

Fe-DOPED Co-Sb NANOWIRES USING ELECTROCHEMICAL METHODS

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Abstract. CoSb₃ is the most promising thermoelectric material to replace PbTe-based alloys because it displays remarkable electrical properties. Thermoelectric properties of CoSb₃ are largely affected by doping. In addition, thermoelectric properties are affected by the dimensionality of the material, especially when high aspect ratio nanowires are considered. Our approach to develop high-efficiency thermoelectric materials is to combine the chemistry and the size effects to fabricate nanostructured materials with high figure of merit (ZT). This work presents our latest results on electrochemical doping of CoSb₃ nanowires with iron for high temperature thermoelectric materials. Iron doped Co-Sb skutterudite nanowires were grown by electrochemical methods using template synthesis. Detailed electrochemical characterization as well as chemical, structural and morphological characterization (SEM, EDS) were performed.

1. Introduction

Recently, there is a great interest in developing nanostructured materials for thermoelectrics using sustainable techniques at low temperature. Among other methods to produce nanomaterials, electrochemistry can be used to grow nanostructures using template synthesis [1-3]. Combining chemistry and size effects to create new thermoelectric materials has the potential to result in a significant improvement in the power to weight ratio of the thermoelectric device.

Thermoelectric devices transform heat directly into electricity based on the Seebeck effect. Performance of a thermoelectric material is based to the merit (ZT) of the material:

$$ZT = S^2 \sigma T / k \quad (1)$$

where S is the Seebeck coefficient, σ is electrical conductivity, k is thermal conductivity and T is temperature.

CoSb₃ is the most promising thermoelectric material to replace PbTe-based alloys because it displays remarkable electrical properties [4]. Doping of CoSb₃ affect the transport properties of this material [5-16], including Hall mobility, Seebeck coefficient, and electrical conductivity, which depend strongly not only on the carrier concentration but also on the donor impurities [17].

Iron is one of the elements that was investigated as a donor impurity in CoSb₃ skutterudite [18]. It was shown that the carrier concentration increased with increasing Fe doping content but the carrier mobility decreased with increasing doping content, which indicates that the hole mean free path was reduced by the impurity scattering [19]. Also, thermal conductivity was considerably reduced by Fe doping and the lattice contribution was dominant in the Fe-doped CoSb₃ skutterudites [8, 18-21].

This paper shows that Fe-doped Co-Sb nanowires can be obtained using electrochemical template synthesis. While deposition parameters still need to be optimized, we present the fabrication method and the characterization of Fe-doped Co-Sb nanowires.

2. Material and methods

2.1. Materials

Solutions containing iron, cobalt and antimony were prepared by dissolving 0.003 M Sb₂O₃ and 0.155 M CoSO₄·7H₂O, 0.017M FeSO₄·7H₂O (Electrolyte A) or by dissolving 0.003 M Sb₂O₃ and 0.138 M CoSO₄·7H₂O, 0.034M FeSO₄·7H₂O (Electrolyte B) in aqueous solutions containing 0.125 M C₆H₇KO₇ (potassium citrate monobasic) and 0.196 M C₆H₈O₇ (citric acid). The use of citrate and citric acid is to increase the solubility of Sb₂O₃ by forming complexes and reduce the gap between the deposition potential of antimony and that of cobalt.

All reactive were purchased from Sigma-Aldrich. Deionized water (Milli Q 18-M Ω) was used for preparing solutions and for rinsing. The solution was purged with N₂ for at least 10 min before deposition.

Gold sputtered PCTE membranes (GE Water & Process Technologies, PA, USA) were used as a substrate for electro-deposition. The rough side of a 200 nm PCTE membrane was first sputtered with Au using a sputtering device for 5 min. A piece of double sided copper tape was then placed in contact with the Au-coated side of the membrane. Finally the two pieces were sandwiched between two single sided plastic tapes with a circular cut-out, exposing Au to the electrolyte. The circular cut-out had an approximate area of 0.198 cm² with a pore density of approximate 10⁶ pores/cm². A diagram of the set-up is shown in Figure 1.

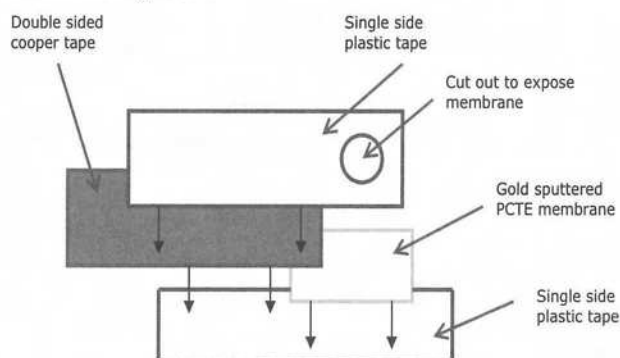


Figure 1 The experimental set-up for the working electrode.

