One-Dimensional Single-Crystalline Bismuth Oxide Micro/Nanoribbons: Morphology-Controlled Synthesis and Luminescent Properties

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Based on a facile vapor-phase transport method without any catalyst and template, one-dimensional single-crystalline bismuth oxide (Bi2O3) micro/nanoribbons were fabricated on silicon substrates in large quantities and morphology-controlled fabrication of Bi2O3 was achieved from a single precursor. The widths of Bi2O3 ribbons varied from 0.2 to 20 μm depending on the deposition temperatures. The thickness was in the range of 0.1–2 μm and the length reached several hundred micrometers and even millimeter range. The detailed composition and structural analysis confirmed the single-crystalline nature of α-Bi2O3 micro/nanoribbons with monoclinic structure. The photoluminescence spectrum of a single Bi2O3 ribbon showed a broadband emission from 450 to 750 nm in the visible region, consisting two peaks located at 589 and 697 nm which were primarily originated from the impurity ions and crystal defects. A self-catalyzed vapor–solid model was proposed to account for the growth mechanism of Bi2O3 ribbons with different morphologies.

Keywords: Bi2O3 Micro/Nanoribbons, Vapor Phase Transport, Photoluminescence.

1. INTRODUCTION

Research in one-dimensional (1D) metal oxide nanostructures with different morphologies has attracted considerable attention owing to their dimension-dependent physical properties and unique applications in nanoscale electronic and optoelectronic devices in recent years.1,2 Bismuth oxide (Bi2O3) is an interesting material and very important in modern solid-state technology owing to its unique structure and physical properties, such as a phase-dependent energy band gap (2.85 eV for α-Bi2O3 and 2.58 eV for β-Bi2O3), high refractive index, high dielectric permittivity (εr = 190), high oxygen ion conductivity (1.0 S cm−1), and good photoconductivity and photoluminescence (PL).3–6

Although bulk Bi2O3 has been widely used in various technological fields such as the third-order nonlinear optical glass, oxide-conductors, solar cells, and gas sensors, the synthesis of 1D Bi2O3 has not been widely investigated till now. However, controlled fabrication of Bi2O3 nanostructures is of great importance for both physical research and potential applications in photocatalyst, sensors and optoelectronic devices. Among the five polymorphs of Bi2O3 that are α-Bi2O3 (monoclinic), β-Bi2O3 (tetragonal), γ-Bi2O3 (body centered cubic), δ-Bi2O3 (cubic), and μ-Bi2O3 (triclinic), α-Bi2O3 exhibits p-type electronic conductivity (dominated by hole charge carriers) at room temperature.4,7 However, reports on controlled fabrication of pure single α-crystalline Bi2O3 nanostructures is very limited and the reported morphologies are nanoparticle, nanosquaresheet and nanorod.8–11 Thus, both from fundamental and application viewpoints, it is meaningful to develop a simple and effective method to achieve dimensionally-controlled high-quality α-Bi2O3.

Herein, we report a simple and effective approach of fabricating single crystalline α-Bi2O3 micro/nanoribbons with length up to several hundred micrometers with controllable morphologies. Single crystalline α-Bi2O3 micro/nanoribbons were synthesized simultaneously at two temperature regions of 550–650 °C and 650–850 °C, respectively.
2. EXPERIMENTAL DETAILS

The synthesis was carried out in a horizontal tube furnace by vapor-phase transport (VPT) method without any template or catalyst. The VPT system used in our experiment can be found elsewhere. The source material used was Bi$_2$O$_3$ powder (99.999%, Strem Chemicals, Inc.) mixed thoroughly with graphite powder (weight ratio 1:1), which was placed at one end of a small quartz tube. Si(100) wafers serving as the substrate were ultrasonically cleaned with acetone, isopropyl alcohol, and deionized water in sequence, each for 15 minutes, and was dried in pure nitrogen gas flow before being placed at the other end of the small quartz tube. The central temperature of the furnace was increased to 1000 °C at a rate of 10 °C min$^{-1}$ and kept for 60 min under a constant Ar flow of 250 sccm (standard cubic centimeters per minute) and O$_2$ flow of 2 sccm. The substrates were located at a temperature region of 550–850 °C according to the predetermined furnace temperature profile. After 60 min evaporation, the small quartz tube was drawn out of the furnace and cooled down to room temperature. A wool-like layer of light yellow color was found on the substrates.

The morphology and crystal structure were characterized by scanning electron microscopy (SEM, JEOL JSM-5600LV, operated at 10 kV), X-ray diffraction (XRD, Rigaku, operated at 40 kV) with Cu K$_{α1}$ radiation ($λ = 1.5418$ Å), and transmission electron microscopy (TEM, JEM-2010, operated at 200 kV). The chemical composition was analyzed using X-ray photoelectron spectroscopy (XPS, KRATOS, AXIS ULTRA) using a monochromatized Al K$_{α}$ X-ray source (1486.6 eV). All XPS spectra were calibrated by C 1s peak (284.9 eV) to compensate the charging effect. Raman scattering spectra of the samples were measured by a Renishaw Ramanscope with an argon laser operating at 514.5 nm as the excitation source. The PL spectrum of a single Bi$_2$O$_3$ microribbon was recorded by a Renishaw inVia Raman microscope with 325 nm laser excitation.

