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Growth of β-Ga_2O_3 Nanorods and Photoluminescence Properties

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β-Ga_2O_3 nanorods were successfully fabricated through annealing Ga_2O_3/Mo films deposited on the Si (111) substrate by radio frequency magnetron sputtering technique. The morphology and structure of the as-synthesized nanorods were characterized by X-ray diffraction, scanning electron microscopy, high-resolution transmission electron microscopy, and energy dispersive X-rays spectroscopy. The results show that the formed nanorods are single-crystalline Ga_2O_3 with monoclinic structure. The diameters of nanorods are 200 nm and lengths typically up to several micrometers. A photoluminescence spectrum at room temperature under excitation at 325 nm exhibits two strong blue-light peaks located at about 413.0 nm and 437.5 nm, attributed to the recombination of bound electron–hole exciton in β-Ga_2O_3 single crystal. The growth process of the β-Ga_2O_3 nanorods is probably dominated by conventional vapor–solid mechanism.

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1. Introduction

One-dimensional nanomaterials (nanotubes, nanowires, and nanorods) have attracted intensive experimental and theoretical interests due to their novel physical properties and potential application for nanodevices [1]. Recently, one-dimensional nanostructures of semiconductive oxides such as ZnO, SnO_2, In_2O_3, and CdO have been successfully synthesized [2]. Monoclinic gallium oxide (β-Ga_2O_3) with a band gap of 4.8 eV is chemically and thermally stable. And Ga_2O_3 is also expected to have potential applications for optoelectronic devices such as flat-panel displays, optical emitters, and solar energy conversion devices

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because of its particular conduction and luminescence properties [3, 4]. Nanostructures of Ga_2O_3 will be of particular interest for these applications. β-Ga_2O_3 nanomaterials have been successfully synthesized by various techniques such as arc discharge of GaN powder [5], evaporation of bulk Ga [6], annealing of Ga_2O_3 powder with carbon nano-tubes [7]. However, up to now, there is a rare report on the synthesis of gallium oxide nanostructures by annealing Ga_2O_3 films deposited on Si (111) substrates.

In this paper, we develop a novel method to synthesize β-Ga_2O_3 nanorods by annealing Ga_2O_3/Mo films deposited on the Si (111) substrate by a radio frequency magnetron sputtering technique. This growth method allows a continuous synthesis and produces a large quantity of single-crystalline β-Ga_2O_3 nanorods at relatively high purity and low cost. Moreover, if β-Ga_2O_3 nanorods can be prepared on Si, it will pave the way for integration of future devices with developed Si integrated circuit technology.

2. Experimental

The Ga_2O_3/Mo films were deposited in turn on Si (111) substrates by sputtering a Mo target and a sintered Ga_2O_3 (99.99%) target using a JCK-500A radio frequency (RF) magnetron sputtering system with 7.8×10^{-4} Pa as base pressure. The distance between targets and substrates was 8 cm. Then argon gas (99.999%) was introduced into the chamber at the pressure of 2 Pa and the RF power was adjusted to 150 W. The sputtering time was 5 min for Mo layers and 90 min for Ga_2O_3 films, respectively.

After sputtered, the Ga_2O_3/Mo films were annealed under flowing ammonia in a horizontal tube furnace. First flowing N_2 gas was introduced into the tube for 5 min to flush out the residual air and then the samples were annealed for 20 min with a flow rate of 500 ml/min at 950°C. After being annealed, the samples were taken out for characterization.

X-ray diffraction (XRD, Rigaku D/max-rB Cu K_α), scanning electron microscopy (SEM, Hitachi S-570), high-resolution transmission electron microscopy (HRTEM, Tecnai F30), energy dispersive X-ray spectroscopy (EDX) attached to the HRTEM instrument and fluorescence spectrophotometer (PL, LS50-B) were carried out to examine the structure, surface morphology, composition, and optical properties of the synthesized samples.

