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Fabrication of δ-Bi_2O_3 Nanowires

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δ-Bi_2O_3 nanowires were successfully fabricated using a thermal enhanced process on electroplated Bi nanowires. Bi was first prepared using template-assisted electroplating. After thermal modification at 350°C for 12 h in air, Bi_2O_3 nanowires with high-temperature phase (δ-phase) were obtained. A Bi/Bi_2O_3 core-shell structure was examined by high-resolution transmission electron microscopy (HRTEM) after the Bi nanowires heated at 250°C for 12 h. The oxidation reaction of Bi occurred at temperatures below the melting point of Bi (271.3°C). According to the analysis of HRTEM, the formation of high-temperature δ-phase is caused by the coherent relationship between Bi and Bi_2O_3 nanowires.
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Bi_2O_3 was used as a good dielectric material in many applications such as optical coatings and capacitors. δ-Bi_2O_3 was also of the highest oxygen ionic conductivity (1 S/cm at 800°C) for high-temperature electrochemical application such as solid oxide fuel cells (SOFCs) and oxygen pumps. However, the presence of the highest ionic conductivity was due to the fluorite structure with 25% anionic vacancies. Hence, δ-phase was the only favored structure for solid electrolyte. Owing to its defective structure, the δ-phase is only stable at 723 to 823°C and may be stabilized by adding some rare earth oxide.[1-5] Solid-state synthesis of doped bismuth oxide was widely investigated to obtain a stable δ-phase with fluorite structure.[6-11] For SOFC application, a nanostructure established at the anode/electrolyte interface would increase the triple phase boundary (TPB) to minimize the concentration polarization causing the degradation of voltage. To obtain an anode/electrolyte interface with nanostructure, a facile process was studied here to form nanowires of solid electrolyte using anodic alumina oxide (AAO) template. Electroplating was a useful method for filling materials into nanoporous AAO templates. Based on Swizter's research, single-crystal δ-phase Bi_2O_3 was obtained by electrodeposition at low temperature.[12,13] Thus, nanostructured δ-Bi_2O_3 may be fabricated using an electrodeposition process with an AAO template. However, according to Swizter's work, the electrolyte solution used was consisted of 2.5 M KOH which would dissolve AAO membrane. In this work, metallic Bi nanowires were fabricated by electroplating in an ethylene glycol/water electrolyte solution containing $Bi(NO_3)_3 \cdot 5H_2O$. δ-Bi_2O_3 nanowires were obtained by heat-treatment at temperatures greater than 250°C. These Bi_2O_3 nanowires were characterized by high-temperature X-ray diffraction (HTXRD), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM).

Experimental

Preparation of AAO template.—The nanoporous Al_2O_3 membrane was fabricated by anodization of Al metal. An Al sheet (99.997% purity; Alfa aluminum foil; Johnson Matthey, Ward Hill, MA) of 1 mm thick was used as the starting material for anodization. One-step anodization was then conducted in 0.3 M oxalic acid solution under a constant voltage of 40 V in a thermostated bath. The anodized specimens were then immersed in a saturated $HgCl_2$ solution to remove the remaining aluminum substrates, and pore opening was then conducted by chemical etching in 10 wt % phosphoric acid solution at 30°C to remove the barrier layer. A 20 nm thick Pt layer was deposited on the backside of the porous alumina as the working electrode.

Electroplating of Bi nanowires.—The deposited Pt layer served as the working electrode in a conventional three-electrode cell for electrodeposition using a potentiostat/galvanostat (263A). A graphite plate was used as the counter electrode. The electrolyte solution was composed of 48.57g $Bi(NO_3)_3 \cdot 5H_2O$ 700 mL ethylene glycol and 300 mL distilled water. To ensure a stable electrodeposition process, the solution was stirred for 1 day to remove the bubbles. Owing to the neutral solution, the AAO template would not be dissolved during deposition process and remained its nanoporous structure. Hence, the electrochemical method was applied at −0.15 V *vs*. Ag^+/AgCl reference electrode for 10 h to overfill the AAO template with Bi. After rinsing with distilled water, the deposited samples were pasted on a solid substrate (Au coated Si wafer) by Ag adhesive. The specimen was bathed in 3 M aqueous NaOH for 2 h to dissolve the AAO template. To remove the residual NaOH solution, the samples were also immersed in water for 30 min and rinsed with distilled water several times.