To explore the structural and optical properties of a single Bi$_2$O$_3$ nanoribbon by TEM and PL characterizations, the nanoribbons were ultrasonically removed from the growth substrate and then transferred onto a carbon-coated copper grid and a clean silicon wafer by dropping an ethanol-nanoribbon suspension. All the characterizations were performed at room temperature.

3. RESULTS AND DISCUSSION

3.1. Morphology Characterization

Large quantities of light yellow products were collected at a wide deposition temperature region from 550 to 850 °C. Figures 1(a–c) show the typical low-magnification SEM images of Bi$_2$O$_3$ micro/nanostructures grown at different temperature regions, i.e., (a) region I: 550–650 °C, (b) region II: 650–750 °C, (c) region III: 750–850 °C, respectively. Figures 1(d–f) are the corresponding enlarged SEM images of Figures 1(a–c), respectively. In the low temperature region I, large quantities of nanoribbons were observed with thickness of ~100 nm, width in the range of 0.2–1 μm, and length up to several hundred micrometers and even several millimeters. In the medium temperature region II, microribbons with thickness of 0.4–2 μm, width of 2–10 μm and length up to several hundred micrometers were observed. In high temperature region III, the width of some microribbons further increase to more than 20 μm while the thickness and the length did not show much change compared to region II.

3.2. Composition and Structural Analysis

Figure 2(a) shows a typical XRD pattern of the products. All the diffraction peaks can be indexed as monoclinic α-Bi$_2$O$_3$ with lattice constants of $a = 5.849$ Å, $b = 8.169$ Å, $c = 7.512$ Å and $β = 112.98°$ (ICPDS 41-1449), indicating single phase of our products. Figure 2(b) shows the typical Raman scattering spectra recorded from the 1D Bi$_2$O$_3$ micro/nanostructures with an excitation wavelength of 514.5 nm, for a low frequency range ranging from 50 to 600 cm$^{-1}$. The peak positions of the Raman scattering throughout the whole deposition temperature regions are similar. All 14 peaks agree well with the literatures, which further confirms that the nanostructure is composed of monoclinic α-Bi$_2$O$_3$. The Raman bands observed in the region below 120 cm$^{-1}$ are mainly attributed to the displacements of Bi atoms while those above 150 cm$^{-1}$ are mainly due to the displacements of the O atoms. Raman bands in the range of 120–150 cm$^{-1}$ are defined by the displacement of both Bi and O atoms. XPS survey scan of the Bi$_2$O$_3$ micro/nanoribbons (Fig. 2(c)) shows the presence of Bi, O and C. Figures 2(d and e) show the high resolution XPS spectra of O 1s and Bi 4f in the Bi$_2$O$_3$ micro/nanoribbons, respectively. The quantification analysis of the XPS peaks show that the Bi/O atomic ratio is about 2:3, which is consistent with the given formula of Bi$_2$O$_3$ and former XRD and Raman results. Figure 2(f) shows the high resolution TEM (HRTEM) image recorded near the edge of a Bi$_2$O$_3$ nanoribbon. The measured lattice spacing of 2.0 Å corresponds to the spacing between (010) planes of α-Bi$_2$O$_3$. The white arrow indicates that the Bi$_2$O$_3$ nanoribbon grows along the [010] direction. The selected area electron diffraction (SAED) pattern shown in Figure 2(g) is in good agreement with the monoclinic crystal structure of α-Bi$_2$O$_3$ taken along the [001] zone axis. Additionally, an amorphous layer with width of ~4 nm can be found at the edge of the nanostructures.

3.3. Optical Properties

Figure 3 shows the room temperature PL spectrum of a single Bi$_2$O$_3$ microribbon using a He–Cd laser (325 nm)
as the excitation source. A wide broad-band emission from 450 to 750 nm was observed, which can be well presented by the two Gaussian-shaped peaks centered at 589 and 697 nm, respectively. The full widths at half maximum of the two bands are \( \sim 130 \) and \( \sim 80 \) nm, respectively. The 589 nm emission can be attributed to different valence states of Bi ions such as \( \text{Bi}^{3+} \), \( \text{Bi}^{2+} \) or Bi cluster.\(^{4,15,16}\) The red/near-infrared emission may be ascribed to the recombination between the defect levels in the band gap or from the conduction band to defect levels.\(^{4}\)

3.4. Growth Mechanism Discussion

The growth mechanism of Bi\(_2\)O\(_3\) can be attributed to the self-catalyzed vapor–solid (VS) mechanism instead of conventional vapor–liquid–solid (VLS) process since no metal catalyst was used in the growth process.\(^{17}\) To investigate the growth mechanism, we conducted two control experiments under the same growth condition except (1) only using Bi\(_2\)O\(_3\) powder as the source material and (2) conducting the experiment in an open-end quartz tube (without any carrier gas and open to the atmosphere). In both experiments, no Bi\(_2\)O\(_3\) products were collected on the Si substrates which can be understood by the high melting point of Bi\(_2\)O\(_3\) and low vapor pressure of Bi\(_2\)O\(_3\) at atmosphere. Thus, Bi or Bi suboxides played an important role for the nucleation of Bi\(_2\)O\(_3\) micro/nanostructures. The formation mechanism is similar to that of other metal oxides fabricated by VPT method such as ZnO.\(^{18,19}\)

