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Electrochemically deposited thermoelectric $Bi_2(Se,Te)_3$ nanowires

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The processes associated with the electrodeposition of thermoelectric $Bi_2(Se,Te)_3$ nanowires are reported along with an analysis of the composition, morphology and structure of resulting material. Electrochemical behavior was examined using cyclic and linear voltammetry techniques. Energy dispersive X-ray spectrometry (EDX) indicates that the composition of self-standing $Bi_2(Se, Te)_3$ wires can be controlled by the electrodeposition method. The composition of $Bi_2(Se,Te)_3$ wires prepared at a potential of -0.01V vs SCE is close to $Bi_2Te_{2.7}Se_{0.3}$.The structure and morphology of $Bi_2(Se,Te)_3$ nanowires were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

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1. Introduction

Progressive growth in world energy demand and the likely impact of global warming determined taking into consideration of residual heat recovery by using on a large scale of thermoelectric (TE) generators. On the other hand, the thermoelectricity advance could permit to replace with Peltier cooler the cooling based on compression. The performance of a thermoelectric material is represented by the dimensionless figure of merit, $ZT = \frac{S^2\sigma T}{\kappa}$, where S, σ, κ and T are Seebeck coefficient, the electrical conductivity, the thermal conductivity and the temperature in Kelvin, respectively. The term “thermoelectric material” is usually attributed to the materials with ZT>0.5. In the last 40 years, the best TE materials have ZT value between 0.75 and 1. When ZT value increases to infinite, the TE device efficiency reaches the efficiency limit of the Carnot cycle, applicable to the all thermal machines. Nanostructured thermoelectric semiconductors [1-7] are a promising material to convert waste heat to electricity for energy regeneration due to improvement of Seebeck coefficient and thermal conductivity reducing. Among various thermoelectric materials, bismuth telluride based alloys [8] are the most used in the fabrication of TE devices. In this paper, the electrochemical synthesis of $Bi_2(Se,Te)_3$ nanowire array from nitrate- EDTA solution was investigated using cyclic and linear voltammetry measurements.

2. Experimental

Electrochemical experiments were conducted potentiostatically in a conventional three-electrode cell configuration at room temperature. Platinum and a commercial saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. $Bi_2(Se,Te)_3$ wires were synthesized using as template a track etched membrane (polycarbonate membrane). Prior electrodeposition, polycarbonate membrane with a thickness of 27μm, pore diameter of about 500 nm and 10^8 cm^{-2} pores density was covered by sputtering with a thin gold film. This film was thickened by electrochemical deposition of palladium and copper successive layers. The surface area of the membrane exposed at electrodeposition solutions was $1cm^2$. For SEM and XRD measurements, after the electrodeposition process the polymer membrane was dissolved in dichloromethane. The electrochemical measurements were carried out with an Autolab PGSTAT 30 potentiostat/galvanostat connected to a computer. The semiconductor wires were imaged using a field emission scanning electron microscope Quanta InspectF equipped for chemical composition measurements with an EDX device from EDAX. X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance type X-ray diffractometer, in focusing geometry, equiped with copper target X-ray tube and LynxEye one-dimensional detector.

3. Results and discussion

According to the E-pH Pourbaix diagram [9], bismuth telluride is a stable compound over the entire range of pH as a bulk material, at potentials more negatives than 0.5V/NHE (normal hydrogen electrode). In acid medium, tellurium is soluble as $HTeO_2^+$ in a narrow range at low pH, around pH=0 and bismuth is soluble as Bi^{3+} at pH<2; consequently, Bi_2Te_3 can be electrodeposited at pH=0. In order to synthesize $Bi_2(Te,Se)_3$, in electrochemical bath for Bi_2Te_3 deposition is added the stable specie of Se^{4+}_{aq}, namely H_2SeO_3.

We studied the preparation of $Bi_2(Se,Te)_3$ wires from nitric acid electrolyte containing 3.39mM $HTeO_2^+$, 32.98mM Bi^{3+}, 0.10mM H_2SeO_3, 32.24mM EDTA 2Na, pH=0.