Thermal modification of Bi nanowires.—In this study, the nanowires of Bi_2O_3 were obtained by oxidizing Bi nanowires. HTXRD (Rikagu Multuflex) was used for characterizing the oxidation of metallic Bi nanowires at various temperatures in air. The specimen was placed in the high-temperature attachment for HTXRD analysis. With the heating rate of 10°C/min, the temperatures of specimens were held at 50, 150, 250, 350, 450, and 550°C for 30 min. The scanning condition was 2°/min from 20 to 80° of 2θ angles with 30 kV and 20 mA Cu kα radiation. According to the HTXRD results, as-fabricated specimens were also annealed at 250, 350, and 450°C for 12 h in air atmosphere. To collect the nanowires for TEM analysis, the nanowires were scraped off and dispersed in ethanol. Then, several drops of alcohol were to put on the 325 mesh copper grid. A transmission electron microscope (TEM, JEOL-3010) and electron diffraction (ED) attached to HRTEM were used for structural analysis of single nanowire.

Results and Discussion

Fabrication of metallic bismuth nanowires array.—Although, Bi nanowires have been successfully prepared in nitric acid solutions,[16-20] in this study, to avoid the dissolution of AAO template, an organic solvent, ethylene glycol, was chosen to dissolve bismuth nitrate prentahydrate. After applying a voltage of −0.15 V *vs*. Ag^+/AgCl reference electrode for 10 h, Bi was also successfully deposited by electroplating and filled into the nanopores of AAO in the neutral electrolyte solution. Figure. 1 shows the SEM of Bi nanowires after removal of AAO template. Consequently, the Bi metal deposited in the pores of AAO template was exposed and became free-standing Bi nanowires. The inset clearly shows the Bi nanowire array with an average diameter of 47 nm that is close to the pore diameter of AAO template.

Oxidation of metallic bismuth nanowires.—HTXRD was used for characterizing the phase transformation of bismuth nanowires in air atmosphere. The *in situ* HTXRD was taken from an as-fabricated

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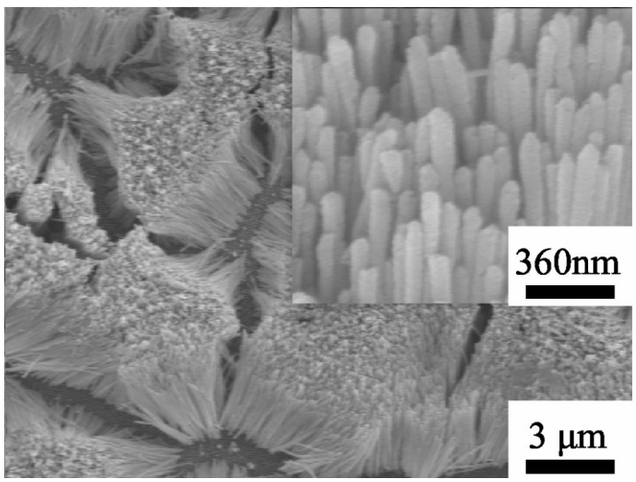
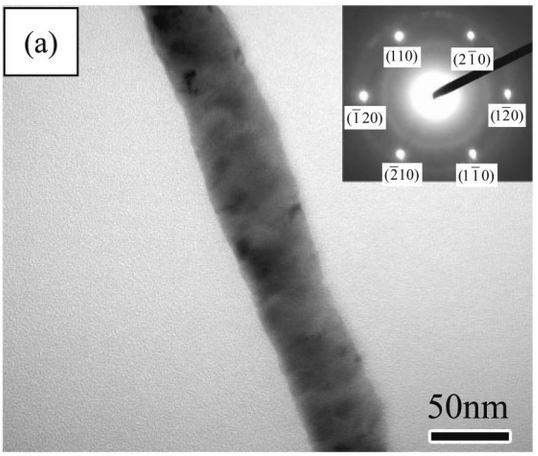


Figure 1. SEM of Bi_2O_3 nanowires array.



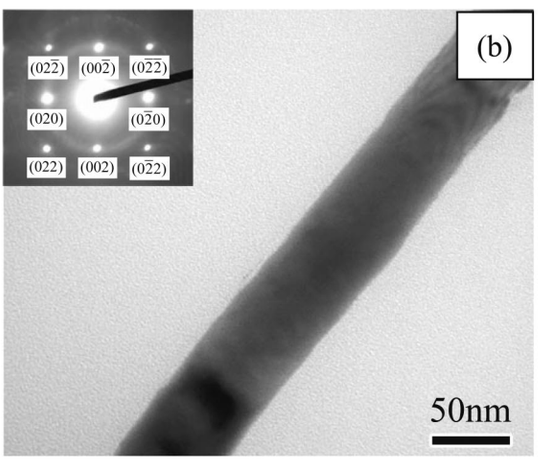


Figure 3. TEM images and SAED patterns of (a) as-fabricated Bi nanowire (b) δ-Bi_2O_3 nanowire.

