

Synthesis of β -Ga₂O₃ Nanowires by Laser Ablation

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A simple laser ablation method has been employed for the synthesis of β -Ga₂O₃ nanowires. The as-synthesized products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and room-temperature photoluminescence. The synthesized β -Ga₂O₃ nanowires have diameters of 15–50 nm and lengths up to several micrometers, and a few of the nanowires appear to have ring-shaped structures. Photoluminescence of the bulk β -Ga₂O₃ nanowires shows a stable and broad green emission band centered at 497 nm, which has a blueshift of 30 nm from β -Ga₂O₃ powder. Possible growth mechanisms of the β -Ga₂O₃ nanowires are briefly discussed.

1. Introduction

Monoclinic gallium oxide (β -Ga₂O₃), one of the transparent conducting oxides, is intrinsically an insulator with a wide band gap of 4.9 eV, and it becomes an n-type semiconductor when synthesized under reducing conditions.^{1,2} β -Ga₂O₃ is useful as insulating oxide layers for all gallium-based semiconductors and can also be applied as an optical limiter for ultraviolet light and an oxygen gas sensor.³

Because of the remarkable electronic, optical, and mechanical properties of one-dimensional (1D) structures (nanotubes or nanowires), the fabrication of the 1D structures from various materials has been attracting much attention in mesoscopic physics and nanodevices.^{4–6} Nanoscaled gallium oxide with a large ratio of surface area to volume is expected to have special conduction and semiconductor properties, which may find applications in optoelectronic devices. This expectation has led to a considerable interest in growth of β -Ga₂O₃ nanowires. For example, β -Ga₂O₃ nanowires have been synthesized by electric arc-discharge of GaN powder based on the mechanism of catalytic step growth, or high temperature heat treatment of GaAs crystal via a vapor–liquid–solid (VLS) growth process.^{7–9} In both cases, the catalytic metals are required to generate energetically favorable sites for confining and directing the growth of β -Ga₂O₃ nanowires. Other methods, such as the carbothermal reduction reaction, the physical evaporation method, or the thermal annealing route, have also been developed for the growth of β -Ga₂O₃ nanowires,^{10–12} in which the growth process involves reactions at high temperatures. Recently, the laser ablation technique has been successfully used for the synthesis of semiconductor nanowires of various materials including silicon,^{13–16} germanium,^{14,17} III–V,^{18,19} and II–VI compounds.¹⁸ In this study, using pressed β -Ga₂O₃ powder as a target, a simple laser ablation method has been exploited for the synthesis of β -Ga₂O₃ nanowires, in which no catalytic metals and no high reaction temperature were required. The optical properties of the as-grown β -Ga₂O₃ nanowires have been investigated, and possible growth mechanisms are briefly discussed.

2. Experimental Procedure

The synthesis system used here has been described in detail elsewhere.²⁰ Briefly, a quartz tube (outer diameter, 42 mm; length, 80 cm) was mounted horizontally inside a high-temperature furnace. A Ga₂O₃ target (made by compacting β -Ga₂O₃ powder with a hydraulic press) was located at the center of the tube, and an alumina substrate was placed downstream of the target (the distance between the substrate and the target was about 6 cm). After evacuating the system by a mechanical rotary pump to a pressure of 3×10^{-2} Torr, a carrier gas of high-purity argon mixed with 5% hydrogen was kept flowing through the tube at a rate of 50 sccm and a pressure of 350 Torr in the tube. When the furnace was heated at a rate of 10 °C/min to 800 °C, the beam of a KrF excimer laser (Lambda Physik Co., Germany) with a wavelength of 248 nm and a pulse frequency of 10 Hz was then used to ablate the target. The laser power was 350 mJ per pulse with a pulse duration of 34 ns. The size of the laser spot on the target was about 1 mm \times 3 mm. The total duration of the ablation was 5 h. During the whole ablation process, the temperature, pressure, and the carrier gas flow rate were kept constant. After the ablation was stopped and the furnace cooled to room temperature, the resulting products were collected from the alumina substrate for characterization and measurement.