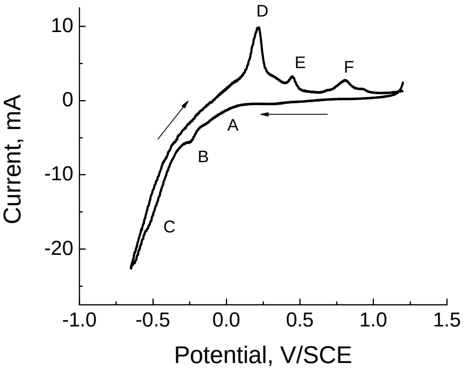

Fig. 1. Cyclic voltammogram of a Au/Pd/polycarbonate membrane electrode in a nitric acid solution containing 3.39mM $HTeO_2^+$, 32.98mM Bi^{3+}, 0.10mM H_2SeO_3 and 32.24 mM EDTA 2Na; pH=0; scan rate 5 mV/s; T = 25 ˚C; electrode surface area 1cm^2.

The reduction waves observed on the cyclic voltammogram (Fig.1) during the cathodic scan at 0.06, -0.239 and -0.523 V/SCE are attributed to the underpotential deposition of $Bi_2(Se,Te)_3$, reduction of $HTeO_2^+$ at H_2Te and hydrogen evolving, respectively. The marked waves observed on the anodic branch of the voltammogram at 0.21 and 0.44 are in connection with the oxidation of bismuth from the top of $Bi_2(Se,Te)_3$ wires and oxidation of $Bi_2(Se,Te)_3$ at bismuth, respectively. This assignment is consistent with previous reports [9-11].The wide peak at 0.81V (peak F) was attributed to oxidation of the palladium support [12].

The reactions responsible for the deposition process at 0.06V, labeled A on the cyclic voltammogram from the Fig. 1 are described as (1-4):

$$HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te + 2H_2O \quad (1)$$

$$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O \quad (2)$$

$$3Te + 2Bi^{3+} + 6e^- \rightarrow Bi_2Te_3 \quad (3)$$

$$3Se + 2Bi^{3+} + 6e^- \rightarrow Bi_2Se_3 \quad (4)$$

They involve the reduction of $HTeO_2^+$ and H_2SeO_3 adsorbed onto the electrode to produce Te and Se, respectively; these initiate the reduction of Bi^{3+}.The potential at which reduction is observed is more positive compared with the reduction of solution containing only $HTeO_2^+$ (H_2SeO_3) or only Bi^{3+}, for comparable concentrations. This process is known as underpotential deposition due to the anodic shift of the deposition potentials as a result of adsorption of the reactants and formation of the compound on the surface of the electrode.

The reduction wave B (at -0.239V) is attributed to the formation of $Bi_2(Se,Te)_3$ via the reactions (5-8):

$$HTeO_2^+ + 5H^+ + 6e^- \rightarrow H_2Te + H_2O \quad (5)$$

$$H_2SeO_3 + 6H^+ + 6e^- \rightarrow H_2Se + 3H_2O \quad (6)$$

$$3H_2Te + 2Bi^{3+} \rightarrow Bi_2Te_3 + 6H^+ \quad (7)$$

$$3H_2Se + 2Bi^{3+} \rightarrow Bi_2Se_3 + 6H^+ \quad (8)$$

At this potential the deposition rate of $Bi_2(Se,Te)_3$ is large and the obtained semiconductor material has a bad quality.

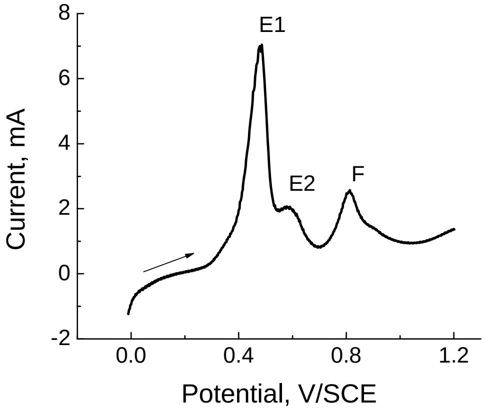

Fig. 2. Linear voltammogram of a Au/Pd/polycarbonate membrane electrode recorded after electrodeposition of $Bi_2(Se,Te)_3$ for 10min at a potential of -0.01V; scan rate 5 mV/s; T = 25 ˚C; electrode surface area 1cm^2.

