Ordered $CoSb_3$ Nanowire Arrays Synthesized by Electrodeposition

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Highly ordered $CoSb_3$ nanowire arrays have been fabricated successfully by direct current electrodeposition from aqueous solution into the pores of a porous anodic aluminum oxide (AAO) template. Extensive characterization of the as-synthesized sample has been performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDS). The analysis indicates that the $CoSb_3$ nanowires are single crystals with highly preferential orientation and the atomic ratio of Co to Sb is very close to 1:3.

Skutterudite compounds have stimulated great interest because they are promising thermoelectric (TE) materials suitable for several advanced applications.[1,2] Binary skutterudites have a body-centered cubic (bcc) crystal structure with space group $Im\bar{3}$, and is a very narrow, direct-band-gap semiconductor, which have the general formula MX_3 where M is Co, Rh, or Ir and X is P, As, or Sb.[3] In the skutterudite family, $CoSb_3$-based compounds have attracted by far the greatest interest. Not only it is with some of the best TE characteristics, but also the constituent elements are abundant, less volatile, and less expensive than most alternative skutterudities.

Single crystal, powder, and thin film of $CoSb_3$ have all been fabricated and analyzed,[4] but nanowires have not been reported in the literatures. Recent studies indicate that the thermoelectric properties of nanowires will be enhanced significantly compared with bulk materials.[5] The Seebeck coefficient can be increased because of the enhancement of electronic state density near E_F and the reduction of the lattice contribution to the thermal conductivity. Low-dimensional systems have already shown improvement in the thermoelectric figure of merit. In this paper, we report the successful AAO-template growth of large-area, continuous, and ordered $CoSb_3$ nanowires by controlling the solution concentrations, the potentials, and the pH at room temperature.

Alumina template with pore size of 60 nm was prepared by a two-step anodization process as described elsewhere.[6] With a voltage of 1.1 $V_{DC.}$ nanowire arrays of $CoSb_3$ were electrodeposited into the pores of the template in a three-electrode plating cell with a saturated calomel electrode (SCE) as reference electrode at 25 °C. The solutions used consisted of 0.01 M SbO^+, 0.10 M Co^{2+}, and 0.14 M tartaric acid. The Sb precursor must be dissolved in the presence of the tartaric acid before addition to the Co^{2+} solution in order to achieve the correct solubility. The pH of the solution was adjusted to 2.5 by adding 1 M HCl. The wire composition is sensitive to the pH value of the electrolyte solution. If pH of the solution is too low, Co composition will very low.

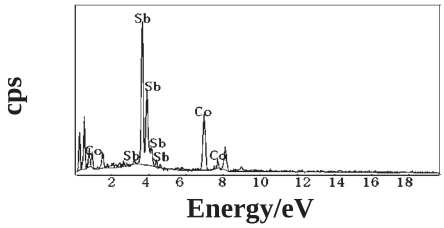

Figure 1. EDX spectrum of the as-synthesized nanowires and then dried in air at room temperature for further analysis.

The as-grown products were characterized and analyzed by X-ray diffraction with Cu Kα radiation ($\lambda = 1.5406$) in the range of $20° \leq 2\theta \leq 105°$ and scanning election microscopy. Transmission electron microscopy and selected-area diffraction (SARED) were employed to characterize the individual $CoSb_3$ nanowires. The chemical composition of the nanowires was determined by energy dispersive spectrometry (EDS).

Figure 1 shows the EDS examination which demonstrates the stoichiometry of the products. Within the uncertain of the EDS system, the ratio of cobalt to antimony (other signals from the AAM) is found to be approximately 1:3 as expected. Figure 2 shows the X-ray diffraction (XRD) pattern of the $CoSb_3$ nanowires embedded in AAO template. The XRD exhibits that only (420) and (840) peaks are discernible corresponding to a bcc structure with the lattice constant of $a = 9.024$ Å. These structure characters highly fit the XRD data of bulk material $CoSb_3$. Therefore, both XRD and EDX analyses show that the produced nanowires have been successfully alloyed in pure cubic-phase $CoSb_3$ by the electrochemical deposition technique in our conditions. In addition, the unique existent of (420) and (840) peaks indicates that all of the single $CoSb_3$ nanowire seems to be the single crystalline and preferentially oriented in the (420) direction along the nanowire axes. Furthermore, the X-ray rocking curve for (420) reflection has been examined to reveal the consistency of the orientation of the wires. As shown in the inset of Figure 2b, the diffraction is a sharp peak with a half maximum (FWHM) only 2.72°, preferential orientation within 1.36° of the

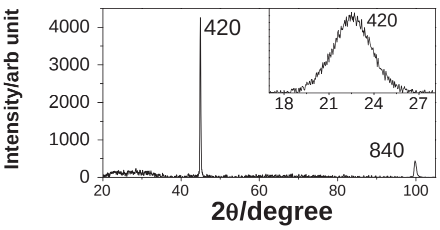

Figure 2. X-ray diffraction (XRD) spectrum of $CoSb_3$ nanowire arrays embedded in porous alumina template. Inset is the X-ray rocking curve for (420) solution.