Powder X-ray diffraction (XRD; Siemens D-500 with Cu K α radiation and a normal $\theta - 2\theta$ scan) was used to characterize the phases in the collected products. Morphological observation and the structural analysis of the products were carried out with transmission electron microscopy (TEM; Philips, CM20 and CM200 FEG) operated at 200 kV. TEM samples were prepared by conventional dispersing followed by carbon film fishing (the as-synthesized nanowires were dispersed into methanol first, and then we dipped carbon film (on a copper grid) into the methanol to catch the nanowires, and finally let the methanol vaporize). Photoluminescence (PL) spectra were recorded at room temperature by an image-intensified detector ICCD and a spectrometer (SpectraPro 500i; Acton Research Corporation), using a pulsed Nd:YAG laser (355 nm) as an excitation source with energy in the range of μ J.

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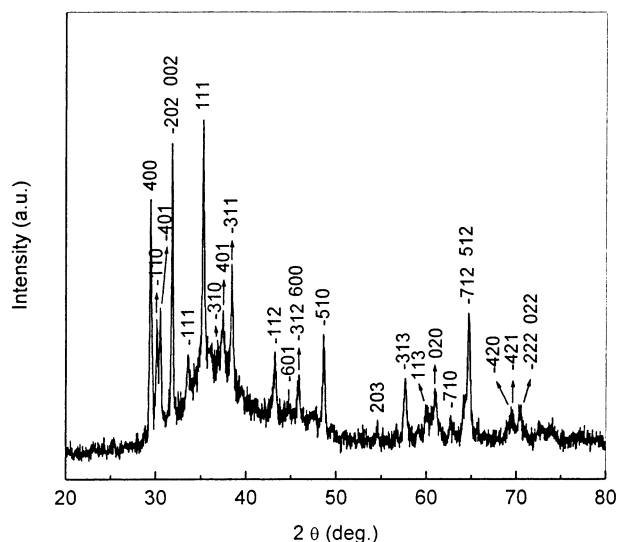


Figure 1. XRD pattern recorded from the as-synthesized products.

3. Results and Discussion

The resulting product, which appeared like a piece of white wool-like material, was deposited on the alumina substrate. Figure 1 shows the XRD pattern of the as-synthesized product. All of the diffraction peaks in the pattern can be indexed to those of the monoclinic structure of β -Ga₂O₃. After refinement with a least-squares fit, the measured lattice constants were $a = 12.229$, $b = 3.036$, $c = 5.786$ Å, in good agreement with the reported values of β -Ga₂O₃ in the literature (JCPDS, Powder Diffraction File No. 41-1103: $a = 12.227$, $b = 3.0389$, and $c = 5.8079$ Å). No peak associated with the other crystalline forms of the gallium oxides was detected in the pattern. The results suggested that the deposited product contains virtually only one crystalline phase of β -Ga₂O₃ and the other crystalline phases are below the detection limit.

Figure 2a shows a low-magnification TEM image revealing the general morphology of the deposited β -Ga₂O₃. It can be seen that the sample consists mainly of straight nanowires with diameters of 15–50 nm and lengths up to several micrometers (average aspect ratio is about 100). It is of considerable interest that a few of the wires appear to display coiled rings with an average diameter of about 700 nm or equivalently a contour length of 2.2 μ m (as shown in the inset of Figure 2a). Neither nanoparticles nor other morphologies were observed in the examined sample. (When the samples' plane was tilted in the TEM, we have not found the diameters' variations of the prepared Ga₂O₃ nanowires. So, we do not believe that the prepared Ga₂O₃ displayed the nature of nanobelt-like.) Figure 2 parts b and c are two selected area electron diffraction patterns taken from two different single nanowires; the patterns correspond to those of the [102] and [203] zone axis of the monoclinic phase of β -Ga₂O₃, respectively. Several diffraction patterns taken from different positions of the same wire along its length without further tilting of the sample always give the same pattern. This confirms the single-crystalline nature of the wire.

