



Ga₂O₃ nanowires grown on GaN–Ga₂O₃ core–shell nanoparticles using a new method: Structure, morphology, and composition

Hongdi Xiao^{a,*}, Haiyan Pei^b, Wenrong Hu^b, Bo Jiang^b, Yingbin Qiu^a

^a School of Physics, Shandong University, Jinan 250100, PR China

^b School of Environmental Science and Engineering, Shandong University, Jinan 250100, PR China

ARTICLE INFO

Article history:

Received 1 April 2010

Accepted 17 July 2010

Available online 23 July 2010

Keywords:

Ga₂O₃ nanowires

GaN–Ga₂O₃ core–shell nanostructures

Heat-treated GaN nanoparticles

ABSTRACT

Ga₂O₃ nanowires grown on GaN–Ga₂O₃ core–shell nanoparticles were prepared through heat-treating GaN powder method which comprises a pre-nitridation process in the flow of N₂ gas and a post-oxidation process in the air at 1200 °C. XRD and EDS patterns indicated that the heat-treated GaN powders were a powder mixture of GaN and Ga₂O₃. SEM, TEM, HRTEM and SAED images revealed that some nanowires that grow out from the edge of the GaN–Ga₂O₃ core–shell nanostructures with atomically smooth interfaces were monoclinic Ga₂O₃. Large blue-shifts in vibration frequency of Ga–N bonds observed in the FTIR spectrum could be contributed to size confinement effect and internal strains in GaN nanoparticles.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Nanotubes, nanorods and nanowires of various semiconductor materials have drawn much attention in recent years, due to their novel physical properties and new promising application in nano-devices. Among them, monoclinic Ga₂O₃ with a wide band gap of 4.9 eV is a promising candidate for potential applications such as transparent conducting material, flat-panel displays, optical emitters and solar energy conversion devices [1–3]. Various kinds of one-dimension (1-D) nanostructural Ga₂O₃ have been grown by different methods such as thermal evaporation method [4], microwave plasma chemical vapor deposition (MPCVD) [5], arc discharge [6], and laser ablation [7]. Due to most cases using a catalyst in synthesizing Ga₂O₃ 1-D nanostructures, these methods were comparatively complicated.

Recently, some studies on thermal stability of GaN nanopowders in N₂ or O₂ gas have been performed [8,9]. These studies found that (1) annealing over 200 °C resulted in the oxidation of GaN nanopowders in oxygen ambient; (2) annealing over 1120 °C led to the decomposition of GaN nanostructures in nitrogen ambient. According to the above properties of GaN nanostructures, a method which comprises a pre-nitridation process in the flow of N₂ gas and a post-oxidation process in the air at 1200 °C has been developed. This novel and efficient method comprises two reactions, namely the decomposition of GaN in N₂ gas and the oxidation of Ga metal in the air at 1200 °C. In this paper, we found that this method can not only reduce defects in GaN nanostructure but also lead to the formation of

a novel structure, namely Ga₂O₃ nanowires grown on GaN–Ga₂O₃ core–shell nanoparticles.

2. Experimental section

In our experiment, GaN nanopowders prepared by ammonolysis of Ga₂O₃ powders at 950 °C were used as the starting material [10]. The GaN-containing quartz boat was loaded into the center of a horizontal quartz tube placed in a conventional tube furnace. The nanopowders were annealed under flowing nitrogen with 300 ml min⁻¹ at 1200 °C. After annealing for 30 min in the flow of N₂ gas, the quartz boat was immediately taken out and exposed to air. The nanopowders annealed at 1200 °C, therefore, were natively cooled to room temperature in the air.

D8 Advance X-ray diffractometer (XRD), Vertex-70 Fourier transform infrared (FTIR) system, Hitachi H-8010 scanning electron microscopy (SEM), JEM-2100 high resolution transmission electron microscopy (HRTEM), and energy dispersive X-ray fluorescence (EDX) attached on the JEM-2010 were applied to examine the structure, morphology, and composition of oxidized GaN nanopowders.