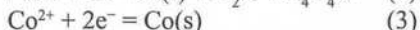
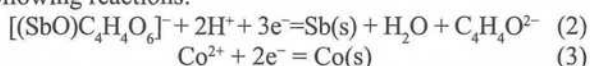
2.2. Methods

The pulsed electrodeposition of Fe-doped Co-Sb nanowires was carried out in a new, innovative, three-electrode cell setup in which a gold foil was used as auxiliary (counter) electrode and a saturated Ag/AgCl electrode was used as reference electrode. The electrolyte was prepared using deionized water. The equipment for electrodeposition is a Parstat 4000 potentiostat/galvanostat operating in fast potential pulse mode between -1 V and at -0.4 V vs. Ag/AgCl for 600s with a pulse rate of 0.01s. The deposition temperature was controlled at 65 °C using a hot plate magnetic stirrer.

The electrodeposition process of nanowires involves diffusion, adsorption and reaction. For Co-Sb nanowires the alloying process could be described as follows:

1) Diffusion and adsorption of $[(\text{SbO})\text{C}_4\text{H}_4\text{O}_6]^-$ and Co^{2+} ions onto the Au electrode surface induced by the electric field applied between the two electrodes.

2) Adsorbed $[(\text{SbO})\text{C}_4\text{H}_4\text{O}_6]^-$ and Co^{2+} acquire electrons to form elemental Sb and Co according to the following reactions:



3) Reduced Sb and Co atoms react with each other to form CoSb_3 . Thus, the overall reaction can be expressed as: $\text{Co}^{2+} + \text{Fe} + [(\text{SbO})\text{C}_4\text{H}_4\text{O}_6]^- + 2\text{H}^+ + 5\text{e}^- = \text{Co/Fe-Sb}(\text{s}) + \text{H}_2\text{O} + \text{C}_4\text{H}_4\text{O}_6^{2-}$ (4)

Additionally, Fe will be co-deposited with Co and substitute Co in the Co-Sb unit cell.

3. Results and discussion

3.1. Co-deposition of Co, Fe and Sb

Figures 2 present a typical deposition curve for samples obtained by fast57 potential pulse techniques. For all samples the deposition current is negative, in the miliampere domain.

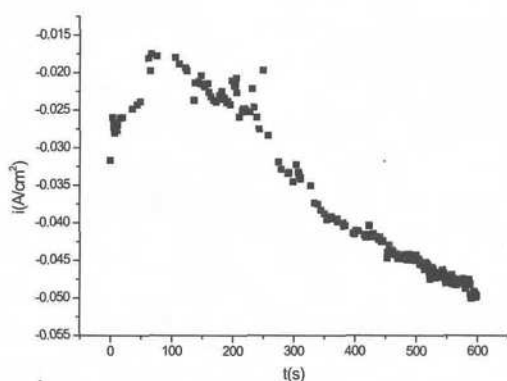


Figure 2 Typical current-time plot recorded during the fast potential pulse deposition of Fe-doped Co-Sb NWs.

3.2. Spectroscopic analysis and morphology characterization of Fe-doped CoSb₃ nanowires

Surface morphology, structural and elemental analysis of electrodeposited coating, composition of nanowires formed on the working electrode were studied using scanning electron microscopy (SEM) with Environmental

Scanning Electron Microscope FEI/Phillips XL 30 ESEM at 0.7 Torr pressure.

A key issue in fabricating Co-Sb nanowires is to control the nanowire composition and obtain a certain stoichiometry [22]. Figure 3 shows the Energy Dispersive Spectrometry (EDS) spectrum and SEM images for Fe-doped Co-Sb nanowires obtained from electrolyte A. On the surface of the electrodes appear a bundle of Fe-Co-Sb nanowires. The presence of Au and Cu in the scan is due to sample setting.

The nanowires obtained by pulsed electrodeposition are straight and sturdy. We obtained nanowires with an approximate length of 5-7 μm and a diameter of 200 nm corresponding to the diameter of the pores. Overgrown nanowires present the typical mushrooms structures at the point where the nanowires reach the surface. Figure 4 shows the EDS and elemental mapping on nanowire array. Superimposing the elemental color coding over the SEM image illustrates the difference in composition between nanowires and mushroom caps. Elemental analysis performed on mushroom caps showed a Fe:Co:Sb ratio of 1:29:38, while the Fe:Co:Sb ratio was 1:8:3 on nanowire. The Fe:Co ratio for nanowires is higher than mushroom caps. Also, it looks like the more Sb in the mushroom cap correlates with less Fe. A similar difference in composition between nanowires and mushroom cap has been previously observed in the Co-Sb system [1]. Moreover, there is a striking difference between mushroom caps and thin film. Because mushroom caps should grow similar to thin films, this finding is quite unexpected. We will continue to study the electrochemical behavior of the dopant and investigate the influence of deposition parameters on the composition of the deposit (i.e., nanowires, mushroom caps or thin films).

