$Bi_{2-X}Sb_XTe_3$ THICK THERMOELECTRIC FILMS OBTAINED BY ELECTRODEPOSITION FROM HYDROCHLORIC ACID SOLUTIONS

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A method to produce composition modulated $Bi_{2-x}Sb_xTe_3$ alloys by electrodeposition has been developed. The electrolyte, which consists in a HCl 6M (pH = 0) aqueous solution, allows for the co-deposition of bismuth, antimony and tellurium to be accomplished at room temperature on glassy carbon, platinum or nickel electrode. The composition of the films, their crystal structures and morphology were studied as function of electrochemical parameters and bath composition. It is shown that the electrodeposits are monophasic and exhibit a polycrystalline state. The electrical resistivity was of the order of 7-10 mΩcm, whereas the electrodeposition rate value was 30-50 μm/h for the films with good thermoelectric properties.

1. Introduction

The electrochemical synthesis of various compounds, such as CdS, CdSe, CdTe, GaAs, GaSb, $CuInX_2$, MoX_2, Bi_2X_3 (where X = S, Se, Te) has been already successfully realized [1-6]. The electrochemical methods are enough a relatively simple procedures that allow for the deposition of thermoelectric films onto electrodes of variable geometry and preparation of specific materials necessary for solving the thermal management of electronic devices [7]. Semiconductor films are mostly polycrystalline. $Bi_{1-x}Sb_x$ alloys are very attractive materials for thermoelectric refrigeration at low temperature using Ethinghausen effect [8-9], whereas $Bi_{2-x}Sb_xTe_3$ compounds are the best thermoelectric materials both for thermoelectric refrigeration (by Peltier effect) and for thermoelectric power generation (by Seebeck effect) [10-11].

The aim of this work is to study the bismuth-antimony-tellurium ternary alloys with good semiconductor characteristics, suitable for thermoelectric application by exploring two electrochemical processes of deposition (potentiostatic or galvanostatic deposition). Both processes are based on the co-reduction of bismuth, antimony and tellurium ions in an aqueous medium containing complexing agents (chloride). Complexation brings the reduction potentials of Sb and Bi close to each other, thus allowing co-deposition in spite of differences in the standard electrode potentials. This fact allows for a good control on Sb/Bi ratio in the electrodeposited $Bi_{2-x}Sb_xTe_3$ ternary alloys.

2. Experimental details

A computer driven Sycopel potentiostat/galvanostat was used for cyclic voltammetric analysis.

Voltammetric experiments were carried out in a conventional three-electrode cell in a thermostat (25 °C). The working electrode was a rotating vitreous carbon disc (3 mm diameter, BAS-

RDE); the rate of rotation was 500 rpm. The electrochemical potentials of the working electrode were measured and expressed by reference to a saturated calomel electrode (SCE). The counter electrode was a platinum wire. For long time electrodeposition a platinum electrode (1 cm^2) was used as working electrode.

The electrolytic baths were prepared with deionized water. To ensure the stability and the solubility of antimony[III] and bismuth[III] species in solutions the electrolyte was a solution containing concentrated hydrochloric acid in order to form chloride complexes (BiCl$_4^-$ and SbCl$_4^-$). The Sb[III] containing solutions were prepared by dissolution of SbCl$_3$ in 6M hydrochloric acid solution. The Bi[III] containing solutions were obtained in the same way, by dissolution of Bi$_2$O$_3$. The Te[IV] solutions were obtained by dissolution of TeO$_2$ in NaOH, followed by neutralization and pH ajusting at pH = 1. All reagents were from Merck p.a. grade. X-ray diffraction data were obtained with a X-ray diffractometer (DRON 2). The morphology was studied using a scanning electron microscope (AMR Model 1000 SEM). The elemental analyses of the electrodeposited films removed from their suports were performed by atomic absorbtion spectrometry, AAS (Solar, Unicam 969). The stoichiometric determination analyses by AAS were reproducible up to 0.5-1%. The electrical resistivity measurements of the removed films were made using a van der Pauw technique [12]. The Seebeck coefficient was measured with a home-made apparatus.

3. Results and discussion

The electrochemical behavior of Bi[III], Sb[III] and Te[IV] ions and their mixtures were investigated using cyclic or linear sweep voltammetry.

3.1. Investigations of solutions containing a single ion species

Typical cyclic voltammograms obtained with solutions containing a single ion species are shown in Fig. 1, whereas the corresponding polarization curves are presented in Fig. 2.