3. Results and discussion

The XRD patterns of the as-synthesized and heat-treated GaN powders are shown in Fig. 1. The XRD data in Fig. 1(a) are well matched with the hexagonal GaN with wurtzite structure (JCPDS card no. 2-1078) [10]. The diffraction peaks marked by indices of lattice planes in Fig. 1(b) correspond to the monoclinic Ga₂O₃ structure with lattice constants $a = 1.223$ nm, $b = 0.305$ nm, $c = 0.581$ nm and $\beta = 103.7^\circ$, being in good agreement with the literature (JCPDS card no. 43-1012). The diffraction peaks located at 32.36°, 34.54° and

* Corresponding author. Tel.: +86 531 88364329.

E-mail address: hd Xiao@sdu.edu.cn (H. Xiao).

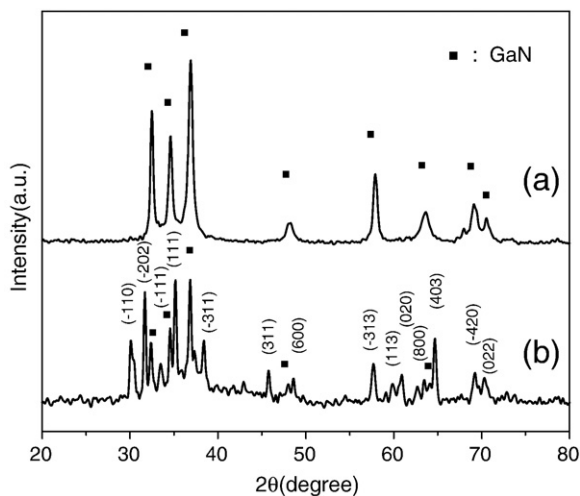


Fig. 1. XRD pattern of as-synthesized GaN powders (a) and heat-treated GaN powders at 1200 °C (b).

36.86° correspond to the (100), (002) and (101) faces of hexagonal GaN, which confirms the existence of GaN crystal in the heat-treated GaN powders. When GaN is fully relaxed, the corresponding peaks are located at 32.44°, 34.64° and 36.99°. These shifts towards the smaller angle side indicate an increase in the lattice parameter which means the presence of internal strains in the crystal [11].

Fig. 2 displays the infrared absorption of the samples. High-energy-shift of 17–61 cm^{-1} for ω_T vibration frequency of Ga–N bonds is observed in comparison with the calculated value of 560 cm^{-1} [12]. Some authors deduced that these results were caused by the size confinement effect or the presence of impurities, defects and internal strains [13–15]. The size of as-synthesized GaN nanoparticle was found to be in the range of 150–300 nm in the literature [10], so the blue-shift of 17 cm^{-1} should be ascribed to the defects such as

vacancy of N. For the heat-treated GaN samples, the blue-shift of 61 cm^{-1} shown in Fig. 2(b) could be explained by two possible mechanisms. One is the size confinement effect. As Ga_2O_3 layers form from the surface towards the center of GaN, the GaN nanoparticle size gets smaller and smaller eventually reaching dimensions comparable to or less than the confinement size. Another possible cause is internal strains, confirmed by the XRD data, in the particles. Most defects near the GaN surface could be consumed into the oxide layer, so these two factors could all contribute to the blue-shift of the infrared absorption. Two new bands corresponding to 466 and 670 cm^{-1} are found in Fig. 2(b), indicating that the bonding between Ga and O is formed in the samples. Furthermore, two absorption peaks at 1632 and 3438 cm^{-1} should contribute to hydrogen stretch modes which come from H_2O adsorbed by the nanopowders when the samples were investigated at room temperature in the air.

