

The Electrodeposition of High-Density, Ordered Arrays of Bi_{1-x}Sb_x Nanowires

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Recent studies indicate that thermoelectric (TE) materials with improved efficiencies can be obtained through quantum confinement.¹ These results have stimulated research in the synthesis of nanowires of efficient bulk TEs because nanowires are the most highly confined materials that still retain electrical connectivity. Since a single nanowire does not carry a high enough current for TE applications, synthetic methods that yield highly dense nanowire arrays are of particular interest. Here we report the synthesis of dense arrays of Bi_{1-x}Sb_x nanowires with $>5 \times 10^{10}$ nanowires/cm² over an area of >2 cm². The individual wires are crystalline and highly oriented, with diameters of 40 nm and a composition of $x = 12$ –15 atom % Sb.

Bulk Bi_{1-x}Sb_x alloys are a good choice for study because they are among the best n-type low-temperature TE materials ($20 < T < 220$ K). For alloys with 12% Sb, the dimensionless figure of merit, *ZT*, is 0.88 at 80 K.² The properties of the alloy change dramatically with composition, and the Bi-rich alloys have large TE efficiencies.³ Dresselhaus et al. predicts a $ZT = 1.25$ –1.5 for nanowires with diameters of 35–45 nm and 10–15% Sb.⁴ The sensitivity of the properties of this alloy to composition, coupled with the potential to tune the electronic structure of the material through quantum confinement, offers intriguing possibilities for achieving a higher *ZT* than is attainable in the bulk.

The challenge in studying these alloys hinges on the difficulties of preparing homogeneous samples. There is a clear size and composition dependence of the magnetoresistance of sub-100-nm diameter nanowires of Bi_{1-x}Sb_x ($0 \leq x \leq 0.15$) made by pressure injection into a porous alumina template.⁵ However, detailed compositional analysis of 200-nm diameter nanowires made by pressure injection indicate that the concentration of Sb is heterogeneous along the length of the wire due to constitutional supercooling.⁶ Electrodeposition is an attractive alternative for filling the high-aspect ratio pores of alumina templates under ambient conditions.⁷ This method provides exquisite control over the composition and growth rate. Here we report the effects of solvent, solution concentrations, and potential on the composition and quality (crystallinity and morphology) of the resulting nanowire arrays.

Electrodeposition from aqueous solutions has been utilized for the deposition of thick films of Bi_{1-x}Sb_x of varying composition⁸ as well as for the deposition of elemental Bi⁹ and Sb¹⁰ wires. For these depositions, high concentrations of complexing agents were added to the electrochemical bath to increase the solubility of Sb salts. We have shown that dimethyl sulfoxide (DMSO) is a good alternative to water due to the higher solubility of Sb salts in DMSO¹¹ and that the composition of the resulting alloy is related

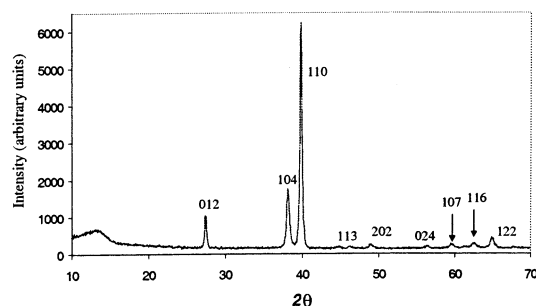


Figure 1. XRD of 40-nm Bi–Sb wires after the electrode layer has been removed mechanically. The high intensity of the 110 peak shows that the wires are oriented and that the preferred wire axis is $\langle 110 \rangle$.

to the ratio of Bi and Sb salts in solution. As described below, we have used conditions similar to those used to fabricate thick films and 200-nm nanowires to fabricate 40-nm nanowires with the predicted optimal composition of Bi_{0.85}Sb_{0.15}.

Alumina templates were prepared as described elsewhere.¹² Nanowires of Bi_{1-x}Sb_x were electrodeposited into the pores of the template in a three-electrode cell (EG&G PAR model 273 potentiostat/galvanostat) at 25 °C. The solutions used consisted of Bi(NO₃)₃·5H₂O and SbCl₃ (both Sigma Chemicals 99.97%) dissolved in DMSO (Fisher, 99.9%). The volume of the bath was 20 mL. Different Bi(NO₃)₃·5H₂O:SbCl₃ concentrations (0.06:0.02 M, 0.05:0.03 M) and different voltages (from –0.75 to –1.25 V vs Hg/Hg₂SO₄) were studied.

The wire composition is most sensitive to the concentrations of the Bi and Sb salts. For electrolyte compositions of 0.06 M Bi(NO₃)₃·5H₂O:0.02 M SbCl₃, and for a range of deposition potentials, the resulting nanowire arrays had a low Sb composition (1–7 atom % Sb) as determined by energy dispersive spectroscopy (EDS, JEOL 6300 SEM). By tuning the solution composition to 0.05 M Bi(NO₃)₃·5H₂O:0.03 M SbCl₃ we were able to increase the Sb content of the wires to 12–15 atom %, the range that is predicted to give optimum TE efficiency.