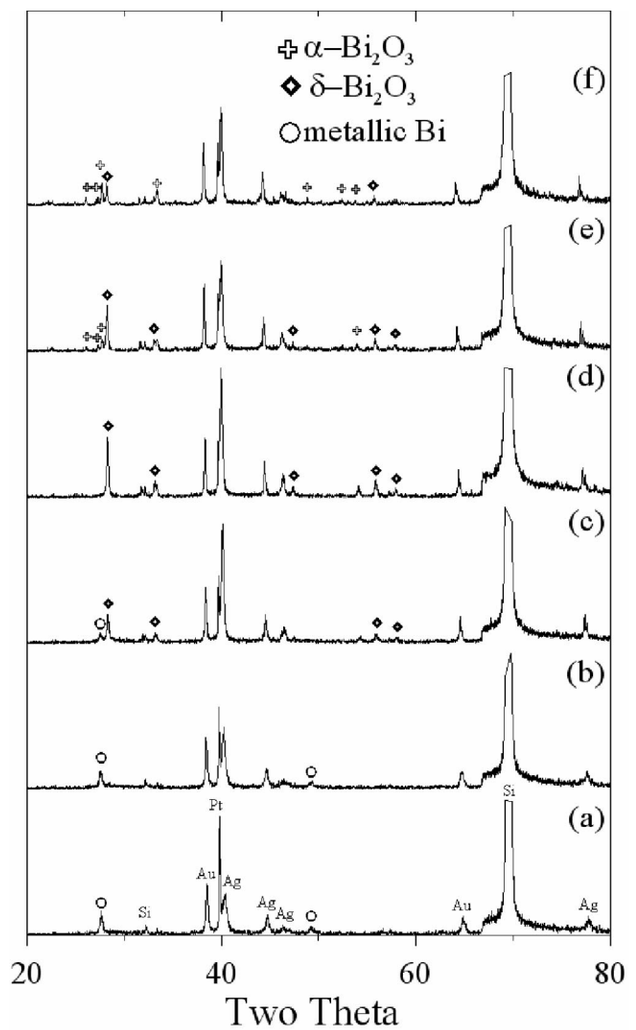


Figure 2. HTXRD traces of metallic Bi nanowires at (a) 50, (b) 150, (c) 250, (d) 350, (e) 450, and (f) 550°C.

specimen after heated from 50 to 550°C at interval of every 100°C for 30 min. Figure 2a-f shows the XRD patterns of bismuth nanowires heated at temperatures ranging from 50° to 550°C. In Fig. 2a, the reflections of bismuth with rhombohedral lattice were observed, while the reflections of Si, Ag, Au, and Pt are from the substrate, adhesive, conductive layer and retained electrode. Figure 2a-d show the XRD patterns of heat-treated bismuth nanowires. In Fig. 3c, the reflections representing the cubic lattice of δ-Bi_2O_3 were observed. Thus, the oxidation of bismuth nanowires began around 250°C.

The increasing intensity of cubic reflections indicates that the extent of Bi oxidation increased with increasing temperature. Although it is known that the equilibrium phase of Bi_2O_3 at temperatures below 723°C is α-Bi_2O_3, δ-Bi_2O_3 was formed due to the oxidation of nanosized bismuth. Similar phase stabilization of δ-Bi_2O_3 was also observed in the electrodeposition δ-Bi_2O_3 film.[12,13] In addition, δ-Bi_2O_3 film could also be synthesized by thermal evaporation method.[14,15] However, owing to some restricted condition of AAO template, thermal enhanced method was a preferred way to fabricate δ-Bi_2O_3 nanowires array. The reflection intensity of δ-phase decreased as the temperature increased up to 550°C as Fig. 2e and f show. This implies that the as-oxidized δ-Bi_2O_3 was a metastable phase. Consequently, the phase transformation of Bi_2O_3 nanowire from δ to α phase occurred as the temperature increased to

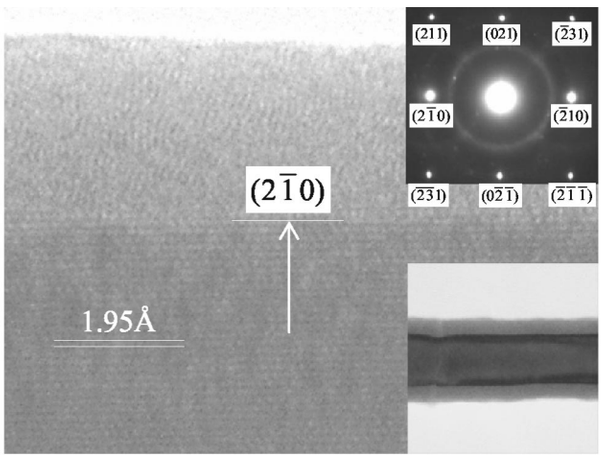


Figure 4. HRTEM images and SAED pattern of Bi nanowire annealed at 250°C for 12 h.

