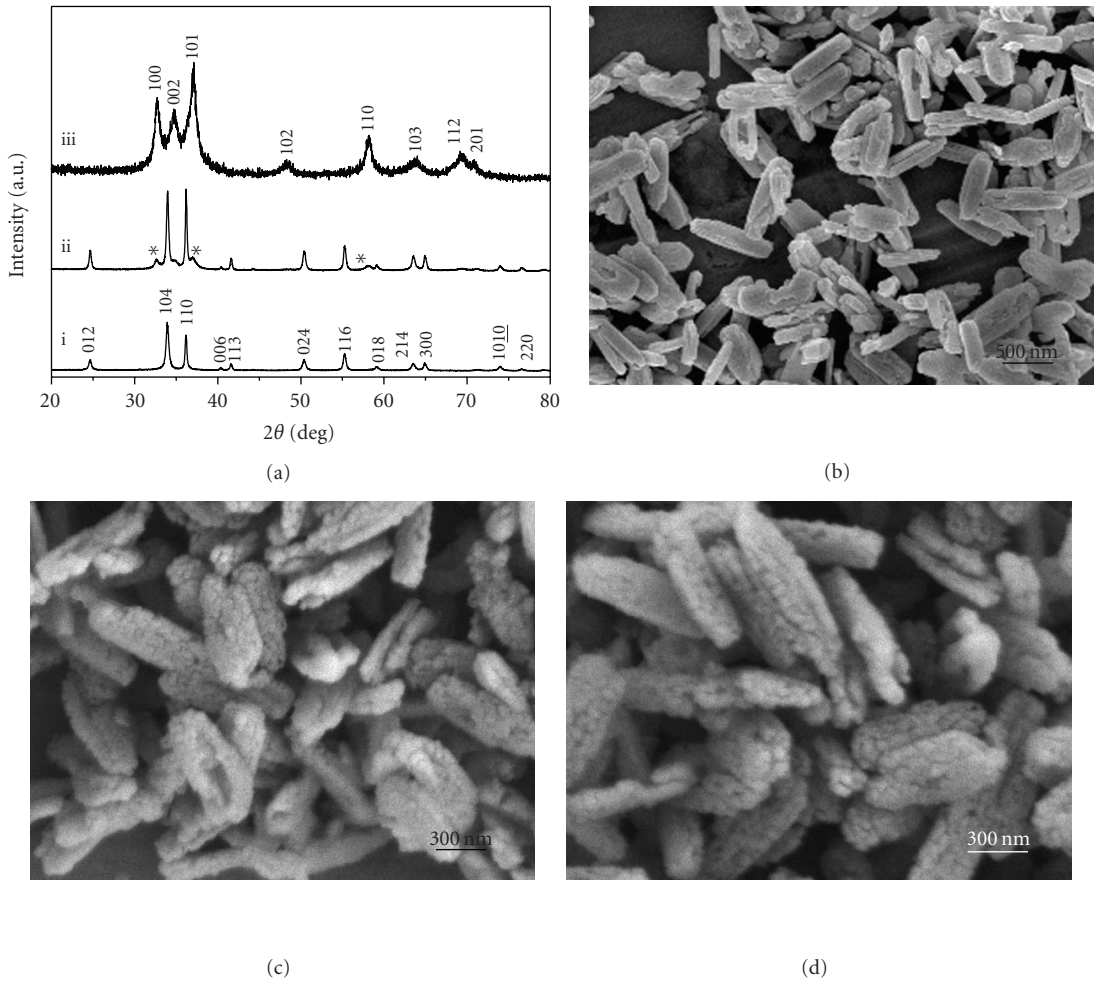

Figure 5: (a) i, ii, and iii are the XRD patterns of the products shown in (b), (c), and (d), respectively. ((b)–(d)) FESEM images of the products obtained at 600°C for 15 minutes, 1 hour, and 5 hours, respectively.

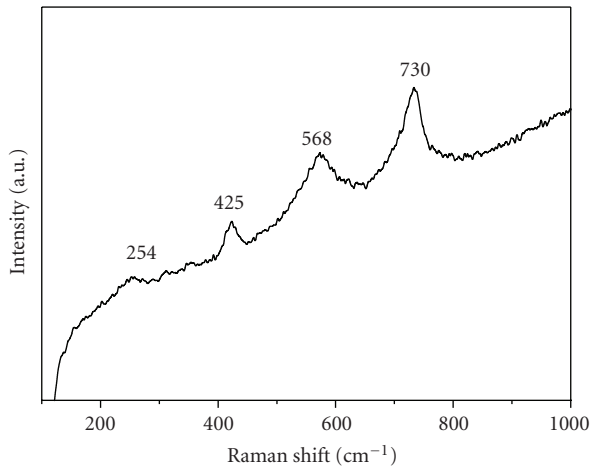

Figure 6: Raman spectrum of the as-prepared GaN nanorods.

