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H.W. KIM✉
J.H. MYUNG
S.H. SHIM
C. LEE

Growth of Bi_2O_3 rods using a trimethylbismuth and oxygen mixture

School of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea

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ABSTRACT We have successfully grown the rod-like structures of bismuth oxide (Bi_2O_3) on silicon substrate by a reaction of a trimethylbismuth (TMBi) and oxygen (O_2) mixture without using any catalyst. We have characterized the samples by means of X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The products consisted of bundles of rod-like structures. The Bi_2O_3 rods were of monoclinic structure.

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1 Introduction

Bismuth oxide (Bi_2O_3) is an interesting material characterized by significant band gap, high refractive index and dielectric permittivity, as well as marked photoconductivity and photoluminescence [1–3]. All these characteristics make Bi_2O_3 suitable for several applications such as microelectronics [4], gas sensors [5], optical coatings [6], and ceramic glass manufacturing [7].

Since there has been much interest in one-dimensional (1D) nano-scale or sub-micron scale materials due to their potential in mesoscopic physics and nanodevice technique considerable efforts have been placed on the synthesis and characterization of those materials over the past several years.

Up to the present, not many researchers have demonstrated the deposition of Bi_2O_3 1D structures; Bi_2O_3 needles were fabricated by the hydrothermal method [8] and Bi_2O_3 nanotubes were prepared by a self-sacrificing template method [9]. Recently, Bi_2O_3 rods was reported to grow by means of halide chemical vapor deposition (CVD) [10]. In this communication, we demonstrate the production of Bi_2O_3 rod-like crystals using a reaction of a trimethylbismuth (TMBi) and O_2 mixture. We have employed the bare silicon (Si) substrate without metal catalyst, which will pave the way for integration of future devices with developed Si integrated circuit technology.

✉ Fax: +82-32-860-7544, E-mail: hwkim@inha.ac.kr

2 Experimental

Bismuth oxide was deposited on Si(100) substrates using an metalorganic CVD (MOCVD) system shown in Fig. 1 [11]. O_2 and TMBi were used as oxygen and bismuth precursors, respectively. Before being loaded into the reactor, the substrates were precleaned with acetone and methanol. Ar was used for carrying TMBi. The flow rates of O_2 and TMBi were set at 30 and 20 standard cubic centimeters per minute (sccm), respectively. The bubbler of TMBi was maintained at −5 °C. The pressure in the reactor during the growth was kept at 1 Torr and the growth was conducted for 1 h. Since our preliminary experiments indicated that few 1D structures were found to grow at substrate temperatures below 400 °C, the growth temperature in this study was set to 450 °C.

The structural properties of the as-grown products were investigated using X-ray diffraction (XRD) with Cu K_α radiation ($\lambda = 0.154056$ nm), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) with energy-dispersive X-ray (EDX) spectroscopy attached. For TEM observation, the products were ultrasonically dispersed

