Formation of bicrystalline β-Ga_2O_3 nanorods

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Over the past few years, attention has been focused on the study of one-dimensional (1D) nanomaterials, due to their novel physical properties steming from the reduced dimensions and due to their promising applications to advanced devices and technologies [1–3]. Semiconductor oxides are widely used as the base materials for transparent conducting oxide, photoelectronics, and gas sensors [4–7] and among them, gallium oxide (Ga_2O_3) with a wide bandgap of 4.9 eV [8] has great potential applications. Accordingly, many researchers have prepared 1D Ga_2O_3 nanostructures, such as nanowires, nanobelts, nanosheets, and nanorods by d.c. arc discharge [9, 10], metalorganic chemical vapor deposition [11], and evaporation or thermal heating [12–19].

Although the 1D bicrystalline nanostructures have been reported for ZnO [20], Si [21], SiC [22], CuO [23], and ZnS [24], the production of bicrystalline Ga_2O_3 nanostructures, which we believe, has never been reported. These unusual structures offer model systems for the study of charge and mass transport and may serve as templates for novel device structures. In this paper, we first report on the formation of bicrystalline structured Ga_2O_3 nanorods.

Our experiments were performed in a vertical furnace system [25]. The GaN powder with a purity of 99.9% were used as the starting material. The substrates used in our experiments were p-type (1 0 0) Si wafers. They were ultrasonically cleaned for 10 min in acetone solution. The GaN powders and the treated Si substrates, respectively, were placed on the lower and the upper holder in the furnace. The powder-to-substrate distance was 5 mm. The thermal evaporation of the GaN powders was performed at 900° for 2 h with a nitrogen (N_2) flow rate of 500 standard cubic centimeters per minute under a pressure of 1 atm. After evaporation, the substrate was cooled down and subsequently taken out from the furnace. The as-grown deposits were examined by X-ray diffraction (XRD) using a Philips X'pert MRD diffractometer with CuKα_1 radiation ($\lambda = 0.154056$ nm). Scanning electron microscopy (SEM) measurements were carried out with a Hitachi S-4200 field-emission microscope. Transmission electron microscopy (TEM) investigation was made on a Philips CM-200 microscope with an accelerating voltage of 200 kV. The TEM sample was prepared by dispersing the powder in acetone. Imaging was enabled by dispersing few drops of suspension onto carbon coated copper grid.

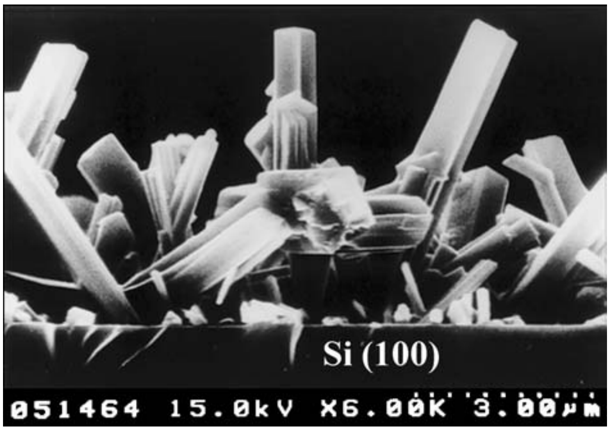

Figure 1. SEM image of deposits.

Fig. 1a is a SEM image of the side view of the deposits, indicating that the deposits consist of an agglomeration of rod-like structures. The growth direction of the rod-like structures is randomized. Statistical analysis of many SEM images shows that the diameters of the rods are about 40–1000 nm and the lengths are mostly less than 6 μm. Fig. 2 shows the XRD patterns of the deposits on Si substrates. The reflection peaks of (004), $(\bar{2}02)$,$(\bar{1}11)$, (111), $(\bar{1}13)$, $(\bar{2}11)$, $(\bar{2}13)$, (015), $(\bar{3}13)$, (020), and $(\bar{2}17)$ correspond to the monoclinic (β-Ga_2O_3 structure with lattice constants a = 5.80 Å,

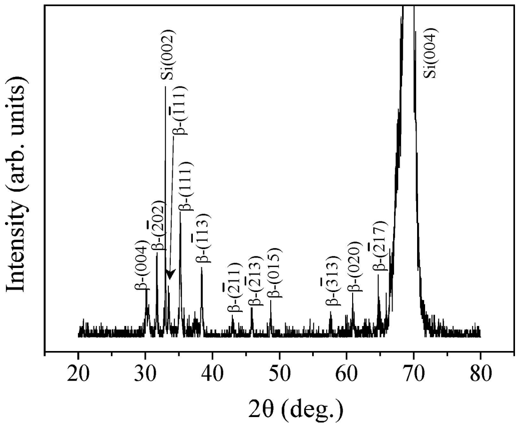

Figure 2. X-ray diffraction pattern recorded from the deposits.