A representative X-ray diffraction pattern (Siemens D5000 diffractometer, Cu K α radiation) of the filled template is shown in Figure 1. All but two peaks can be indexed to the rhombohedral space group $R\bar{3}m$ (to which Bi, Sb, and Bi–Sb alloys belong). The peaks are shifted from the positions expected for a pure Bi sample toward higher 2θ values, indicating that the wires are a Bi–Sb alloy. Peak broadening is observed which may indicate a slight inhomogeneity in the composition of the wires. The relative intensities suggest texturing along a $\langle 110 \rangle$ direction, which is different from the orientation obtained by pressure injection with the normal to $\{012\}$ parallel to the wire axis.⁹

There are two remaining peaks. The broad peak at low angles is due to the amorphous alumina template. A small peak that can be assigned to diffraction from the $\{012\}$ planes of pure Sb is also

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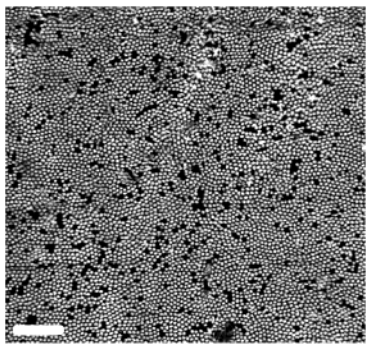


Figure 2. Backscattered SEM image of the bottom of the template containing 40-nm $\text{Bi}_{88}\text{Sb}_{12}$ wires with the Ag-sputtered electrode mechanically polished off. Bright regions are the filled pores; dark regions are where the wires failed to nucleate. Scale bar indicates 1 μm .

observed. However, when the metal electrode backing and approximately 1 μm of the nanowires are removed by mechanical polishing, the peak widths in the X-ray diffraction pattern are narrower, and there is no Sb_{012} peak. Fixed-time EDS point analysis performed at random locations throughout the wire arrays after polishing and systematic line scans along the axis of a single wire both reveal that the composition is homogeneous within 3–5 atom %. We conclude that the Sb is deposited during the initial stages of the electrodeposition process, but once steady-state conditions have been reached, the Bi-rich alloy with a relatively narrow composition range is formed.

To obtain the maximum number of wires, nucleation must occur in all of the pores simultaneously. If nucleation occurs rapidly in a few pores, then these pores will fill, and growth will continue across the top surface. This blocks diffusion of solution down neighboring pores, halting growth. By using potentials that are as positive as possible, which results in slower growth, a high degree of nucleation is achieved. At -0.75 V we observe nucleation in 85–90% of the pores as shown in the scanning electron microscope (SEM) image (Hitachi S-5000) in Figure 2.

The overgrowth of some of the wires occurs after 3 h, as is evident by an increase in the current and roughness on the sample surface. At this point, the majority of the wires are approximately 20–25 μm in length (one-third of the thickness of the template). This corresponds to an aspect ratio of 600 to 1.

An SEM image of a cross section of a template (Figure 3) shows that the wires are dense and completely fill the pores. The sample was prepared by cleaving the template and looking at the sample edge-on. We attribute the slight roughness in the wires to the tendency of this phase to grow dendritically, even at slow growth rates. At higher growth rates (more negative potentials, Figure 3, inset) we observed that the wire diameters are smaller than the pore diameters. We conclude that it is possible to grow wires with diameters that are smaller than the pore diameter by changing the growth potential.

In summary, we have fabricated dense arrays of crystalline $\text{Bi}_{1-x}\text{Sb}_x$ ($0 \leq x \leq 0.15$) nanowires with 40-nm diameters. The composition of the wires is relatively homogeneous, and the wires are highly textured in a $\langle 110 \rangle$ direction. Nucleation occurs in 85–90% of the pores, and the wires grow to one-third the thickness of the template before overgrowth occurs. Faster growth rates (more negative potentials) result in wires with diameters smaller than the pore diameter. We conclude that by tuning the solution concentra-

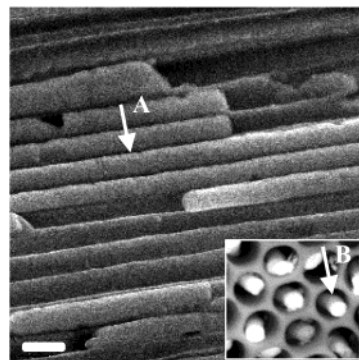


Figure 3. Secondary electron SEM image of a cross-section of the sample shown in Figure 2. (A) Wires are dense and fill the pores completely. (B - inset) Bottom of a template that was filled quickly (at more negative potentials), with voids clearly visible. Scale bar indicates 60 nm for both images.

tions and controlling the growth rate by controlling the potential, the composition, crystallinity, and morphology of the nanowires can be tuned.

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Note Added after ASAP Posting. The version published 2/6/2003 contained errors in the caption to Figure 2. The final version published on the Web 2/7/2003 and the print version are correct.

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