The voltammogram relative to Bi[III]/Bi couple (curve *a* in Fig.1) indicates the occurrence of a well-defined cathodic peak at approximately – 0.3 V electrode potential, suggesting a direct cathodic deposition of elementary Bi (at potentials more negative than –0.275 V) by reduction of BiCl$_4^-$ ion (BiCl$_4^-$ species being more stable than Bi[III] ion in these very concentrated acid solutions).
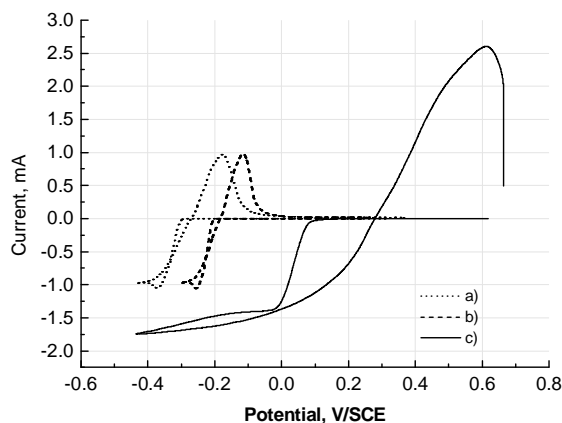

Fig. 1. Cyclic voltammograms in HCl-6M aqueous solution. Working electrode: glassy carbon (7.06 mm^2), rotation rate: 500 rpm, scan rate: 50 mV/s; a) Bi[III] conc. = 0.1M, b) Sb[III]conc. =0.1M, Te[IV] conc. = 0.2M.

Indeed, the X-ray diffraction pattern of the electrodeposited product confirms the formation of Bi metal. The polarization curve (curve *a* in Fig. 2) proves the increasing of cathodic current starting from *ca* –0.28 V and shows a relative independence of current vs. electrode potential in the region –0.25 V to –0.55 V. This diffusion current increases linearly with increasing Bi^{III} concentration in solution. A shift of potential towards more negative values than -0.55V causes the H$_2$ evolution. On the anodic branch of voltammogram, the peak located at E$_{pa}$ = -0.175V corresponds to the redissolution of metallic bismuth. At more positive potential it was not noticed any electrochemical process until O$_2$ evolution (not shown in Fig.1). The coulombic efficiency of Bi deposition may be estimated as the ratio between the electric charge used for stripping Bi deposit (Q$_a$) and the total charge transferred during deposition (Q$_c$). The values of coulombic efficiencies ($\eta = Q_a/Q_c$) were found to be fairly constant with changes in the negative switching potentials (η=90% $\pm$ 2%). The cathodic charge excess is certainly due to formation of nonperfectly adherent product on the electrode (vitreous carbon here).

The curve *b* in Fig.1 represents a cyclic voltammetry curve for reduction of SbCl$_4^-$ ion to metallic Sb (cathodic branch) and electro-oxidation of fresh deposited Sb (anodic branch). During cathodic exploration only one reduction peak, situated at *ca* –0.25 V, occurs. By shifting the potential until –0.6 V (where the reduction of H$^+$ begins) a constant diffusion current is recorded, due to the electrodeposition of antimony metal. Reversing the sweep towards positive values of potential causes the occurrence of a sharp anodic peak (E$_{pa}$ = - 0.1V) corresponding to Sb film stripping. The potential of this anodic peak has a value more positive than the observed anodic peak for Bi/Bi^{III} system. Because $\Delta E_p = E_{pa}-E_{pc}$ is larger for the antimony system the process appears to be less reversible than the bismuth system in this electrolyte.

Referring to the polarization curve of Bi^{III}ion, the black metallic product obtained after a cathodic scan (Fig. 2 curve *b*) was analysed by X-ray diffraction and consists in elementary antimony. For this system, the cathodic (Q$_c$) and anodic (Qa) charges are slightly different. The variation in the Q$_a$/Q$_c$ ratio can be interpreted on the basis of hydrogen formation for the most negative potentials, causing a nonadherent powder electrodeposit.
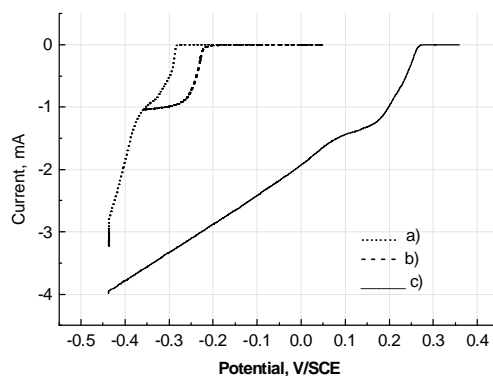

Fig. 2. Polarization curves in HCl-6M aqueous solution. Working electrode: glassy carbon (7.06 mm^2), rotation rate: 500 rpm, scan rate: 1 mV/s; a) Bi^{III}conc. = 0.1M, b) Sb^{III}conc. = 0.1M, Te^{IV}conc. = 0.2M.

