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One-dimensional structures of Bi_2O_3 synthesized via metalorganic chemical vapor deposition process

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Abstract

We have demonstrated the synthesis of one-dimensional (1D) structures of bismuth oxide (Bi_2O_3) by a reaction of a trimethylbismuth (TMBi) and oxygen (O_2) mixture at 450 °C. Scanning electron microscopy showed that the product consisted of 1D materials with width or diameters less than 1 μm and lengths up to several tens of micrometers. The X-ray energy dispersive spectroscopy revealed that the materials contained elements of Bi and O. The results of X-ray diffraction and selected area electron diffraction pattern indicated that the obtained Bi_2O_3 were crystalline with monoclinic structure.

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Keywords: A. Nanostructures; B. Chemical synthesis; C. Transmission electron microscopy

1. Introduction

The discovery of carbon nanotubes has initiated an exciting, challenging, and rapidly expanding research field for one-dimensional (1D) nanostructures [1]. Since 1D nanostructures are of great interest for their novel physical properties [2–6], considerable efforts have been placed on the synthesis and characterization of those materials over the past several years.

The bismuth oxide (Bi_2O_3) has attracted great attention due to their applications in several technological fields, such as oxide-ion conductors, piezo-optic materials, solar cells, gas sensors, and ceramic glass manufacturing [7–11]. Additionally, Bi_2O_3 is a component of various important electroceramic oxides including Bi–Sr–Ca–Cu–O superconductors [12,13], and Sr–Bi,Ta–O/Sr–Bi–Nb–Ta–O ferroelectric oxides, which have applications in non-volatile computer memories [14].

In contrast to their scientific and technological importance, the synthesis of 1D structures of Bi_2O_3 has not received great attention; Yang et al. synthesized Bi_2O_3 nanotubes (NTs) by oxidizing the bismuth NTs in air [15] and Takeyama et al. reported the growth of Bi_2O_3 rods using BiI_3 and O_2 [16]. In this letter, we report the fabrication of crystalline 1D materials of Bi_2O_3 using a reaction of a trimethylbismuth (TMBi) and O_2 mixture.

2. Experimental

A schematic illustration of the metalorganic CVD (MOCVD) reactor used in our experiments was previously reported [17]. We used p-type Si(100), precleaned with acetone and methanol, as starting materials onto which a layer of Au (about 50 nm) was deposited by the radio frequency magnetron sputtering. In the growth process of Bi_2O_3, TMBi and O_2 were used as the Bi and O sources, respectively, with Ar as the carrier gas. The temperature of TMBi bubbler was fixed at −5 °C. The Ar and O_2 gas flow rates, respectively, were set to 20 standard cubic centimeters per minute (sccm) and 30 sccm. The reactor pressure of approximately 1 Torr was maintained during the growth for 1 h. The substrate temperature was measured to be approximately 450 °C. After cooling down to room temperature, a thin layer of wool-like material was found on the surface of the substrate.

The resulting material was characterized by X-ray diffraction (XRD, X'pert MRD-Philips) using Cu K_α radiation ($\lambda = 0.154056$ nm), scanning electron microscopy (SEM, Hitachi S-4200), and transmission electron microscopy (TEM, Philips CM-200) with energy-dispersive X-ray (EDX) spectroscopy installed. TEM specimens were prepared by

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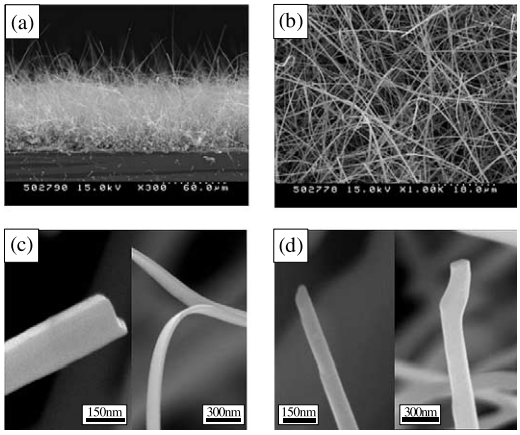

Fig. 1. (a) Side-view and (b) plan-view SEM image of the products. (c, d) Enlarged SEM images showing the individual 1D structures.

sonicating in alcohol by ultrasonic treatment, and subsequently dropping onto a porous carbon film supported on a copper grid.

3. Results and discussion

The whole substrate surface was found to be covered with the uniform film of dense structures (Fig. 1(a)). Fig. 1(b) shows the typical plan-view SEM image of the deposits, indicating that this raw material consists of aggregates of 1D structures. The SEM images reveals that the growth direction of the structure is randomized. Fig. 1(c) shows the nanostructures with a rectangular cross-section, indicating that it has the thickness less than 1/3 of the widths. Fig. 1(d) shows the 1D structures with a circular cross-section. Close examination reveals that both straight and curved morphologies are apparent and no metal particle can be seen at tips of the 1D structures (Fig. 1(c) and (d)). Statistical analysis of many SEM images shows that most structures have average diameters or widths ranging from 60 to 800 nm and the lengths reach up to several tens of micrometers.

