\(\beta\)-Ga\(_2\)O\(_3\) Nanowires and Nanobelts Synthesized by Using GaAs Powder Evaporation

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We report the synthesis and characterization of \(\beta\) (monoclinic)-Ga\(_2\)O\(_3\) nanowires and nanobelts prepared by using GaAs powder evaporation under a low vacuum condition (300Torr). As-grown \(\beta\)-Ga\(_2\)O\(_3\) nanostructures were synthesized based on the well-known vapor-liquid-solid (VLS) mechanism by employing a Au thin film and vapor-solid (VS) reaction. Dense and uniform Ga\(_2\)O\(_3\) nanowires with a diameter of 80 nm were synthesized at a higher temperature (800 °C), while various nanostructures including nanowires and nanobelts were found around 650 °C. The crystalline structures and the chemical compositions of the as-synthesized \(\beta\)-Ga\(_2\)O\(_3\) nanostructures were characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectrometry (EDS).

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I. INTRODUCTION

Growth of well-fabricated nano-scale materials are important for elucidating the fundamental physics at the nano-scale, eventually leading to creation of novel functional materials useful for future electrical/optical devices [1]. Specifically, one-dimensional (1D) nanostructures, such as nanowires, nanotubes, and nanobelts, have attracted much attention owing to their importance in understanding the fundamental concepts of the roles of both dimensionality and quantum size effects and to their potential applications as the building blocks for electronic/optical nano-devices [2-4]. Among various 1D nanostructure materials, gallium oxide with a monoclinic structure, a compound with wide bandgap energy of 4.9 eV at room temperature [5], has drawn considerable attention due to its potential applications in optoelectronic devices, including flat-panel displays, gas sensing, and solar energy conversion [6-8]. The synthesis of \(\beta\) (monoclinic)-Ga\(_2\)O\(_3\) nanostructures have been achieved through various methods, including arc discharge, laser ablation, thermal oxidation, and carbothermal reduction [9-12]. In previous works on \(\beta\)-Ga\(_2\)O\(_3\) nanostructures, it was proposed that the growth of \(\beta\)-Ga\(_2\)O\(_3\) nanostructures with different morphologies, sizes, and microstructures were mainly controlled by the temperature and reaction process [13,14]. To the best of our knowledge, little literature has been reported on the growth of \(\beta\)-Ga\(_2\)O\(_3\) nanostructures by GaAs evaporation and on the understanding of the variation in the morphology of \(\beta\)-Ga\(_2\)O\(_3\) nanostructures with the growth conditions.

In this paper, we report the synthesis and characterization of \(\beta\)-Ga\(_2\)O\(_3\) nanowires and nanobelts prepared by using GaAs powder evaporation under a low vacuum state (300 Torr). As-synthesized \(\beta\)-Ga\(_2\)O\(_3\) nanostructures were characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive spectrometry (EDS). This study provides useful information for creating the nano-electronic devices building blocks and for tuning the properties of those nano-device.

II. EXPERIMENTS AND DISCUSSION

The synthesis of \(\beta\)-Ga\(_2\)O\(_3\) nanostructures was conducted in a conventional horizontal tube furnace with a 25 mm inner-diameter quartz tube. GaAs powders (Sigma Aldrich) were positioned in the center of the quartz tube. A Au thin film on a cleaned Si wafer (50 mm in length and 10 mm in width) was deposited (thickness of less than 100 nm) by DC magnetron sputtering, and the Au-deposited Si wafer was then placed downstream in the quartz tube. 50 nm away from the GaAs powder. After evacuation of the quartz tube to ~5 mTorr, a high-purity Ar flow was set at a constant rate of 100 sccm, which led to a constant process pressure of 300 Torr. Before heating the furnace, a moveable thermocouple was inserted in the furnace to measure the temperature distribution on the substrate. The furnace was heated to
1050 °C for 5 min and was kept at this temperature for 60 min. The local temperature of the Au-coated Si substrate was precisely measured and was found to be in a range of 650 °C to 800 °C. After the growth, the furnace was slowly cooled down to room temperature. The product was then characterized using X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation, scanning electron microscopy (SEM, FEI Nova NanoLab 200), and high-resolution transmission electron microscopy (TEM, JEM-3000F, equipped with an energy dispersive X-ray spectroscopy unit).

After the synthesis, a gray-colored product was found on the Au-coated Si substrate. Fig. 1 shows the typical XRD pattern of the obtained product. All the strong peaks in this pattern can be readily indexed to β (monoclinic)-Ga2O3 structures (JCPDS card, No. 43-1012). Peaks associated with the GaAs phase (JCPDS card, No. 80-0016) are also partially detected, which can be considered to be GaAs particles that did not decompose during the synthesis procedure.

A SEM image of the as-synthesized product is shown in Fig. 2(a) and (b). Fig. 2(a) displays a typical SEM image of the as-synthesized Ga2O3 nanowires obtained at 800 °C. Dense and uniform Ga2O3 nanowires were found with diameters of ~80 nm and lengths exceeding ~10 μm. At the end of the individual nanowire, the Au catalyst is clearly seen in Fig. 2(a), which can be explained by the Au-nanoparticle-mediated vapor-liquid-solid (VLS) mechanism [15]. For the substrate at lower temperature (~650 °C), the morphologies of the as-synthesized products were changed from nanowires to mixed nanostructures, including nanowires and nanobelts, with high-yield. A typical SEM image in Fig. 2(b) shows that Ga2O3 nanobelts were synthesized with widths in the range of several tens to several hundreds of nanometers and with lengths up to ~0.5 μm. In our case, these nanobelt structures might have been formed via the well-known vapor-solid (VS) reaction [16]. However, there is a notable difference in that the Au catalyst was also observed at the tips of the nanobelts in our case, as contrary to the typical catalyst-free VS reaction. The nanowires grown at 650 °C, shown in Fig. 2(b) were seen to have similar morphology as the as-synthesized nanowires obtained at 800 °C, and with average diameter of 80 nm and lengths up to 20 μm. The VLS reaction using Au nanoparticle and VS method will be discussed later in this paper.