The curve *c* in Fig.1 shows a voltammogram for a HTeO$_2^+$ion containing solution. During a cathodic scan, a reduction wave with large currents begins at about +0.25 V, due to the electrodeposition of tellurium on electrode surface. The tellurium deposit occurs by a mechanism involving the electroreduction of HTeO$_2^+$ to H$_2$Te gas, followed by a chemical reaction between H$_2$Te with HTeO$_2^+$ to yield tellurium:

$$HTeO_2^+ + 5H^+ + 6e \rightarrow H_2Te + 2H_2O \tag{1}$$
$$2H_2Te + HTeO_2^+ \rightarrow 3Te + 2H_2O + H^+ \tag{2}$$
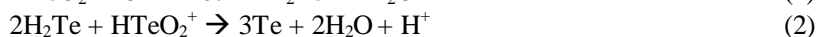
A reverse potential sweep causes the tellurium stripping, illustrated by an anodic peak at +0.6 V, a positive value substantially more higher than the observed potentials for Bi and Sb dissolution. This fact proves once again that tellurium has non-metallic properties. The grey compact product obtained was also analysed by X-ray diffraction and corresponds to elementary tellurium. The coulombic efficincies were found to be around 80% during electrolysis at negative potentials, between +0.1V and -0.4V. Extending to more negative potentials leads to the producing of a nonadherent powder.

3.2. Investigation of solutions containing Bi^{III}, Sb^{III} and Te^{IV} ions mixtures

Figs. 3 and 4 are related to a more complex situation, where the electrolyte contains two electroactive species, namely either $BiCl_4^-$ and $HTeO_2^+$ ions or $SbCl_4^-$ and $HTeO_2^+$ ions (in a higher concentration of $HTeO_2^+$) dissolved in a very concentrated solution HCl 6M. The polarization curve represented by the curve *b* in Fig.3 exhibits several electrode potential regions, according to the various processes which take place on the rotating disc of vitreous carbon.
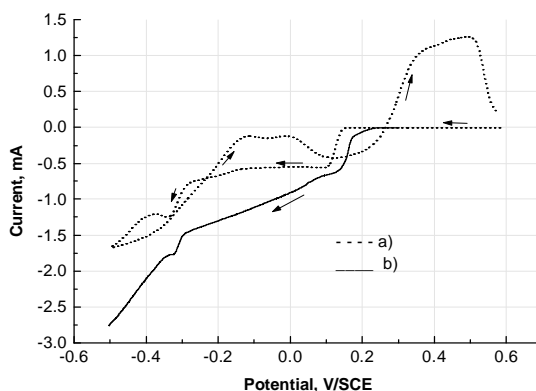

Fig. 3. The voltammogram (*a*), scan rate 50 mV/s and polarization curve (*b*), 1 mV/s for Bi-Te alloy electrodeposition. Working electrode: glassy carbon (7,06 mm^2), rotation rate: 500 rpm; Bi^{III}conc. = 0.06M, Te^{IV}conc. = 0.08M.

Thus, starting from an equilibrium potential of +0.2 V, the first cathodic reaction develops with the participation of $HTeO_2^+$ ion, which is converted to H_2Te gas (in the potential range +0.2 V to +0.1 V) according to equation (1).

The initial formation of gaseous H_2Te is a condition for inducing the next process, a chemical reaction with $HTeO_2^+$ participation (equation (2)).

The existence of the chemical deposition step of tellurium by reaction (2) is proved the constancy of the cathodic current in the potential region from +0.1 V to -0.15 V. By shifting the potential more cathodically, a new chemical reaction involving H_2Te gas and Bi^{III} ions takes place:

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

The chemically deposited Bi_2Te_3 binary compound is, however, unstable in the region -0.15 V to –0.3 V, due to the more positive polarization of electrode than the formal potential of Bi^{III}/Bi couple. The increase of current on voltammogram is explained by the formation of a coarsely crystallysed Bi_2Te_3 compound, a phenomenon that enhances the actual surface area of electrode. A substantial formation of Bi_2Te_3 stable film was performed electrochemically at more negative potentials, but in a narrow range of potentials (-0.3 V to –0.35 V):

$$2 \; Bi^{3+} \; + \; 6 \, e \; + 3 \; Te \; \rightarrow Bi_2Te_3 \tag{4}$$

Obviously, by overcoming this region at more negative potentials than –0.35 V, the electrodeposition of the metallic bismuth predominates; the beginning of H$_2$ evolution is also expected.