Firstly, in the high-temperature region, carbon reduced Bi\(_2\)O\(_3\) into Bi or Bi suboxides (Bi\(_{2x}\)O\(_x\), \( x < 1.5 \)) by the following reactions:

\[
\begin{align*}
C + 1/2O_2 & \rightarrow CO \\
2\text{Bi}_2\text{O}_3 + 3C & \rightarrow 4\text{Bi} + 3\text{CO}_2 \\
\text{Bi}_2\text{O}_3 + 3\text{CO} & \rightarrow 2\text{Bi} + 3\text{CO}_2 \\
\text{Bi}_2\text{O}_3 + (3 - 2x)\text{CO} & \rightarrow 2\text{Bi}_2\text{O}_3 + (3 - 2x)\text{CO}_2
\end{align*}
\]

Carbon might directly react with Bi\(_2\)O\(_3\) or first react with oxygen to form CO. Then Bi\(_2\)O\(_3\) powders were reduced into Bi or its suboxide under a reducing atmosphere with CO presence.
Secondly, the Bi and BiO vapor with a low melting point would evaporate and be continuously transferred to the low-temperature region to form nanosized droplets, which are ideal nuclei for Bi$_2$O$_3$ nanostructure growth. These droplets can enhance the adsorption and diffusion of Bi oxides at the tips of Bi$_2$O$_3$ nanostructures during growth.

Finally, due to further oxidation, the concentration of oxygen in the droplets increases, and then Bi$_2$O$_3$ nanostructures started to form as given by:

$$4\text{Bi} + 3\text{O}_2 \rightarrow 2\text{Bi}_2\text{O}_3$$

$$2\text{BiO}_x + (3/2 - x)\text{O}_2 \rightarrow \text{Bi}_2\text{O}_3$$

Figure 4 shows the proposed growth process of temperature-dependent Bi$_2$O$_3$ micro/nanostructures. Bulk quantities of products are found in all temperature regions from I to III, however, the average width of the ribbons increases gradually from region I to III. According to Blackley and Jackson’s proposal, the nucleation probability can be expressed as:

$$P_n \propto \exp\left[-\frac{\sigma^2 \pi}{(k^2 T^2 \ln \alpha)}\right]$$

where $\sigma$ is the edge energy per atom, $k$ is the Boltzmann constant, $T$ is the temperature in Kelvin, and $\alpha$ is the
supersaturation ratio in the vapor. Based on this equation, two-dimensional (2D) nucleation events will increase when the temperature and supersaturation of the gas reactant are increased. The dependence of $P_N$ on $T$ and $\alpha$ has been verified in other metal oxide growth by VPT method.\textsuperscript{21–24}

In our case, both the temperature and supersaturation of the gas reactant are higher in the region closer to the source material. Thus, 2D nucleation is predominant in higher temperature region (region II–III) by the agglomeration Bi or Bi suboxide droplets. Since the diffusion length of the seed (Bi or Bi suboxide) droplets is larger at higher substrate temperature, the size of the nucleation droplets are expected to be much larger at higher temperature region III, which corresponds well with the SEM images taken from different regions after synthesis for 1–2 min. Since the mobility of adatom is higher at a higher temperature region in terms of thermodynamics, the adatom BiO\textsubscript{x} molecular species deposited on the base and surface area of the ribbon could move quickly to feed the continuous growth of the ribbon. Therefore, the gradient of deposition temperature and supersaturation level of vapor reactants led the growth of Bi\textsubscript{2}O\textsubscript{3} from nanoribbons (region I) to microribbons (regions II and III).

4. CONCLUSION

In summary, 1D single crystalline Bi\textsubscript{2}O\textsubscript{3} micro/nanoribbons have been synthesized for the first time in a single process by the VPT method without the presence of any catalyst or template. The product morphologies are temperature-dependent, thus can be collected from different temperature regions. The widths of Bi\textsubscript{2}O\textsubscript{3} ribbons varied from 0.2 to 20 \textmu m and the thickness was in the range of 0.1–2 \textmu m and the length reached millimeter range. The composition and structural analysis by XRD, XPS, HRTEM, and Raman scattering spectra confirmed the single-crystalline nature of Bi\textsubscript{2}O\textsubscript{3} micro/nanoribbons. PL spectrum from a single Bi\textsubscript{2}O\textsubscript{3} microribbon showed a defect-related broadband emission in the visible region. The growth of Bi\textsubscript{2}O\textsubscript{3} ribbons is controlled by the self-catalyzed VS mechanism and
different morphologies were related to the temperature and supersaturation gradient.

References and Notes


Received: 10 November 2009. Accepted: 24 February 2010.