3. Results and discussion

The overall structure and phase purity of as-synthesized products were characterized by XRD. Figure 1 shows a typical XRD pattern of the white layer deposited on the substrate surface. All relatively sharp diffraction peaks can be perfectly indexed to β-Ga_2O_3 with a monoclinic structure, which is in good agreement with the reported values of β-Ga_2O_3 with the lattice constants $a = 12.24$ Å,

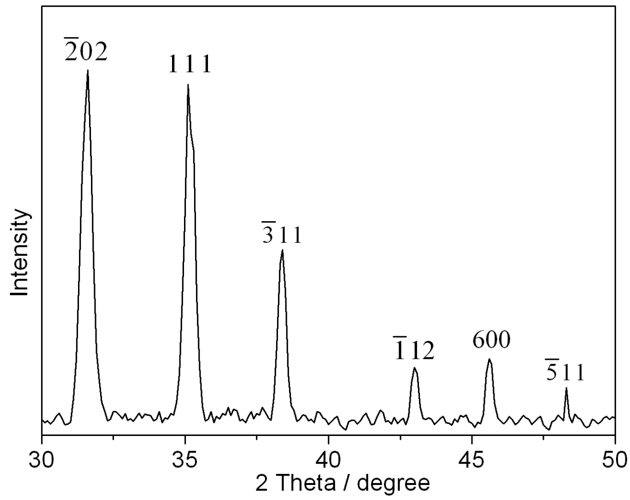

Fig. 1. XRD pattern of the β-Ga_2O_3 nanorods annealed at 950°C for 10 min.

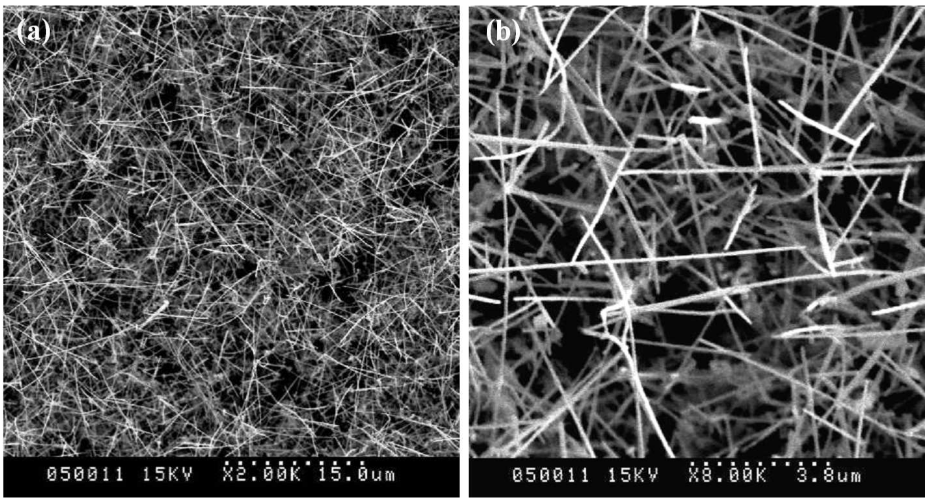

Fig. 2. SEM images of the β-Ga_2O_3 nanorods: (a) the lower magnification SEM image, (b) the higher magnification SEM image.

b = 3.04 Å, c = 5.81 Å, β = 103.76° (JCPDS: 41-1103). Moreover, no diffraction peaks from other impurities are found within the detection limit, indicating that the product on the substrate is predominantly a single β-Ga_2O_3 phase with high purity. The sharp diffraction peaks also reveal that the β-Ga_2O_3 nanorods prepared have a high crystalline quality.

The SEM image shown in Fig. 2a reveals that the products consist of a large quantity of rod-like nanostructures crossing each other and distributed randomly on the Si substrate. In fact, the whole substrate surface is found covered with the nanorods by the full-scale observation of SEM. Figure 2b exhibits the high--magnified SEM image. It reveals that the nanorods possess diameters of about 200 nm with lengths typically up to several micrometers, however, tens of micrometers nanorods can also be observed occasionally on TEM image, which results in a large aspect ratio. Most of the nanorods are straight and uniform along the entire length. It is to be noted that the nanorods have a very flat surface and a particle has never been found at the tip of the synthesized nanorods.