550°C. Hence, the oxidation reaction of metallic bismuth caused the formation of metastable δ-Bi_2O_3. As the temperature increased, the equilibrium phase of α-Bi_2O_3 was obtained.

TEM analyses of Bi and Bi_2O_3 nanowires.—According to HTXRD results, the oxidation of Bi nanowires was clearly observed at 350°C. Hence, the Bi nanowires were annealed at 350°C for 12 h. Figure 3a shows the TEM image of single Bi nanowire. Again, the diameter of Bi nanowire is ~47 nm. The inset shows the select area diffraction pattern (SAED) of Bi nanowires along [001] zone axis of a rhombohedral lattice ($R\bar{3}m$). The electron diffraction pattern shown in Fig. 3b was corresponding to the [100] zone axis of cubic δ-Bi_2O_3 ($Fm\bar{3}m$). Compared to Fig. 3a, the diameter of the δ-Bi_2O_3 nanowire (50 nm) is greater than that of Bi nanowire (42 nm). That is because the density of Bi_2O_3 (8.9 g/cm^2) is less than that of Bi metal (9.8 g/cm^2). The TEM results suggested that Bi_2O_3 nanowires with metastable δ-phase could be synthesized at 350°C.

HRTEM observation of core-shell Bi/Bi_2O_3 nanowire.—In preparation of nanostructure materials, the effect of nanoscale on the crystal structure was very important. Some studies pointed out that δ-Bi_2O_3 film could be synthesized by oxidation of thermal evaporated Bi.[14,15] In addition, δ-Bi_2O_3 film was also prepared by electrochemical method.[12,13] Hence, the formation of δ-Bi_2O_3 nanowires was not due to the nanostructure. To investigate the interface between Bi and δ-Bi_2O_3, nanowires with core-shell structure was prepared. According to the HTXRD result as shown in Fig. 2c, both Bi and Bi_2O_3, were present. To further investigate the oxidation process of Bi nanowires, the specimen was annealed at 250°C for 12 h. From the TEM images shown in Fig. 4, a core-shell structure was formed after oxidation. An obvious interface of Bi/Bi_2O_3 was observed. From the HRTEM image, obvious lattice image with d-spacing of 1.95 Å was found in the center of the nanowire. The SAED pattern from the same zone axis is also shown on the HRTEM image. According to the identification of pattern, the diffraction was along $[\bar{1}2\bar{4}]$ zone axis. Hence, based on the orientation and its d-spacing, the lattice line shown in Fig. 5 was imaged as $(2\bar{1}0)$ planes. In addition, the $(2\bar{1}0)$ plane in Bi was coherent with the (110) plane in Bi_2O_3. A schematic diagram of the lattice relationship between

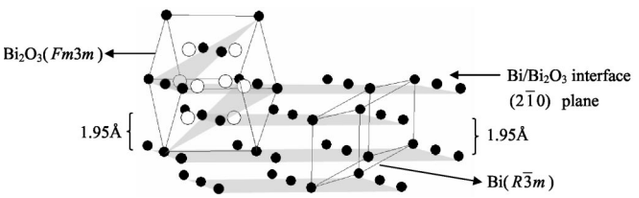


Figure 5. A schematic diagram of the lattice relation between Bi and Bi_2O_3.

Bi and Bi_2O_3 is shown in Fig. 5. As Fig. 5 showed, the arrangement of Bi atoms was similar to that in Bi_2O_3. It was suggested that the formation of δ-Bi_2O_3 was due to the following two steps. First, Bi atoms reacted with oxygen and formed Bi-O ionic bonding. Second, the lattice was adjusted to favor the formation of δ-Bi_2O_3. Although the equilibrium phase of Bi_2O_3 at low temperature was monoclinic, the formation of metastable δ-Bi_2O_3 was clearly enhanced by the coherent relationship at Bi/Bi_2O_3 interface. Once the atomic diffusion is favored at high temperature, the rearrangement of cations and anions caused the transformation of δ-phase to α-Bi_2O_3.

Conclusions

With the assistance of AAO template, metallic Bi nanowires were first obtained by electroplating at applied voltage −0.15 V. After heat-treatment at 350°C, Bi transformed to δ-Bi_2O_3. Because little volume change was occurred during the thermal modification, the nanowires still remained freestanding. According to the crystal structure, the cationic position in the Bi and δ-Bi_2O_3 structures exhibited similar symmetry. Hence, rhombohedral Bi was of a coherent relationship with cubic δ-Bi_2O_3. From the structure characterization of Bi/δ-Bi_2O_3 interface in this work, it was suggested that the formation of the δ-phase was due to the presence of coherent planes of Bi$(2\bar{1}0)$ and $Bi_2O_3(110)$.

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