Fig. 2 displays the typical XRD spectrum of the products. Apart from the Si- and Au-related peaks which are from the underlying substrate, all recognizable reflection peaks including (002), ($\bar{1}$12), ($\bar{1}$21), (012), ($\bar{2}$02), and ($\bar{2}$23) correspond to

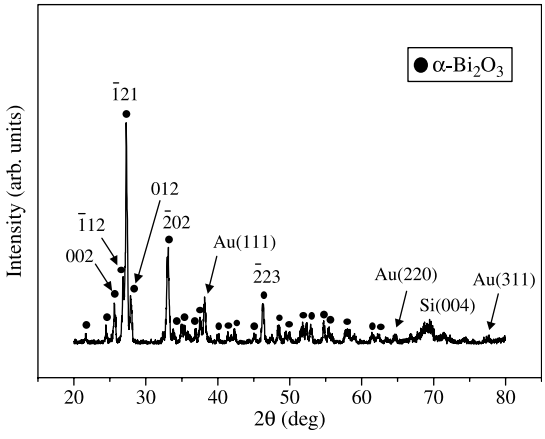

Fig. 2. X-ray diffraction pattern recorded from the products.

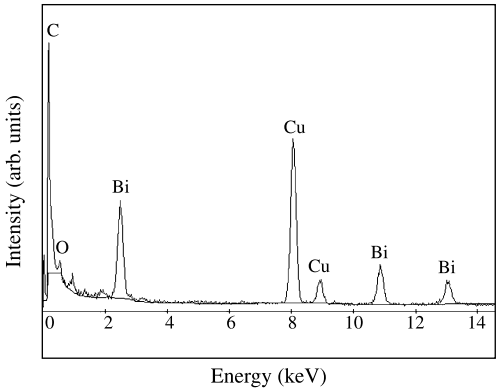

Fig. 3. EDX pattern of a Bi_2O_3 structure.

the monoclinic α-Bi_2O_3 structure with lattice constants a=5.848 Å, b=8.166 Å, and c=7.510 Å (JCPDS: 27-0053), revealing the production of α-Bi_2O_3 deposits.

The EDX analysis indicates that the 1D materials consist of only Bi and O elements, regardless of position, from the stems to the ends (Fig. 3). C peaks and Cu peaks were raised from TEM Cu grid coated with amorphous carbon film. Although we do not know the exact chemical composition, we reveal that the as-synthesized structure comprises Bi and O elements.

Fig. 4(a) shows a representative TEM image of a single 1D structure. The structure has an almost uniform width along

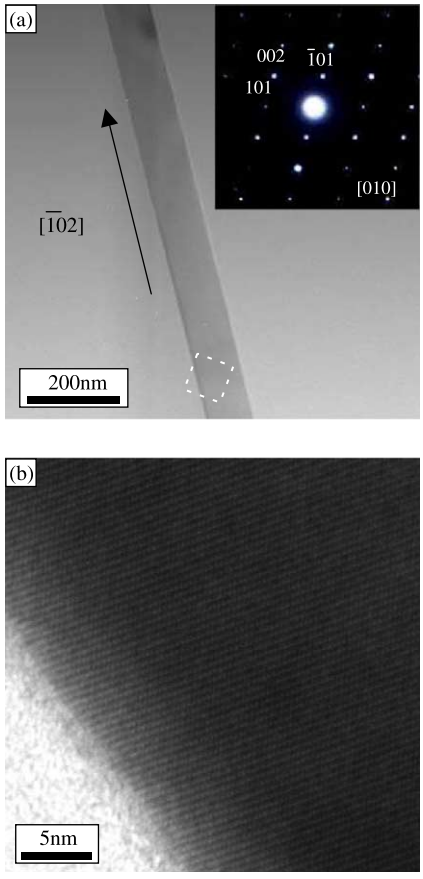

Fig. 4. (a) TEM image of a single structure (inset: corresponding electron diffraction pattern). (b) HRTEM image taken at the area marked with the dotted box in (a).

the length direction. The length direction of the structure, indicated by an arrow, is along the [$\bar{1}$02] direction. Selected area electron diffraction (SAED) patterns, with the incident electron beam parallel to the [010] direction, were recorded perpendicular to the long axis of the structure (inset in Fig. 4(a)). The reflections in the SAED pattern correspond to the lattice planes of bulk Bi_2O_3, indicating that the 1D material is crystalline. Fig. 4(b) shows the visible lattice fringes of the high resolution TEM (HRTEM) image recorded near the edge of the 1D material in Fig. 4(a), suggesting that the 1D material is structurally uniform with a smooth surface.

In the present work, we guess that the Bi-containing vapor which is in ambient or adsorbed on substrate surface combines with oxygen gas, resulting in the formation of solid Bi_2O_3 on the substrate. Although Au-coated Si was used as a substrate material, SEM image, TEM image (not shown here) and EDX measurement coincidently indicated that the structure tips were free of Au-related particles, ruling out the possibility that the growth of Bi_2O_3 in the present route was dominated by a tip-growth vapor–liquid–solid (VLS) mechanism. To investigate the role that Au played in the formation of Bi_2O_3 nanomaterials, the Si substrate without the Au layer was employed in the experiment under the same condition, revealing that thicker but less dense 1D structures were formed on bare Si substrate. At this moment, the specific role of Au layer in the formation of the $Bi_2O_3$1D nanomaterials by MOCVD is not clear. Although we have succeeded in providing a method to fabricate the 1D materials of Bi_2O_3 on a large scale, we believe that further experimental study is needed to fine-tune the growth process and to clearly understand the synthesis mechanism.

4. Conclusion

In summary, we have achieved the growth of Bi_2O_3 1D nanomaterials through the MOCVD technique. We have applied XRD, SEM and TEM techniques to characterize the structure of the samples. Most materials obtained are rectangular or circular cross-sectional shape with width or diameter of 60–800 nm and lengths up to several tens of micrometers. The 1D materials are composed of Bi_2O_3 with monoclinic structure.

Acknowledgements

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