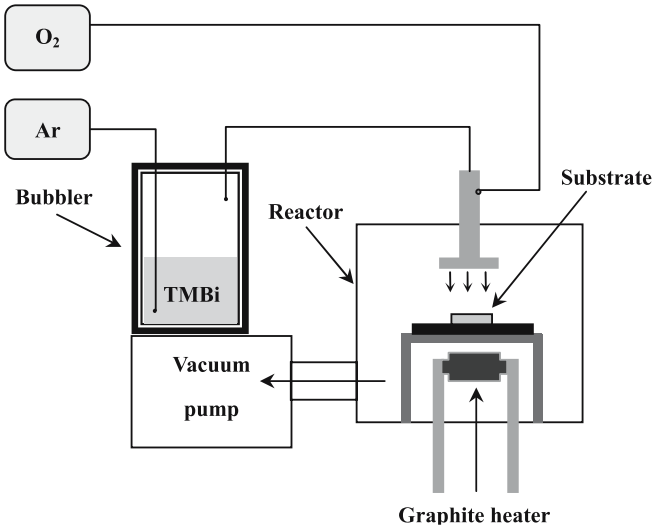

FIGURE 1 Schematic illustration of the apparatus used in this work

FIGURE 2 Typical SEM image of the product at a substrate temperature of 450 °C

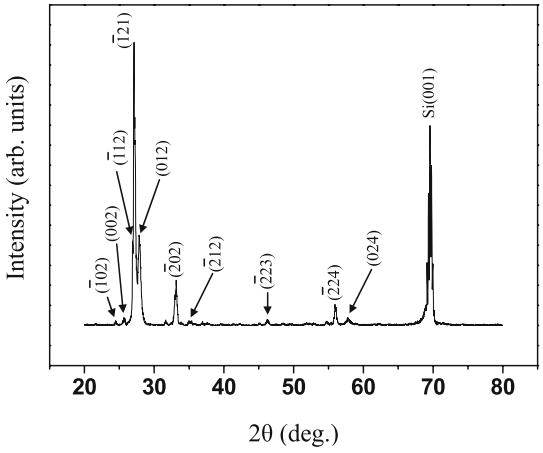

FIGURE 3 XRD spectrum obtained from the product deposited on Si substrate

in acetone and drops were placed on a carbon-coated copper grid.

3 Results and discussion

The whole substrate surface was found to be covered with the uniform film of dense structures. Figure 2 shows the typical side-view SEM images of the deposits at a substrate temperature of 450 °C. The raw material consists of aggregates of 1D structures, with their growth directions randomized. We observe that the diameter of many rod-like structures decreases with increasing the length from the bottom to the top. Statistical analysis of many SEM images shows that most rods have lengths up to several tens of micrometers and have sharp tips of several tens of nanometers in diameter.

Figure 3 shows the XRD spectrum of the products. Apart from the Si-related peak which is from the underlying substrate, all recognizable reflection peaks including (102), (002), (112), (121), (012), (202), (212), (223), (224), and