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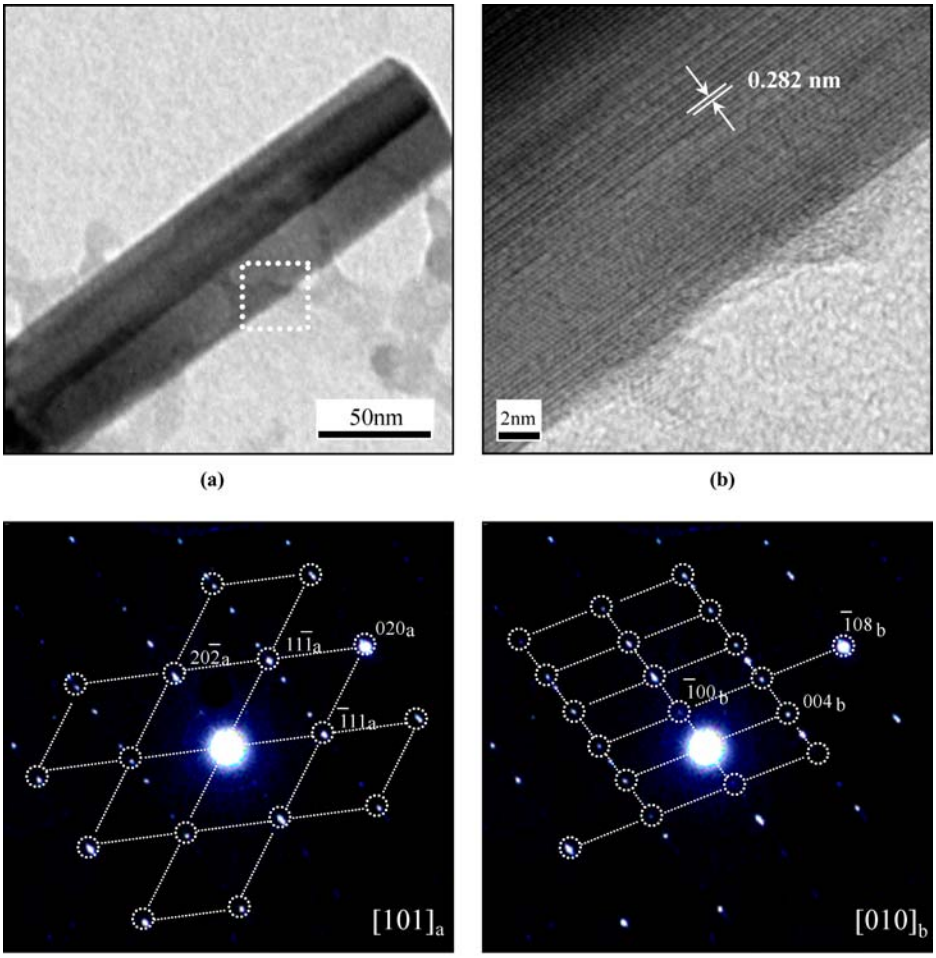

(a) (b)

(c)

Figure 3. TEM characterization of a single (β-Ga_2O_3 nanorod. (a) Low magnification TEM image. (b) High resolution TEM image taken from the boxed region in Fig. 3a. (c) Electron diffraction pattern taken from the whole nanorod region in Fig. 3a, recorded perpendicular to the nanorod long axis. It displays two sets of spotted patterns that corresponds to the $[1\ 0\ 1]_a$ and $[0\ 1\ 0]_b$ zone axises of two monoclinic (β-Ga_2O_3 crystals, respectively.

b = 3.04 Å, and c = 12.23 Å (JCPDS: 11-0370), revealing the production of (β-Ga_2O_3 deposits.

We have performed the further structural characterization of (β-Ga_2O_3 nanostructures by TEM. Fig. 3a shows the low magnification TEM image of a nanostructure, indicating that the nanostructure displays the rod-like shape with a diameter and a length, respectively, of 42 and 200 nm. We found that the average diameters observed in TEM for the isolated nanostructures are obviously smaller than those of the branches of the as-grown deposits observed in SEM (Fig. 1). We surmise that this phenomenon is due to the sample preparation process. After sonification, large-diameter nanostructures cannot be detached from the substrate or tend to fall rapidly to the bottom of the beaker. The visible lattice fringes of the HRTEM image taken from the boxed region in Fig. 3a show that the nanorod is crystalline (Fig. 3b). The interplanar spacing is about 0.282 nm, corresponding to the $(\bar{2}02)$ plane of monoclinic (β-Ga_2O_3. The electron diffraction pattern taken from the whole nanorod region in Fig. 3a is shown in Fig. 3c. The pattern, recorded perpendicular to the nanorod long axis, contains two sets of spotted patterns that corresponds to the $[1\ 0\ 1]_a$ and $[0\ 1\ 0]_b$ zone axises of two monoclinic (β-Ga_2O_3 crystals, respectively. The growth axises of two monoclinic (β-Ga_2O_3 crystals are closely parallel to the $(020)_a$ and $(\bar{1}08)_b$, respectively. We reveal that the observed diffraction pattern can be made by superimposing the characteristic diffraction pattern from one crystal on that from the other crystal. Accordingly, the nanorod consists of two monoclinic (β-Ga_2O_3 crystals. Since only nanostructures with the relatively smaller diameter could be investigated, more study is necessary in order to reveal the exact crystalline nature of the larger-diameter nanostructures. Since no catalysts were intentionally used for the growth of our nanostructures and no nanoparticles or impurities are clearly observed on the tips of prepared nanostructures, we deduce that the growth of (β-Ga_2O_3 nanostructure is a self-catalyzed process.

In summary, we have demonstrated the formation of (β-Ga_2O_3 nanorods via a thermal evaporation method of heating GaN powders at 900°C under N_2 flow. The deposits are composed of an agglomeration of rod-like (β-Ga_2O_3 nanostructures, with the diameter of about 40–1000 nm. Upon sonication in acetone, the deposits break down into rod-like crystals. A single rod with a diameter of 42 nm is found to be a bicrystalline monoclinic (β-Ga_2O_3 structure.

Acknowledgements

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