Fig. 3 shows the SEM morphology of the heat-treated GaN nanopowders. The coexistence of nanowires with nanoparticles was observed. The detailed structure and composition of these nanostructures were further characterized using TEM, SAED, and EDX. A representative TEM image shown in Fig. 4(a) indicates that some nanowires grow out from the edge of the nanoparticles. The HRTEM lattice image of a selected nanowire is displayed in Fig. 4(b). The nanowire clearly shows a lattice spacing of 0.250 nm which corresponds to the (111) plane of $\beta\text{-Ga}_2\text{O}_3$. The selected area electron diffraction (SAED) pattern, shown in the inset of Fig. 4(b), also means that the nanowire is a single crystal $\beta\text{-Ga}_2\text{O}_3$. Fig. 4(c) displays the energy dispersive X-ray (EDX) spectrum of the nanoparticle shown in Fig. 4(a). The Cu-related peaks are due to the presence of Cu grids, so it seems that the components of the nanoparticles are Ga, N and O. This result means that GaN– Ga_2O_3 core-shell nanoparticles could be created by the nitridation oxidation method. In order to confirm this prediction, Fig. 4(d) shows the HRTEM lattice image obtained from the nanoparticles shown in Fig. 4(a). The image clearly illustrates the nanoparticles containing two kinds of crystalline structures (Ga_2O_3 and GaN) and the interface between Ga_2O_3 and GaN being the atomically smooth interface. The measured lattice mismatch between the hexagonal GaN (101) and monoclinic Ga_2O_3 (200) planes is 0.014 nm (hexagonal GaN $d_{101} = 0.242$ nm; monoclinic

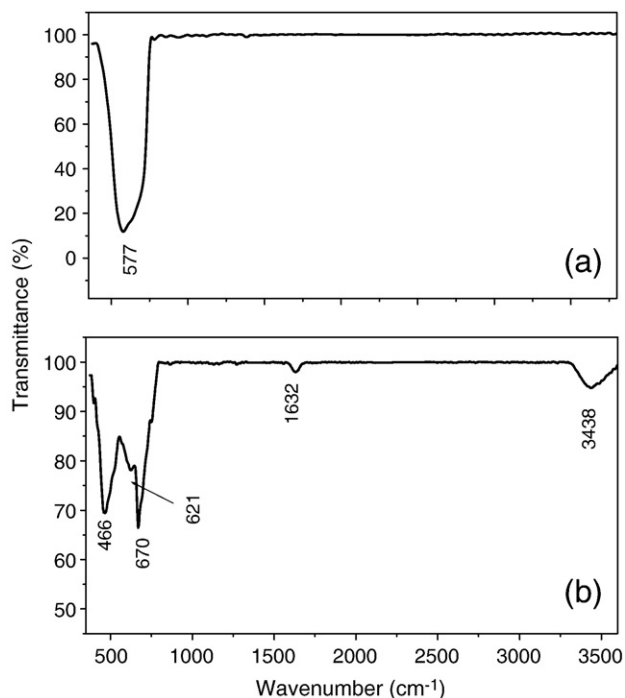


Fig. 2. Transmission infrared spectroscopy of as-synthesized (a) and heat-treated GaN nanopowders (b).

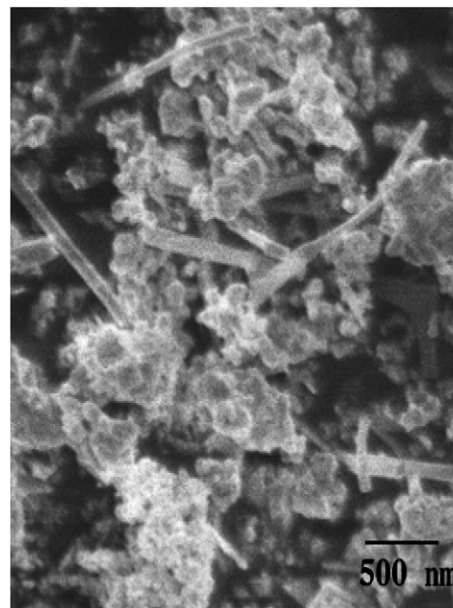


Fig. 3. SEM image of heat-treated GaN nanoparticles at 1200 °C.

Download English Version:

<https://daneshyari.com/en/article/1650075>

Download Persian Version:

<https://daneshyari.com/article/1650075>

[Daneshyari.com](https://daneshyari.com)