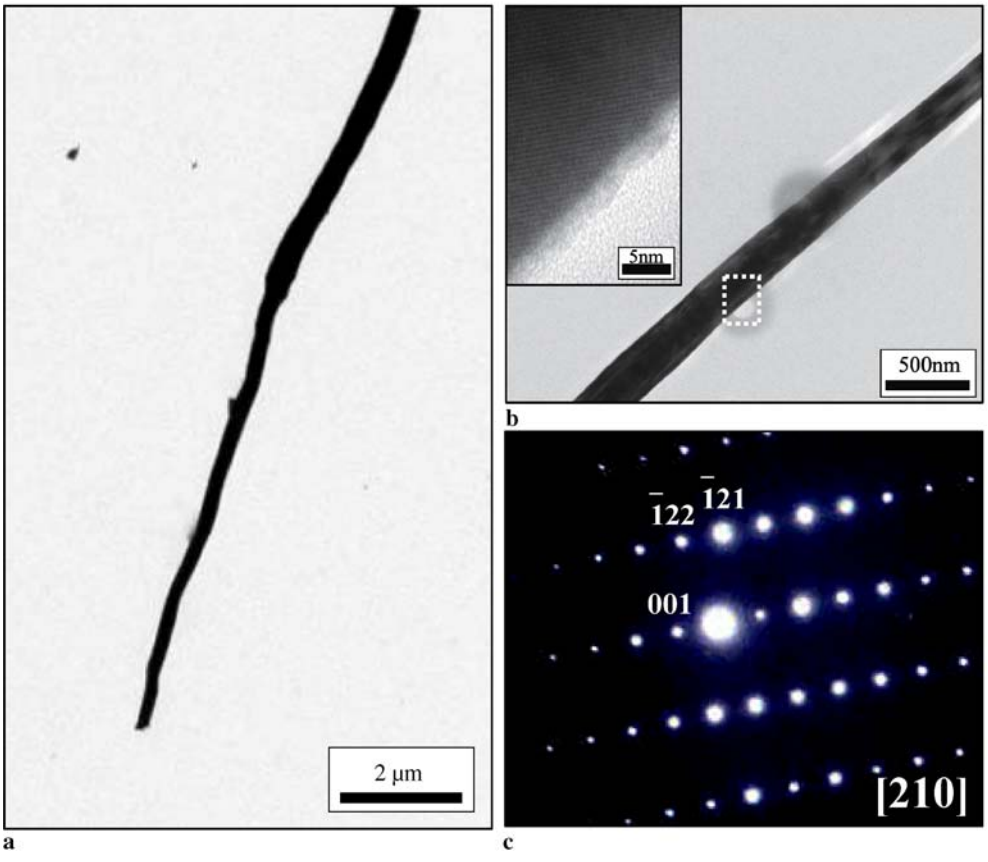

FIGURE 4 (**a**,**b**) TEM image of a single rod (*Inset*: HRTEM image of the marked area). (**c**) Corresponding electron diffraction pattern

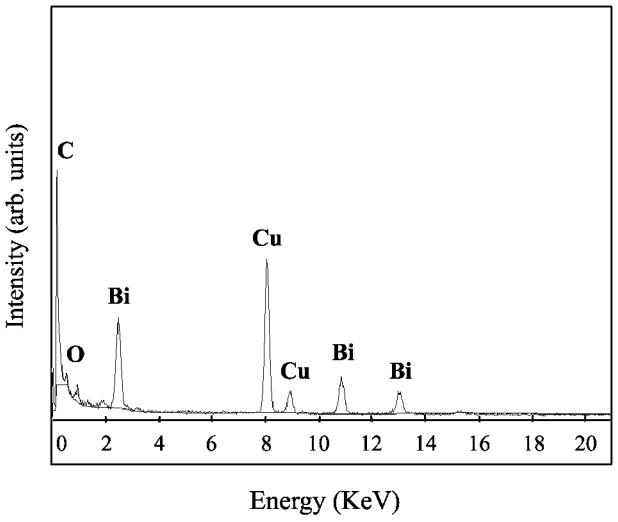

FIGURE 5 EDX spectrum associated with the rod shown in Fig. 4

(024) can be readily indexed to 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). No obvious reflection peaks from the impurities, such as unreacted Bi or other bismuth oxides, were detected, indicating the high purity of the products.

Figure 4a shows a low magnification TEM image of a rod, with its diameter gradually decreasing from bottom to the tip and with no nanoparticle at its tip. Figure 4b is a TEM image of a rod which shows a relatively smooth surface along the length direction. The upper left inset in Fig. 4b shows the High resolution TEM (HRTEM) image of the area marked in Fig. 4b. The visible lattice fringes imply that the rod may be single crystalline. Figure 4c shows the selected area electron diffraction (SAED) pattern which was recorded perpendicular to the rod long axis. It can be indexed for the [210] zone axis of crystalline monoclinic α-Bi_2O_3 structure. The SAED pattern was found to be independent of position in the 1D structure, from the bottom to the tip. In the EDX spectrum depicted in Fig. 5, only peaks associated with Bi and O elements are present. The Cu and C shown in the spectrum originate from the TEM Cu grid coated with amorphous carbon film. Although it is difficult to determine the Bi/O ratio of the rod quantitatively due to the uncertainty of intensity of the EDX detection, we reveal that the rods comprise Bi and O, agreeing with XRD analysis.

In the present work, no metal catalyst was used and thus no particle was observed at the ends of the 1D structures. Therefore, we surmise that the growth mechanism can be understood on the basis of a self-catalytic process with the characteristics of vapor–solid (VS) growth mechanism. Herein, during the process, we surmise that the TMBi vapor in ambient or adsorbed on the substrate surface combines with oxygen gas, resulting in the formation of solid Bi_2O_3 rods on the substrates. More investigation is underway to derive the detailed mechanism for the formation of Bi_2O_3rod-like structures.

4 Conclusions

We have achieved the growth of Bi_2O_3 rods directly on Si substrates through the MOCVD technique at a substrate temperature of 450 °C. The as-synthesized product consists of the rod-shaped materials with lengths up to several tens of micrometers. The Bi_2O_3 rods were crystalline with monoclinic structure.

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