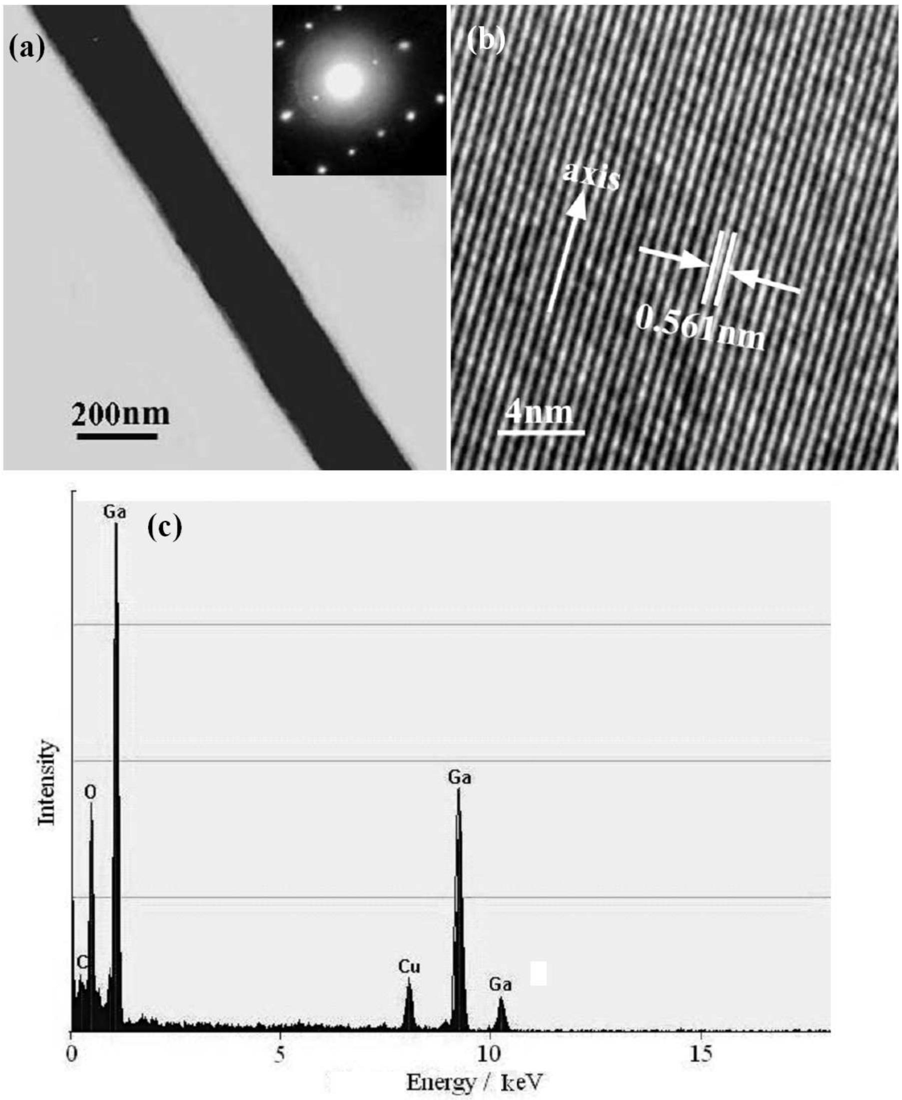

Fig. 3. The image with lower amplification of β-Ga_2O_3 nanorods (a) and the inset — corresponding SAED pattern; the high-resolution image (b); the EDX spectrum showing the chemical compositions of the products (c).

Further structural and elemental analyses of the individual Ga_2O_3 nanorod were performed using TEM. A low-magnified image of an individual nanorod is displayed in Fig. 3a. It shows that the nanorod has a uniform diameter of about 200 nm, which is straight and possesses a fairly clean surface without any particles. It appears to be homogeneous in diameter along the major axis. The inset in the upper-right-hand corner of Fig. 3a presents the corresponding selected area electron diffraction (SAED) pattern with a [110] zone axis, also revealing that the nanorods are single-crystal β-Ga_2O_3, which is in accordance with the XRD result. Figure 3b shows the HRTEM lattice image of the nanorod. The clear lattice fringes confirm that the synthesized nanorods are single crystal. In the image, the interval of the closest interplanar distance is about 0.561 nm, which corresponds to that of the crystal (001) plane of β-Ga_2O_3, indicating that the growth direction of the nanorod is parallel to the fringes of the (001) plane. Furthermore, the lattice is very perfect, which reveals that the nanorod has a high-quality crystal lattice. The EDX spectrum clearly identifies the peaks of Ga, O, C, and Cu shown in Fig. 3c. Since the C- and Cu-related peaks are due to the contamination from the carboncoated copper grids while preparing HRTEM specimens, the spectrum indicates that the components of the sample are Ga and O. The molecular ratio of Ga/O of the nanorods calculated from the EDX quantitative analysis data is close to that of a bulk Ga_2O_3 crystal.