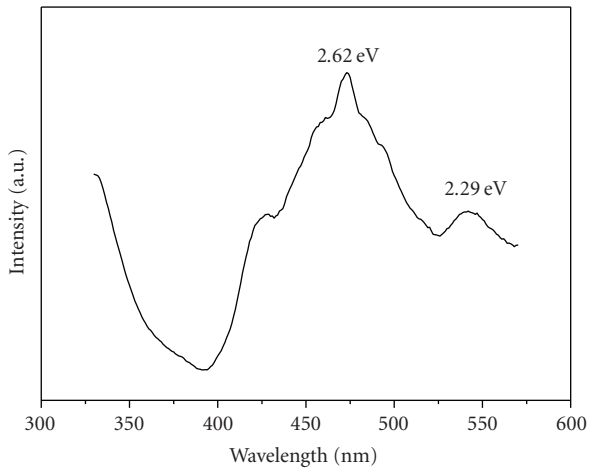

Figure 7: Room-temperature photoluminescence (PL) spectrum of the as-prepared GaN nanorods.

was composed of nanoparticles. All the data show that 600°C is the optimal reaction temperature for preparing wurtzite GaN nanorods.

To substantially understand the process of orthorhombic GaOOH nanorods transformation into wurtzite GaN nanorods, we systematically surveyed the growth process by

analyzing the samples at different growth stages. Figure 5(a) exhibits the XRD patterns of the three products obtained at 600°C for 15 minutes, 1 hour, and 5 hours, indicating that the three products were rhombohedral structure of Ga_2O_3 (JCPDS PDF No. 74-1610, $a = 4.98$ Å, $c = 13.43$ Å), rhombohedral Ga_2O_3 with minor amount of wurtzite GaN, and wurtzite GaN, respectively.

Figures 5(b)–5(d) show the FESEM images of the products obtained at 600°C for 15 minutes, 1 hour, and 5 hours, respectively. As shown in Figure 5(b), when the reaction was processed at 600°C for 15 minutes, 1D skeleton of Ga_2O_3 with relatively smooth surfaces was obtained. When the reaction time was increased to 1 hour, the sample was a mixture of Ga_2O_3 and GaN. The FESEM image (Figure 5(c)) indicates that product consists of nanorods with rough surfaces. Pure GaN could be obtained at 600°C for 5 hours. Figure 5(d) displays the FESEM image of the sample reacting for 5 hours, revealing that GaN nanorods assembled from small nanoparticles were formed. Based on the above investigations, the mechanism includes two steps.

(1) *In the initial step*: the orthorhombic GaOOH nanorods decomposed into rhombohedral Ga_2O_3 nanorods without destroying the 1D framework. As shown in Figure 5(b), the rhombohedral Ga_2O_3 product is composed of nanorods with lengths in the range 400–600 nm.

(2) *Second step*: with reaction time increasing, rhombohedral Ga_2O_3 nanorods transformed into wurtzite GaN nanorods via a high-temperature reaction. When the reaction time was increased to 1 hour, rhombohedral Ga_2O_3 with minor amount of wurtzite of GaN coexisted in the product, and pure wurtzite GaN could be obtained at 600°C for 5 hours. Figures 5(c)-5(d) display the FESEM images of the products obtained at 600°C for 1 hour and 5 hours, respectively, revealing that the initial 1D structural motifs were unaffected.

4. Optical Properties Measurement

Figure 6 is the Raman spectrum of the as-prepared GaN nanorods. The spectrum clearly indicates that Raman peaks appear at about 254, 425, 568, and 730 cm^{-1}. The first-order modes at 568 and 730 cm^{-1} exhibit the feature of red-shifts compared to values of 570 and 735 cm^{-1} for bulk GaN, which is attributed to the nanometer size effect [2]. The second-order Raman modes at 254 and 425 cm^{-1} are assigned to the zone-boundary phonon, activated by crystal imperfections and finite size effects, and the acoustic overtone of wurtzite GaN [6, 7].

GaN is one of the most promising optoelectronic semiconductors in solid-sate devices and its optical properties are directly related to its potential applications. The room temperature photoluminescence (PL) spectrum of the GaN nanorods recorded with excitation wavelength of 300 nm is shown in Figure 7. The PL spectrum exhibits a broad emission band in the range of 2.3–2.9 eV. The blue-emission band with peak at 2.62 eV is attributed to a variety of defects [7]. The green-emission bands with peak at 2.29 eV comes from intrinsic point defects [2, 6]. In a word, the PL emission displays the presence of a high quantity of defects in the as-prepared GaN nanorods. The defects, which can directly serve as radiative centers, may be helpful for electro-optical properties and extend the potential optical and optoelectronic application to the field of high-temperature electron devices.

5. Conclusions

We have demonstrated a convenient chemical route to synthesize wurtzite GaN nanorods via a solid-state reaction. The formation of GaN nanorods involves two steps: first, the orthorhombic GaOOH nanorods decomposed into rhombohedral Ga_2O_3 nanorods; then the rhombohedral Ga_2O_3 nanorods transformed into wurtzite GaN nonorods without destroying the 1D framework. The lengths of the as-obtained wurtzite GaN are in the range of 400–600 nm and the diameters are about 100 nm. The photoluminescence (PL) of GaN nanorods exhibits emission peak in the blue region, which is possibly attributable to the existence of defect.

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