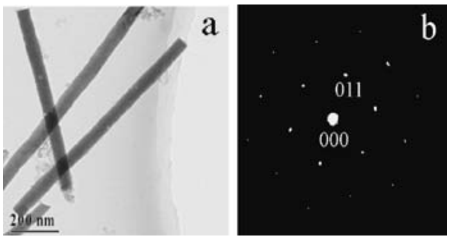

Figure 3. TEM examination for $CoSb_3$ nanowires. (a) morphology and (b) selected-area electron diffraction pattern from individual nanowire.

(420) direction. This observation indicates a perfect preferential orientation of our nanowires. Similar analyses for single crystalline samples of elemental Co nanowires show a larger distribution angle up to 5.6°.[6]

Figure 3a shows the typical TEM image of prepared sample. A number of nanowires are with the average diameter of 60 nm, which is nearly equal to the channel diameter in the AAM. That means that the optimal diameter of the nanowires can be obtained by alerting the channel diameter of the AAM to enhanced thermoelectric response superior to the bulk material. Figure 3b shows the selected-area electron diffraction pattern taken from one nanowire. The sharp SAED dots suggest that the nanowires are the single crystal with a cubic lattice structure corresponding to $CoSb_3$ and without any other product, which further confirms the XRD results.

The alloying process of $CoSb_3$ nanowires could be described by following. Firstly, the Co^{2+} and SbO^+ were transported into the nanochannels of AAM and they were adsorbed on the surface by the electric field force. The adsorbed Co^{2+} and SbO^+ got electrons to produce elemental Co and Sb by the reactions.

$$Co^{2+} + 2e^- = Co(s), \tag{1}$$

$$SbO^+ + 2H^+ + 3e^- = Sb(s) + H_2O. \tag{2}$$

The reduced Co and Sb atoms react with each other to form $CoSb_3$. Thus, the overall reaction can be expressed as:

$$Co^{2+} + 3SbO^+ + 6H^+ + 11e^- = CoSb_3(s) + 3H_2O. \tag{3}$$

Then $CoSb_3$ nucleated, grew and formed the single crystal $CoSb_3$ nanowires in the nanochannels of the template. Because of the electrochemical deposition conditions adapted in this work, not only the chemical reaction according to eq 3 was finished perfectly without other reaction products appeared, but also the product grew in single crystal and preferentially oriented in (420) crystallographic direction.

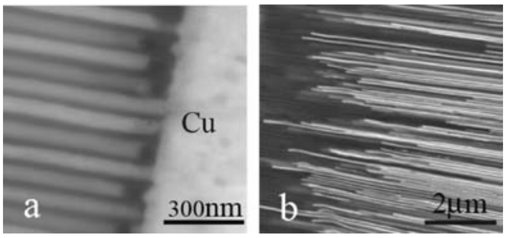

Figure 4. Cross-section view of $CoSb_3$ wire arrays by mechanical polishing: (a) bottom (b) top.

Figure 4a shows the cross-section view of the $CoSb_3$ nanowire arrays. The sample was prepared by cleaving the template and mounting it between two silicon wafers for mechanically polishing. One can see that some wires directly grew from the Cu paint, but some did not contact with the Cu layer, as is evident by the gap between the wires and the paint. This indicates that the nucleation might not occur in all of the pores simultaneously. But the wires are condensed and completely fill the pores, and no sign of unfilled pore can be observed. It implies that the nucleating rate and simultaneity do not affect the filling ratio of pores for $CoSb_3$ nanowire seriously. Turn to wires were with the different length, as shown in the Figure 4b. It may be due to the asynchronism of the nucleation. The previous works indicated that, for the alloys of $A_2^{V}B_3^{VI}$ binary compounds, the achievement of nanowire arrays deposed in large area and in high density determined by the simultaneity of the nucleating.[7] If the nucleation and filling occur rapidly in few pores, the wires will grow continuously, which may block the diffusion of solution down neighboring pores, halting growth.[7] In the present study, however, we found that this effect did not appear in our $CoSb_3$ system and the simultaneity of the nucleation only influenced the wire length.

In summary, large-area, continuous, and ordered $CoSb_3$ nanowires arrays have been produced by use of AAO-template electrodeposition at room temperature. XRD and TEM reveal that the as-deposited $CoSb_3$ nanowires crystallize in bcc structure with (420) orientation along the nanowire axes. It was found that the simultaneity of the nucleation, for $CoSb_3$ nanowire, may not affect filling ratio of pores seriously and only influence the wire length.

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