In our experiment, a particle has never been found at the tip of the synthesized nanorods from the SEM. Therefore, the β-Ga_2O_3 nanorods are most likely produced via a vapor-solid (VS) growth process. We believe the Mo particles probably act as the nucleating sites for embryos [8], which provide growing sites for the later crystal nuclei and oxide source. Furthermore, Mo generally contains O [9], so the Mo layer provides oxide source to feed the growth of Ga_2O_3 nanostructures. The further function of the Mo films during the growth of β-Ga_2O_3 nanostructures is still in progress.

Figure 4 exhibits PL spectrum obtained from β-G_2O_3 nanorods at room temperature. The excitation was conducted under 325 nm ultraviolet light from He–Cd laser. It can be observed that two strong blue-light peaks are located at about 413.0 nm and 437.5 nm, respectively. In the light of the reported emission peak of a bulk Ga_2O_3 single crystal at 435 nm [10], the peak at 438.9 nm should be the emission peak of Ga_2O_3 single crystal. This also illustrates that Ga_2O_3 is obtained under current conditions, which accords with the results of XRD. In our experiment, the samples are annealed in reduction atmosphere and β-Ga_2O_3 nanorods are synthesized at relatively high temperature, which is in favor of the formation of a number of O vacancies (V_{O}) or Ga–O vacancy pairs (V_{Ga}, V_{O}). According to Binet and Gourier [10], after excitation of the acceptor, a hole on the acceptor and an electron on the donor are created. Then an electron on donor formed by oxygen vacancies (V_{O}) is captured by a hole on acceptor formed by gallium vacancies (V_{Ga}) to form a trapped exciton, which recombines radiatively and

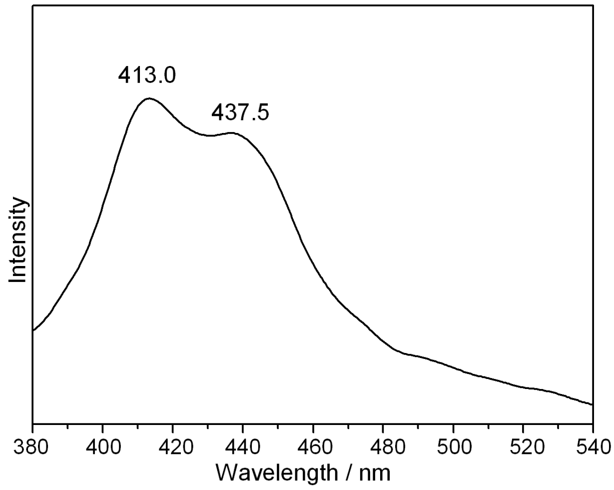

Fig. 4. PL spectrum of β-Ga_2O_3 nanorods.

emits a blue photon. Therefore, the peak located at 438.9 nm may correspond to the recombination of bound electron–hole exciton in β-Ga_2O_3 single crystal. Another peak at 417.8 nm has a blue shift to a shorter wavelength, resulting from the quantum size effect associated with the nanorods [11]. The peak position in the blue emission region has been suggested to depend on the dimension of nanomaterials, as well as the processing conditions [12, 13]. Gallium oxide nanorods may have potential application in active devices such as blue emitters due to their possibilities of strong emission [14]. However, a further work is needed to investigate the PL mechanism of the β-Ga_2O_3 nanorods.

4. Summary

In summary, large-scale fabrication of β-Ga_2O_3 nanorods have been successfully achieved on Si (111) substrates through annealing sputtered Ga_2O_3/Mo films under flowing ammonia at 950°C in a quartz tube. The results show that the as--synthesized products are pure, single-crystalline β-Ga_2O_3 with a monoclinic structure. The diameters of nanorods are 200 nm and lengths typically up to several micrometers through SEM and HRTEM observations. XRD and EDX provide the evidence for the synthesized material to be β-Ga_2O_3. The PL spectrum manifests two strong blue-light peaks located at about 413.0 nm and 437.5 nm, suggesting potential applications in active devices such as blue emitters. The growth process of the β-Ga_2O_3 nanorods is probably dominated by conventional VS mechanism.

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