In order to prepare $Bi_2(Se,Te)_3$ wires we selected from cyclic voltammogram the potentials region where this semiconductor is underpotential deposited. We have grown for ten minutes $Bi_2(Se,Te)_3$ wires into the pores of membrane, at a potential of -0.01V; this electrode was used for linear voltammetry investigations. When the potential of this electrode is scanned from a value of -0.01V towards more positive values (Fig.2) the peak at 0.21V disappears and a supplementary peak (E2) is observed at 0.58V. The composition of $Bi_2(Se,Te)_3$ wires prepared at this potential is close to $Bi_2Te_{2.7}Se_{0.3}$, a preferred composition for n-type elements used in thermoelectric cooling devices. This means that at a potential of -0.01V a quasi-stoichiometric compound was obtained and the oxidation peak at 0.21V, attributed to oxidation of the bismuth deposited in excess disappears. The two closely spaced peaks, E1 and E2 (at 0.48 and 0.58V, respectively) are attributed to oxidation of $Bi_2(Se,Te)_3$ via two steps:

$$Bi_2Te_{2.7}Se_{0.3} + 6H_2O \rightarrow 2.7HTeO_2^+ + 0.3SeO_2 + 2Bi + 9.3H^+ + 12e^- \quad (9)$$

$$Bi \rightarrow Bi^{3+} + 3e^- \quad (10)$$

In the Table 1 are presented the compositions, obtained from EDX measurements, of the $Bi_2(Se,Te)_3$ wire arrays electrodeposited at different potentials. A stoichiometric compound was obtained at potentials around -0.01 V vs. SCE.

Table 1. Atomic percentages as a function of the applied potentials for $Bi_2(Se, Te)_3$ wire arrays.

Potential, V vs SCE	Bi, %	Te, %	Se, %
0.0186	37	52	11
0.00	39	52	9
-0.01	39	54	7
-0.02	43	51	6

At more negative potentials the obtained $Bi_2(Se,Te)_3$ wire arrays contain an excess of bismuth compared with stoichiometric composition (Table 1).

Representative SEM images of self-standing $Bi_2(Se, Te)_3$ wires obtained at different deposition potentials are presented in the Fig. 3. The diameter of prepared $Bi_2(Se,Te)_3$ wires were about 500 nm and their length was around 27 μm. SEM micrograph from Fig. 3 (d) suggests that $Bi_2(Se,Te)_3$ wires prepared in a solution EDTA- nitric acid have a granular structure.

