Novel nanostructures of $\beta$-Ga$_2$O$_3$ synthesized by thermal evaporation

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Abstract

In this study, we report the novel $\beta$-Ga$_2$O$_3$ nanostructures synthesized by the thermal evaporation of Ga droplet in the presence of Au catalysts at 900 $^\circ$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 single-crystalline $\beta$-Ga$_2$O$_3$ nanosheets have lateral dimensions up to several tens of microns. Large arrays of column-like layered crystal $\beta$-Ga$_2$O$_3$ structures that consisted of many nanosheets were formed on the Au-coated silicon substrate under the suitable vapor concentration. These novel $\beta$-Ga$_2$O$_3$ nanostructures are expected to have potential application in functional nanodevices.

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1. Introduction

The synthesis of single-crystalline semiconducting nanostructures such as nanowires and nanobelts has attracted great interest due to their size, morphology-related properties, and their emerging applications in function nanodevices. Monoclinic gallium oxide ($\beta$-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 $\beta$-Ga$_2$O$_3$ nanowires and nanobelts have been lately progressed. Various methods, for example, arc-discharge, laser ablation, thermal evaporation, and carbonthermal reduction, were developed by several research groups [5–12].

Size, dimensionality, and shape play important roles in determining the properties of nanomaterials. So far, most of the nanomaterial researches have been focused on zero-dimensional nanoparticles and one-dimensional nanowires/nanotubes, but very few studies have been carried out on two-dimensional nanosheets [13].

2. Experiment

A vertical quartz tube (outer diam. 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 $\times$ 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 all 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 (HAuCl$_4$), was dipped in the silicon substrate before the reaction and then dried in air [14].

After the tube had been evacuated by a mechanical rotary pump to a pressure of $6 \times 10^{-2}$ 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 maintained at 40 Torr during the experiment. The temperature of the furnace central region was increased at a rate of 30–900 °C min⁻¹, and then maintained at this temperature for 2 h.

The collected products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), 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 scrapped off from the silicon substrates and were directly mounted on Cu folding TEM grids.

3. Results and Discussion

After the furnace was cooled to room temperature, a snow-white wool-like product was deposited on the silicon substrate. The results of XRD (not shown) confirmed that the products were β-Ga₂O₃ ($a_0 = 5.8 \text{ Å}, b_0 = 3.04 \text{ Å}, c_0 = 12.23 \text{ Å}, \beta_0 = 103.42^\circ$, and JCPDS 11-370).

The density and thickness of the deposits gradually decreased with the distance from the source material. Fig. 1 depicts the high-magnification SEM image taken from the zone near the source material. The product consists of many sheet-like structures with large lateral dimensions up to a several tens of microns. The waving and twist shapes of the sheets are apparent, as shown in Fig. 1b, c, further displayed the irregular sheet-shaped characteristic of the nanostructures. Reaphook-like and “Y”-shaped nanosheets are also observed in the product (Fig. 1c, d).

Large arrays of micro-sized β-Ga₂O₃ crystal structures (shown in Fig. 2a) were also formed on the substrate in the zone far from the source material when the furnace temperature were kept at 900 °C for an extended period to 3 h. These column-like crystal structures, several micrometers in diameter, were densely deposited in the preferred normal direction on the silicon substrate, overlap and impinge on other neighboring crystals. Some of the column-like structures, with the polygonal or the rectangular cross-section, protruded from the surface. Close observation in their cross-section indicated that they are layered structures consisting of many nanosheets with uniform thickness about 10–20 nm (Fig. 2b–d).

The structures and morphology of a single β-Ga₂O₃ nanosheet were further characterized using TEM. Fig. 3a shows the typical TEM image of the β-Ga₂O₃ nanosheets with smooth surfaces. The SAED pattern (insert) shows the

Fig. 1. (a) SEM image of large quantities of the nanostructures. (b)–(d) Twisted, reaphook-like, “Y”-shaped nanosheets.

Fig. 2. (a) SEM image of the microsized column-like β-Ga₂O₃ crystals deposited on the silicon substrate. (b)–(d) Rectangular and polygonal column-like crystals consisted of large quantities of layer nanosheets.
single-crystalline structure and can be indexed for the [1 0 1] zone axis of $\beta$-Ga$_2$O$_3$.

In our experiment, the growth substrate and source material were in same temperature zone and no temperature gradient existed. The different morphologies of the products collected from different positions relative to the source material provide evidence that the observed microstructures are strongly dependent on the concentration gradient of the vapor sources. The concentration in the zone nearer to the source materials is higher and supersaturation is easily reached, which offers the higher nucleation rate, resulting in the formation of large quantities of the nanostructures. While at growth sites far away from the source materials, the concentration is low and nucleation rate is small, and the micro-sized column-like crystal structures were formed. Firstly, randomly oriented column-like crystals were formed on the growth substrate. As they grew further, they began to overlap and their growth became physically limited as the misaligned column-like crystal began to impinge on other neighboring crystal, giving rise to the preferred orientation of the large arrays of column-like crystal.

4. Conclusions

In summary, we demonstrated the $\beta$-Ga$_2$O$_3$ nanosheets and their related nanostructures synthesized by thermal evaporation of Ga droplet in the presence of Au catalysts. Large-sized $\beta$-Ga$_2$O$_3$ nanosheets and arrays of column-like layer structure consisting of nanosheets are formed on the different positions of the growth substrate due to different concentrations of vapor. These novel $\beta$-Ga$_2$O$_3$ nanostructures are expected to possess unique properties.

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References