Figure 3 shows a high-resolution TEM image of an individual β -Ga₂O₃ nanowire. Lattice fringes of the (202) planes with a d spacing of 0.28 nm for monoclinic β -Ga₂O₃ can be clearly seen. It also reveals that the wire is single crystalline and the examined region is free from dislocation and stacking faults, whereas the surfaces of the wire terminate with thin (about 1 nm) and smooth amorphous layers. However, vacancy or interstitial defects may

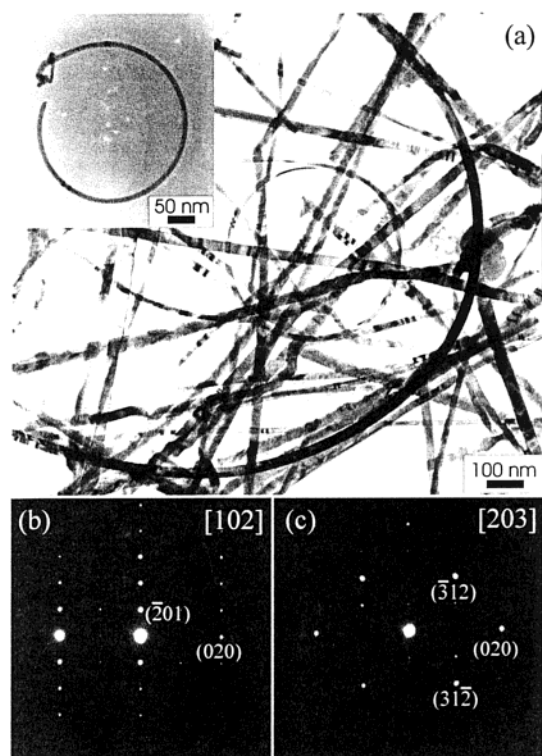


Figure 2. (a) Low-magnified TEM image of the synthesized β -Ga₂O₃ nanowires. (b and c) SAED patterns taken from two different single nanowires.

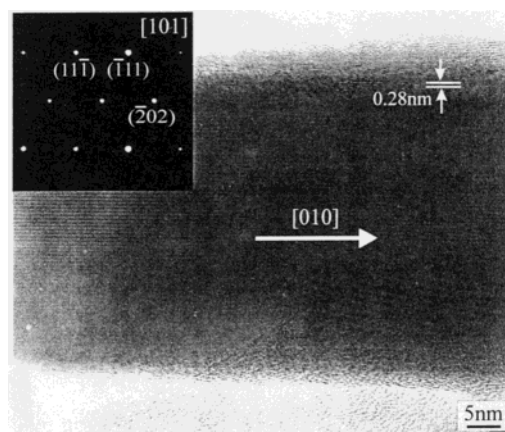


Figure 3. HRTEM image of a single nanowire and its corresponding SAED pattern (inset).

not be visible in the HRTEM observation. The corresponding SAED pattern (in inset of Figure 3) recorded with the electron beam perpendicular to the long axis of this wire can be indexed to the [101] zone axis of β -Ga₂O₃. Further studies of the SAED pattern and HRTEM image demonstrate that the wires grow along the [010] direction (indicated with an arrow).

Figure 4 shows a PL spectrum of the bulk β -Ga₂O₃ nanowires measured at room temperature, which consists of a stable and broad green emission band centered at 497 nm. When it is with the PL feature of β -Ga₂O₃ powders,⁹ the PL of the as-synthesized β -Ga₂O₃ nanowires shows a blueshift of about 30 nm. The PL may originate from the recombination of an electron on a donor formed by oxygen vacancies and a hole on an acceptor formed by gallium vacancies or by gallium–oxygen vacancy pairs.^{9,21,22} It is expected that the present laser ablation

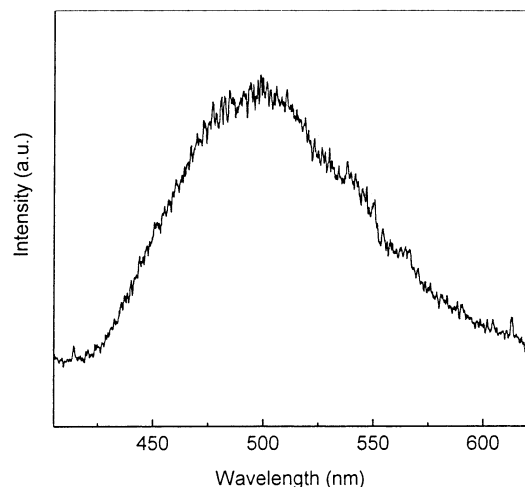


Figure 4. Room-temperature PL spectrum of the bulk β -Ga₂O₃ nanowires.

method should easily produce a considerable density of oxygen and gallium vacancies in the synthesized β -Ga₂O₃ nanowires.

