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TEM Analyses of Bismuth-Antimony Thermoelectric Nanowires

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Background

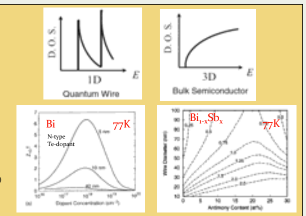
Thermoelectric materials have diverse applications for solid-state cooling and power generation, but at present have poor energy conversion efficiencies. Theory has long predicted that Bi-based nanowires could achieve dramatic improvements in thermoelectric performance through quantum confinement, which creates peaks in the electronic density-of-states that enhance the thermoelectric power factor [1,2]. However, achieving this promise has been difficult, in part because of the experimental challenges of controlling the materials growth in these systems. Key issues include control of composition and crystallinity. Here, we discuss our electron microscopic investigation of BiSb-based nanowires , with the goal of understanding the underlying compositional and microstructural issues necessary for improving nanowire growth and quality.

[1] L.D. Hicks, M.S. Dresselhaus, Physical Review B 47 (19) (1993) 12727.
[2] O. Rabin et al., Applied Physics Letters 79 (1) (2001) 81.
[3] J.P. Dismukes, et al., Journal of Chemical and Engineering Data 13 (3) (1968) 317.

Theory predicts large zT enhancements in nanowires over bulk materials. Enhanced thermoelectric performance is predicted at larger wire diameters in $Bi_{1-x}Sb_x$ alloys than for pure Bi nanowires.
Achieving this theoretical promise will require fine control of composition and crystallinity.

$$zT = \frac{S^2\sigma}{\kappa}T$$

z : thermoelectric figure of merit
T : temperature
S : thermoelectric power (Seebeck coefficient)
σ : electrical conductivity
κ : thermal conductivity



Dresselhaus Adv. Mat. 2007

Dresselhaus and Heremans (2006)

Experimental Details

We are growing BiSb-based nanowires through pulsed electrodeposition into porous anodized aluminum oxide (AAO) templates. These templates are grown on silicon substrates using a tungsten metal "valve-layer" approach that we have employed previously for the growth of Bi2(Te,Se)3 nanowires [4]. Use of the valve layer provides good adhesion for the template while ensuring that the pores remain open to the underlying conductive layer since the W oxidation products from the final stage of anodization can be removed by selective etching. Figure 1 shows a cross-section image of one of our BiSb wire arrays to illustrate the template and layer arrangements. BiSb nanowires are removed from the template by etching the AAO in a phosphoric acid solution.

We are investigating these wires using TEM, studying wire both within the AAO templates as well as individual wires removed from the template and drop cast onto TEM carbon support grids.

[4] S.J. Limmer, et al. Journal of The Electrochemical Society 159 (4) (2012) D235.

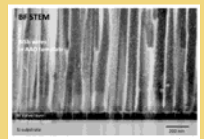


Fig. 1.Cross-sectional image (BF-STEM) of BiSb thermoelectric nanowires electrodeposited into AAO template. Adhesion of the template to the Si substrate is improved with the underlying metal layers. Use of the W valve layer ensures electrical contact to the bottom of the pores.

Composition of the nanowires was measured using energy-dispersive X-ray spectroscopy (EDS) To quantify these measurements, we prepared a bulk BiSb alloy standard. Measured amounts of Bi and Sb were melted together in a quartz tube evacuated to ~5 X 10^{-8} Torr and sealed while under vacuum. The material was melted at 650°C, quenched in ice water, and finally homogenized by annealing at 250°C for 33 days. Homogeneity was verified using EDS in a SEM. Composition of the ingot was measured by Inductively Coupled Plasma Spectroscopy (ICP-OES/MS) (Evans Analytical Group, EAG), giving a compositin of Bi: 68.87 ± 0.62 at% and Sb: 31.13 ± 1.62 at%. Thin sections of the standard were prepared via FIB and EDS data was collected in STEM mode. From the measured x-ray intensities of the Bi and Sb L-series collected from the standard and the concentrations determined by ICP-OES/MS, we calculated a k-factor which was used for our subsequent EDS analysis.

Material synthesis of BiSb ingot for standard

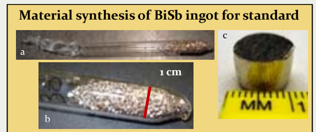


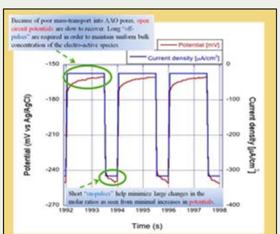
Fig. 2. a. Evacuated sealed quartz tube with Bi and Sb pieces. b. Close-up of Bi and Sb pieces. c. Synthesized BiSb standard ingot.

$$C_B / C_A = k_{AB} (I_B / I_A)$$
$$k_{AB} = (C_B / C_A) * (I_A / I_B)$$
$$C_A + C_B = 1$$

k_{AB} : k-factor (sensitivity factor)
C_A : concentration of Sb
C_B : concentration of Bi
I_A : measured x-ray intensities of Sb
I_B : measured x-ray intensities of Bi

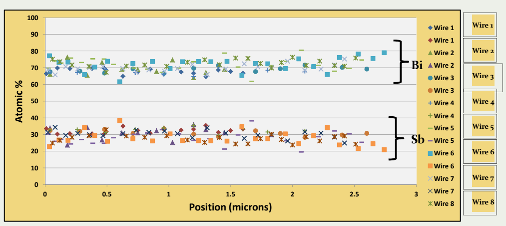
Nanowire Compositional Uniformity

Uniform deposition of alloys into high aspect ratio pores is difficult because of mass transport limitations.