Figure 3 shows TEM images of the products grown at 650 °C. To enable TEM observations of as-synthesized nanostructures, we directly dispersed the products onto a SiN-coated TEM grid. In Fig. 3(a), the Ga2O3 nanobelt has a width of about 150 nm, and the Ga2O3 nanowire has a diameter of ~80 nm. For our experimental conditions, the chemical composition of the Ga2O3 nanostructure can be identified as decomposed elemental Ga from the GaAs powder (melting point ~1240 °C) and residual oxygen originating from the low vacuum state (300 Torr). Further structural investigations of the β-Ga2O3 nanowire were carried out with high-resolution TEM. Fig. 3(b) shows the lattice-resolved HRTEM image ob-
Fig. 3. (a) Low-magnification TEM image of an individual \( \beta \)-Ga\(_2\)O\(_3\) nanowire and nanobelts prepared at 650 \(^\circ\)C. (b) HRTEM image of a \( \beta \)-Ga\(_2\)O\(_3\) nanowire revealing growth along the [020] direction. Their corresponding FFT pattern recorded with the incident beam along the [20\( \bar{1} \)] direction can be indexed to a monoclinic structure.

To examine the chemical composition of the as-synthesized products, we conducted a scanning TEM (STEM) annular dark field (ADF) analysis, as shown in Fig. 4 with an EDS line-scan. Fig. 4(a) shows the EDS line-scan profile along the width direction on the ADF image of the \( \beta \)-Ga\(_2\)O\(_3\) nanowire. From this result, a uniform distribution of elemental Ga (purple) and O (green) was confirmed. Moreover, the faceted line was also found in the \( \beta \)-Ga\(_2\)O\(_3\) nanowire, which can be considered to be a result of a monoclinic single-crystalline growth. Fig. 4(b) displays an EDS line-scan profile along the growth direction superimposed on an ADF image of the top of the \( \beta \)-Ga\(_2\)O\(_3\) nanowire (Au = blue, Ga = green, O = red). Au element was only detected from the body of \( \beta \)-Ga\(_2\)O\(_3\) nanowire whereas elemental Ga and O were observed from the top of the \( \beta \)-Ga\(_2\)O\(_3\) nanowire, which provides evidence for VLS-method growth-mediated Au nanoparticle.

As for the \( \beta \)-Ga\(_2\)O\(_3\) nanowire growth mechanism, Ga from the GaAs powder could be evaporated due to the high vapor pressure of metallic Ga under our experiment conditions [17]. Subsequently, the substrate temperature provides eutectic (\( \sim \)550 \(^\circ\)C) Au-Ga liquid droplets through alloying, which leads to supersaturated Ga-compound crystalline growth [18]. However, residual oxygen under our experiment conditions could not be alloyed with Au, not even at high temperatures [19]. In this regard, \( \beta \)-Ga\(_2\)O\(_3\) nanowire growth can be explained as follows: Firstly, decomposed Ga from GaAs powder starts to form a Ga\(_2\)O\(_3\) compound by reacting with the residual oxygen in the horizontal furnace. The Ga\(_2\)O\(_3\) dissolved Au nanoparticles leads to supersaturated Ga\(_2\)O\(_3\) nanowire growth. Our EDS line-scan profile in Fig. 4(b) provides crucial evidence indicating that single-crystalline Ga\(_2\)O\(_3\) is formed through su-
persaturation, following a Au-Ga$_2$O$_3$ pseudobinary system. In the case of the Ga$_2$O$_3$ nanobelt at 650 °C, the growth mechanism is thought to incorporate both VLS and VS reactions because a Au catalyst was always observed at the top of the Ga$_2$O$_3$ nanobelt and because solidified Ga$_2$O$_3$ atoms at relatively low temperatures enabled single-crystalline lateral growth along the Ga$_2$O$_3$ nanowire's side surface.

III. CONCLUSION

In this work, by using GaAs powder evaporation, we successfully synthesized β-Ga$_2$O$_3$ nanowires and nanobelts. Uniform and dense β-Ga$_2$O$_3$ nanowires grew at temperatures around 800 °C whereas β-Ga$_2$O$_3$ nanobelts were synthesized dominantly at ~650 °C. Using morphological and chemical analyses with electron microscopes, a synthesis mechanism of β-Ga$_2$O$_3$ nanowires and nanobelts is proposed based on VLS and a combined process of VS and VLS, respectively. Through the STEM EDS line-scan, a Au and β-Ga$_2$O$_3$ pseudobinary eutectic system for the supersaturated β-Ga$_2$O$_3$ single crystalline growth is also suggested. The study on various β-Ga$_2$O$_3$ nanostructures here may inspire interest in exploring other various nanostructures and their potential applications in nano-optoelectronic devices.

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REFERENCES