There are two well-accepted growth mechanisms for conventional crystalline whiskers: the screw dislocation mechanism²³ and the vapor–liquid–solid (VLS) mechanism.²⁴ In the screw dislocation mechanism, a screw dislocation line is parallel to the axis of the whisker and provides a spiral step where atoms can easily adhere for the whisker growth. The growth process in the VLS mechanism involves the nucleation and growth of eutectic alloy droplets and the growth of whiskers through droplets owing to supersaturation. In this mechanism, a liquid-forming agent (or so-called catalyst) is thus required. In the present case, no evidence for the existence of screw dislocation was detected either in diffraction contrasted TEM images or in HRTEM images. A catalyst nanoparticle was also not observed on any tips of the synthesized nanowires. It appears that the growth of β -Ga₂O₃ nanowires in the present work cannot be satisfactorily explained by either of the two mechanisms. In our experiment, the observation that the wires formed on the alumina substrate downstream of the target suggests that the growth of the nanowires involves a vapor-forming agent; otherwise, the nanowires will nucleate and grow directly on the target. So, the vapor–solid (VS) mechanism was a reasonable explanation for the growth of the β -Ga₂O₃ nanowires. In fact, heated by the high-temperature plume of the laser ablation, Ga₂O₃ in the target will decompose into Ga₂O vapor (Ga₂O has a sublimation temperature of about 500 °C) and O₂. The Ga₂O vapor is then carried by the carrier gas and transferred along the tube downstream and deposited in the form of nanoclusters by aggregation of Ga₂O molecules on the alumina substrate. As the ablation proceeds, more Ga₂O vapor is generated and more Ga₂O nanoclusters are formed. The as-formed Ga₂O nanoclusters are energetically favorable and serve as the stable sites for rapid adhesion of additional Ga₂O molecules and result in the formation of the Ga₂O nanowires. The formed Ga₂O nanowires are subsequently oxidized by O₂ (from the decomposition of Ga₂O₃) to produce the final β -Ga₂O₃ nanowires. The ring formation process of the nanowires may be caused by physical coiling because of thermal fluctuations during growth, with a significant strain energy because of the increased curvature. On the basis of these discussions, the formation of the β -Ga₂O₃ nanowires is believed to be related to the growth of Ga₂O nanowires in which the Ga₂O nanowires serve not only as a template for directing the growth of β -Ga₂O₃ nanowires but also

as a reactant for the resulting product. The stages leading to formation of β -Ga₂O₃ nanowires are briefly described as follows:

- (1) Laser ablation and decomposition of the starting material β -Ga₂O₃: $\text{Ga}_2\text{O}_3 \rightarrow \text{Ga}_2\text{O vapor} + \text{O}_2$;
- (2) Depositions: $\text{Ga}_2\text{O vapor} \rightarrow \text{Ga}_2\text{O nanoclusters}$;
- (3) The growth of Ga₂O nanowires: $\text{Ga}_2\text{O nanoclusters} \rightarrow \text{Ga}_2\text{O nanowires}$;
- (4) The formation of β -Ga₂O₃ nanowires: $\text{Ga}_2\text{O nanowires} + \text{O}_2 \rightarrow \beta\text{-Ga}_2\text{O}_3 \text{ nanowires}$.

Although no evidence for the existence of screw dislocations was detected in the TEM images of the examined nanowires, some other defects are expected to exist in the synthesized β -Ga₂O₃ nanowires. As indicated by the photoluminescence of the bulk β -Ga₂O₃ nanowires, the stable and broad green emission band may be related to defects such as the oxygen vacancies (or the gallium vacancies) or gallium–oxygen vacancy pairs.

4. Conclusion

A simple laser ablation method has been employed for the synthesis of β -Ga₂O₃ nanowires. The as-synthesized nanowires have diameters of 15–50 nm and lengths up to several micrometers; a few of the nanowires appear to display ring-shaped structures. Room-temperature photoluminescence of the bulk β -Ga₂O₃ nanowires shows a stable and broad green emission band centered at 497 nm, which has a blueshift of 30 nm from β -Ga₂O₃ powder. In contrast to the previously reported synthesis methods, the present laser ablation method required no metallic catalyst and no high-temperature reactions. The formation of the nanowires is believed to involve a VS growth mechanism. By choosing appropriate metal oxides as the target materials, we expect the present method can be extended to synthesize nanowires of other semiconducting metal oxides.

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