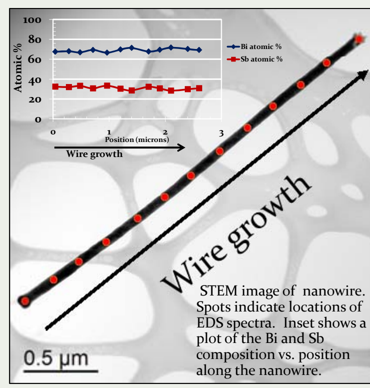


Pulsed electrodeposition can overcome this limitation by providing time for the local composition of the solution to recover between "on" pulses

The as-grown wires exhibit good compositional uniformity, demonstrating the effectiveness of *pulsed electrodeposition* in growing BiSb wires.



EDS measurements from several different BiSb wires. Data was collected in STEM mode on a JEOL 2010F TEM. Compositions were determined using a k-factor derived from the prepared bulk BiSb standard.

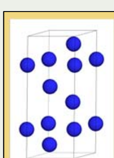


STEM image of nanowire. Spots indicate locations of EDS spectra. Inset shows a plot of the Bi and Sb composition vs. position along the nanowire.

Crystal Structure

Electron diffraction measurements confirm that the wires grow in the expected rhombohedral phase for Bi and its solid solution alloys with Sb.

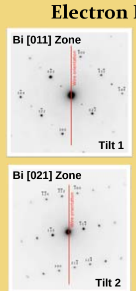
The grain size of the deposited wires is large, with grains typically observed extending at least 0.5 to 1.5 microns along the wire length.



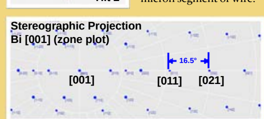
Rhombohedral structure of Bismuth

Bi: space group 166: R-3m
a,b=4.5463Å
c=11.8619 Å

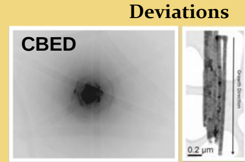
Selected Area Electron Diffraction



Selected Area Electron diffraction patterns obtained at two tilt conditions obtained by tilting nominally about the wire axis by ~15.4° along the (300) Kikuchi band. Patterns obtained from 0.6 micron segment of wire.

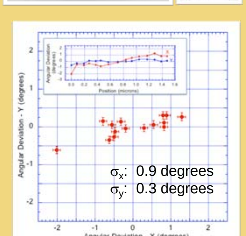


Measurement of Local Angular Deviations

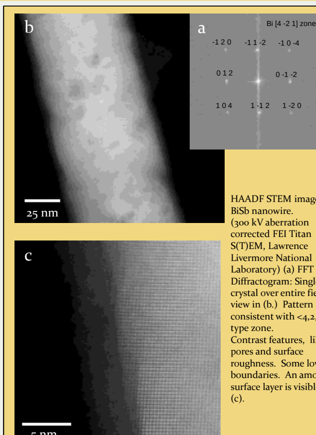


We measure the local angular deviations from shifts in the Kikuchi lines in covergent beam electron diffraction (CBED) patterns obtained from points along the length of the wire

The spread in grain orientation in this wire, characterized by the standard deviation (σ) of the angular deviation measurements, is better than 1 degree.



The larger spread of orientations in x than y, represents a component of twist misorientation about the wire axis.



HAADF STEM images of BiSb nanowire. (300 kV aberration corrected FEI Titan S(T)EM, Lawrence Livermore National Laboratory) (a) FFT Diffractogram: Single crystal over entire field of view in (b.) Pattern consistent with <4,2,-1 > type zone. Contrast features, likely pores and surface roughness. Some low angle boundaries. An amorphous surface layer is visible in (c).

Conclusion

Control of composition and crystallinity will be critical for achieving the enhanced thermoelectric performance in BiSb-nanowires long predicted by theory. TEM analysis is providing useful insight toward this goal. Our results show that pulsed electrodeposition is effective at achieving uniform alloy composition along the wire length and at overcoming the mass transport limitations that could hinder such growth in high aspect ratio AAO templates. Our measurements find that the present wires are somewhat richer in Sb (~30 at %) than the targeted composition (~20 at % Sb), predicted by theory to be optimal for zT enhancement. Thus, these measurements provide feedback for optimization of the growth conditions and bath chemistries. We also find excellent crystalline quality in the as-grown wires, with large grains extending to at least 0.5-1.5 microns along the wire length. Small misorientations observed in the wires likely represent the presence of low angle grain boundaries and dislocations, structural defects that will need to further controlled. Further refinement of the compositional uniformity and crystallinity should be achievable through subsequent annealing of the as-grown wires.

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