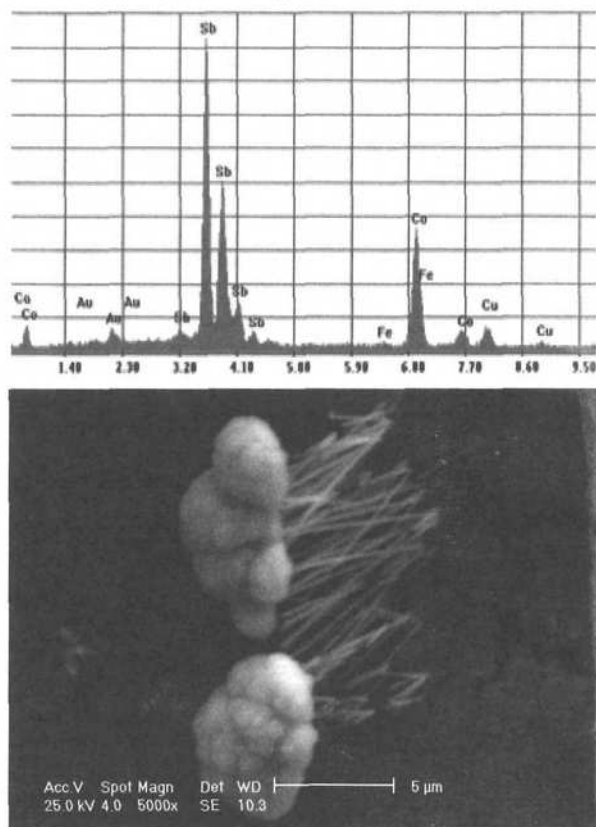


Figure 2 EDS (top) and SEM (bottom) morphologies of nanowires electrodeposited using electrolyte A.

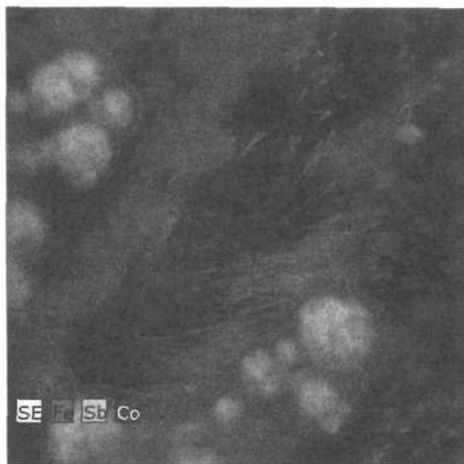


Figure 3 SEM morphologies and elemental mapping of nanowires electrodeposited using electrolyte A.

Fe-doped nanowires obtained in electrolyte B have similar morphologies with those obtained in electrolyte A. The Fe:Co:Sb ratio is 3.5:1:1 for nanowires. Although the electrolyte B contains more iron, it is not clear why the amount of Fe in the nanowire is so high. A more detailed study of the correlation between the amount of Fe in the electrolyte and the amount of Fe in the nanowires is required.

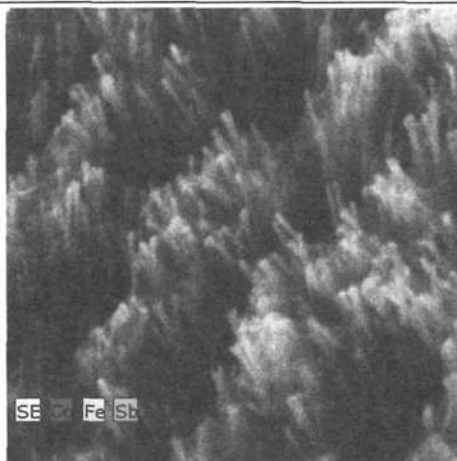
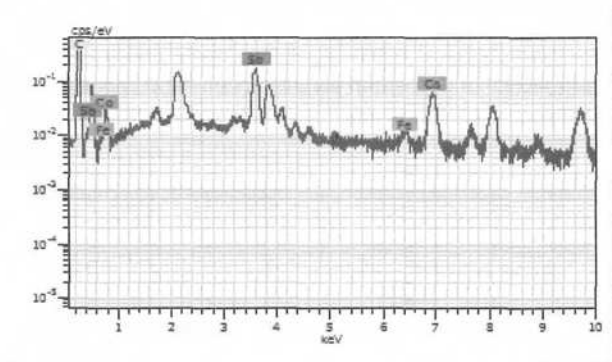


Figure 4 EDS (top), SEM morphologies and elemental mapping on Fe-doped Co-Sb nanowire array

4. Conclusions

We obtained Fe-doped Co-Sb nanowires with various Fe:Co:Sb ratios, which correlate with the amount of Fe in the electrolyte. For depositions performed in electrolyte B, an increase in iron content in the composition of the nanowires was obtained. The electrodeposition method demonstrated for doping semiconductor nanowires opens the doors for new technologies and nanomaterials with unique properties. More investigations are needed to better control and optimize the composition of nanowires for a certain application.

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