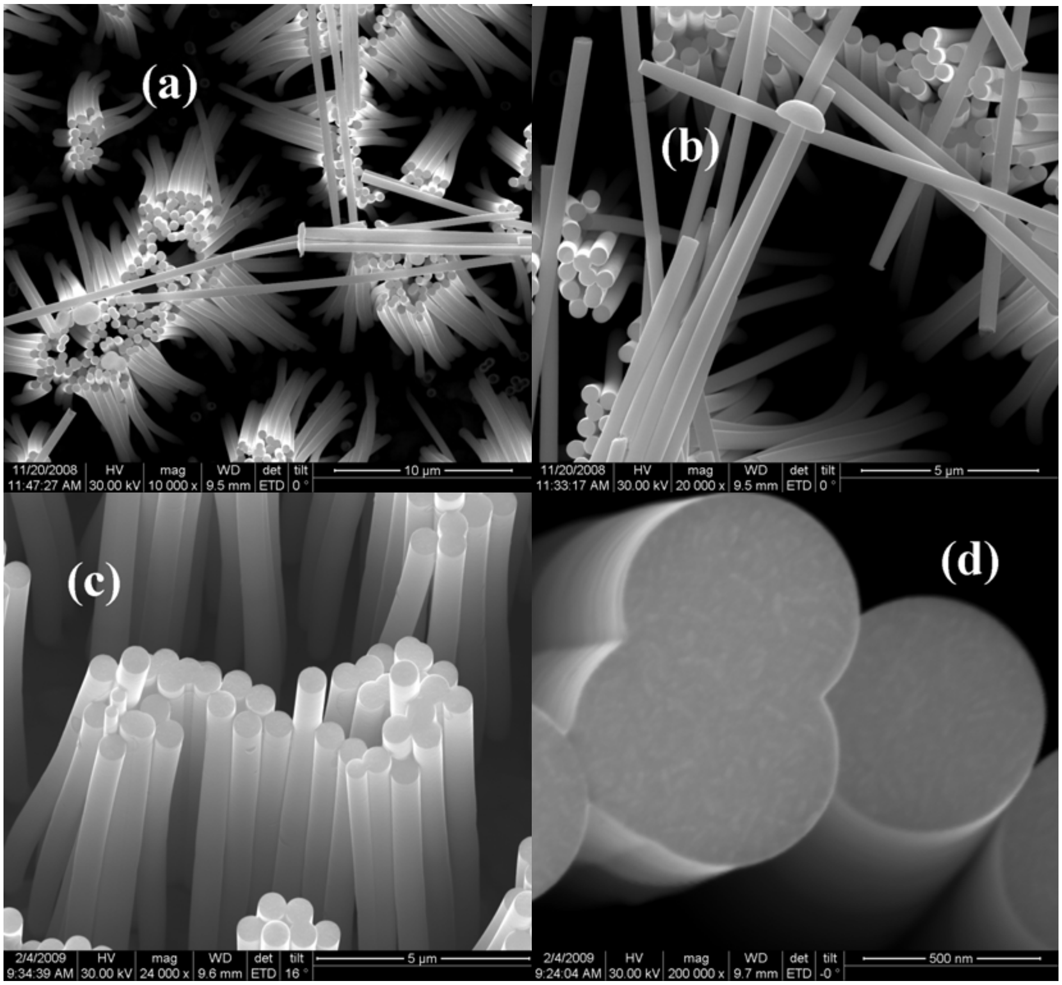

Fig. 3. SEM micrographs of $Bi_2(Se, Te)_3$ wire arrays prepared at potentials (V vs. SCE) 0.0186 (a, b) and -0.01 (c,d).

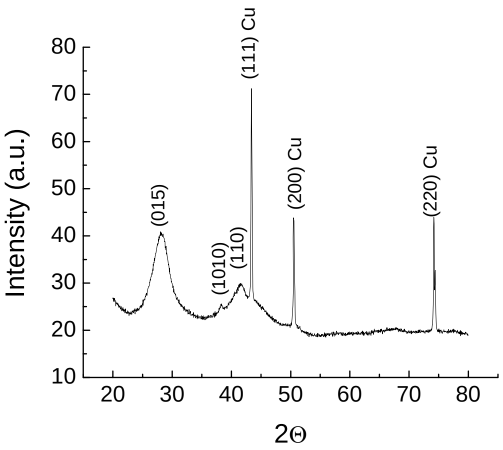

Fig 4. X-ray diffraction pattern of a $Bi_2Te_{2.7}Se_{0.3}$ wire array sample deposited at -0.01V, together with the diffraction peaks of the substrate.

X-ray diffraction pattern of $Bi_2(Se,Te)_3$ wire array, prepared at -0.01V shows characteristic peaks of $Bi_2Te_{2.7}Se_{0.3}$ (Fig. 4). However, the observed peaks are broad, probably due to the presence of nanosized crystallites in the structure of the wires.

4. Conclusions

Voltammetric study of the electrodeposition of $Bi_2(Se,Te)_3$ wire array from nitrate-EDTA solution and EDX measurements showed that at potentials more negative than -0.01V vs SCE was deposited a compound with an excess of bismuth, compared with stoichiometric composition $Bi_2Te_{2.7}Se_{0.3}$. The composition of $Bi_2(Se,Te)_3$ wires prepared at a potential of -0.01V vs SCE is close to $Bi_2Te_{2.7}Se_{0.3}$. XRD and SEM measurements suggested that the obtained $Bi_2Te_{2.7}Se_{0.3}$ wires have a granular structure.

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