β-Ga$_2$O$_3$ nanowires and nanobelts synthesized by thermal evaporation

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Abstract

In this study, we demonstrate the large-scale synthesis of β-Ga$_2$O$_3$ nanowires and nanobelts by simple thermal evaporation of Ga droplet in the presence of Au catalysts at 900°C. The morphology and structure of the products were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The ultra-long single-crystalline β-Ga$_2$O$_3$ nanowires with diameters of about 40 nm exhibit rectangle cross-section shapes. Small amounts of bicrystal nanobelts and ring-shaped nanowires were also observed. The growth process was proposed on the basis of vapour–liquid–solid (VLS) or vapour–solid (VS) crystal growth mechanisms.

1. Introduction

The synthesis of single crystalline semiconducting nanostructures such as nanowires and nanobelts/ribbons has attracted great interest due to their size, morphology-related properties, and their emerging applications in functional nanodevices. Monoclinic gallium oxide (β-Ga$_2$O$_3$) is an important wide band gap material because of good chemical and thermal stability. It has a variety of applications including transparent conducting oxide, optical emitter for UV, and gas sensors [1–4]. The synthesis and characterization of β-Ga$_2$O$_3$ nanostructures have progressed lately. Various methods, for example, arc-discharge, laser ablation, thermal evaporation, and carbon thermal reduction, were developed by several research groups [5–12].

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2. Experiment

A vertical quartz tube (outer diameter 80 mm; length 120 cm) was mounted inside a high-temperature furnace. Analytical grade Ga droplet (0.3 g, purity greater than 99.99%) and the silicon substrate (6 mm × 8 mm in size) were placed on the alumina plate (38 mm in diameter) and positioned horizontally in the central zone of the quartz tube together. The silicon substrate was approximately 5 mm from the edge of the Ga droplet.

To obtain a thin film of Au nanoparticle, a drop of aqueous gold colloidal solution, synthesized by using a mixture of trisodium citrate and tannic acid for the reduction of chloroauric acid (HAuCl₄), was dipped on the silicon substrate before the reaction, and then dried in air [13].

After the tube was evacuated by a mechanical rotary pump to a pressure of 6 × 10⁻³ Torr, a carrier gas of high-purity Ar was kept flowing at a rate of 100 sccm. The pump continually evacuated the system and the pressure inside the tubes was maintained at 40 Torr during the experiment. The temperature of the furnace central region was increased at a rate of 30 °C/min to 900 °C, and then maintained at this temperature for 2 h. After the furnace was cooled to room temperature, a snow-white wool-like product was deposited on the silicon substrate.

The collected products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM at 300 kV). For SEM investigations, the products together with the silicon substrates were directly transferred into the SEM chamber, without destroying the location and orientation of the products on the substrate. For TEM studies, some samples were scraped off from the silicon substrates and were directly mounted on Cu folding TEM grids.

3. Results and discussion

The density and thickness of the deposits gradually decreased with the distance from the source material. Fig. 1a shows the low magnification of the product that was deposited on the silicon substrate. In the zone nearest the Ga droplet, a large quantity of nanostructures, including wire-like, belt-like structures were formed. But sparsely populated nanowires were produced in the zone far from the Ga droplet. The results of XRD (not shown) confirmed that the products

![Fig. 1. (a), (b) The SEM image of the products formed on the Au-coated silicon substrate, showing large quantities of nanowires and nanobelts. (c) A single nanowire with a rectangular cross-section. (d) The curved and twisted nanobelts.](image)
were $\beta$-Ga$_2$O$_3$ ($a_0 = 5.8 \, \text{Å}, \ b_0 = 3.04 \, \text{Å}, \ c_0 = 12.23 \, \text{Å}, \ \beta_0 = 103.42^\circ$, and JCPDS 11-370).

Fig. 1b depicts the high-magnification SEM image taken from the zone near the source material. The most commonly observed structures were ultra-long nanobelts (from tens to hundreds of micrometers in length) having widths ranging from hundreds of nanometers to several micrometers and thickness about tens of nanometers. The waving and twist shapes of the belts are apparent, as shown in Fig. 1d. The nanowires are also observed in the samples. It is to be noted that many of the nanowires exhibit rectangular cross-section, distinct from the common shape of nanowires reported in the literature.

The structures morphology of the $\beta$-Ga$_2$O$_3$ nanostructures were further characterized using TEM. Fig. 2a shows the TEM image of a single $\beta$-Ga$_2$O$_3$ nanowire. The contrast in the image color of the nanowire showed the rectangular cross-section, which is consistent with the SEM results. The inset SAED patterns indicated the single crystalline structure and can be an index to the [110] axis of $\beta$-Ga$_2$O$_3$. $\beta$-Ga$_2$O$_3$ nanobelts with smooth surfaces and uniform widths and twisted nanobelts are depicted in Fig. 2b and 2c, respectively. The ripple-like contrast of the belts in the TEM image was due to the bend contours, as typically observed in the TEM observations of slightly bent thin crystals. Bicrystal-like belts were also observed in the product (Fig. 2d). The SAED pattern obtained from the boundary area between the two belts presented two sets of similar patterns, as shown in Fig. 2c. It can be concluded that the bicrystal was constructed from two belts connected along one axis in a “V” shape.

To investigate the role that Au nanoparticle played in the formation of the $\beta$-Ga$_2$O$_3$ nanostructures, the silicon substrate without the Au nanoparticle was employed in the experiment under the same condition. It is found that few nanowires were formed on the silicon substrate. Moreover, the $\beta$-Ga$_2$O$_3$ nanowires attached to the nanoparticle were discovered at the zone far away from the resource materials when Au nanoparticle was employed, as depicted in Fig. 3a. Fig. 3b also shows a SEM image of the ring-shaped nanowires with branched parts. The Au nanoparticle is located at the tips of the branched nanowires, which is characteristic of the vapour–liquid–solid (VLS) growth mechanisms.
The available evidences suggest that the Au nanoparticle induced the nucleation and growth of $\beta$-Ga$_2$O$_3$ at the initial stage of deposition. In our experiment, the source material and the growth substrate were in the same temperature. Au nanoparticle will adsorb the Ga atom and O atom from the surroundings to form a low-melting-point liquid droplet. The Ga$_2$O$_3$ compound precipitates from the solid–liquid interface when the concentration is of Ga and O atom in the droplet are greater than the saturation threshold.

At the following stage, we propose that vapour–solid (VS) process controls the formation of nanowires and nanobelts. After the initial growth stage, the formed nanowires make the substrate surface rougher, which becomes a favourable position for the nucleation and growth of $\beta$-Ga$_2$O$_3$ nanostructures. No metal catalyst was detected in the nanowires and nanobelts and the growth process was dominated by the VS mechanisms.

4. Conclusions

In summary, we demonstrated the formation of $\beta$-Ga$_2$O$_3$ nanostructures in the presence of Au catalysts using a simple thermal evaporation method at a temperature of 900°C. The single crystalline $\beta$-Ga$_2$O$_3$ nanowires with rectangular cross-section and nanobelts with regular shapes and flat surfaces coexisted in the product. The Au nanoparticle induced the nucleation and formation of $\beta$-Ga$_2$O$_3$ nanowires in the earlier growth stage and vapour–solid mechanism controlled the growth of the nanobelts in the subsequent stage. The $\beta$-Ga$_2$O$_3$ nanowires and nanobelts observed in this study could potentially be used in functional nanodevices. The technique used in this study is an effective approach for the large-scale formation of $\beta$-Ga$_2$O$_3$ nanowires and nanobelts.

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