The electro-dissolution of the corresponding cathodic deposits can be clearly seen by reversing the potential in anodic direction, when several well-defined peaks occur (cyclic voltammetry curve *a* in Fig. 3). For example, the first anodic peak (-0.15 V) may be ascribed to the dissolution of the last deposited Bi film. Actually, its splitted form suggests two steps in the electrodeposition of Bi and two steps in Bi stripping, as well. The second anodic peak (at more positive potentials) is broader in its shape as twins and refers first to dissolution of Bi$_2$Te$_3$ (+0.35 V) and second to dissolution of Te (+0.5 V).

Fig. 4 which illustrates the typical polarization curve and cyclic voltammogram with participation of SbCl$_4^-$ and HTeO$_2^+$ ions can be interpreted in the same manner as Fig. 3. On the polarization curve (curve *b*) one can see again all distinct potential regions like in the cathodic polarization obtained in BiCl$_4^-$ + HTeO$_2^+$ mixture. The reactions (1) and (2) are also valid whereas the reactions (3) and (4) will be replaced by the corresponding reactions (5) and (6):

$$2 \; Sb^{3+} + \; 3 \; H_2Te \; \rightarrow Sb_2Te_3 \; + \; 6 \; H^+ \tag{5}$$

$$2 \; Sb^{3+} \; + 6 \, e \; + 3 \; Te \; \rightarrow \; Sb_2Te_3 \tag{6}$$

The process (6) represents the electrodeposition of the binary compound Sb$_2$Te$_3$ as a stable film. We consider also that at more negative potentials (generally over –0.35 V), Sb deposition may be superposed. Its increased amount gives rise to a more distinct anodic peak representing Sb dissolution (also in two steps).
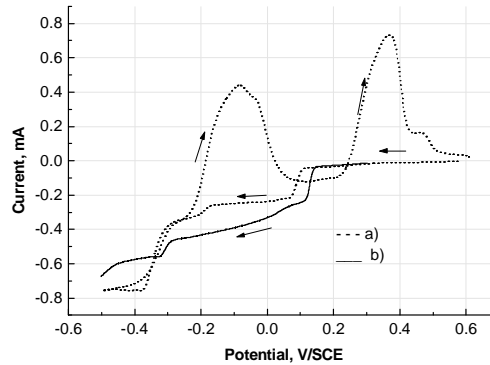

Fig. 4. The voltammogram (*a*), 50 mV/s and polarization curve (*b*), 1 mV/s for Sb-Te alloy electrodeposition. Working electrode: glassy carbon (7,06 mm^2), rotation rate: 500 rpm; Sb^{III}conc. = 0.009 M, Te^{IV}conc. = 0.025M.

However, one can notice on anodic branch of cyclovoltammogram in Fig. 4 a clear separation of succesive peaks in the region of positive potentials, first being attributed to dissolution of binary compound Sb$_2$Te$_3$ (also at + 0.35 V as Bi$_2$Te$_3$ dissolution) and later to dissolution of elementary tellurium (+ 0.47 V, peak of much smaller amplitude).

On the basis of all above discussed we are able now to interpret the complex polarization curve and voltammogram for solutions with BiCl$_4^-$ + SbCl$_4^-$ + HTeO$_2^+$ ternary mixtures. These curves are depicted in Fig. 5.
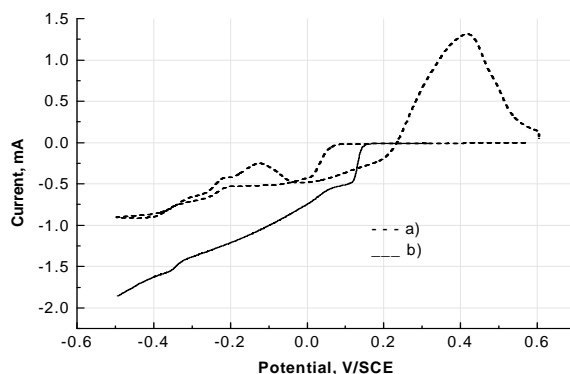
Fig. 5. The voltammogram (*a*), scan rate 50 mV/s and polarization curve (*b*), 1 mV/s for Bi-Sb-Te alloy electrodeposition. Working electrode: glassy carbon (7.06 mm^2), rotation rate: 500 rpm; Sb^{III}conc. = 0.009 M, Te^{IV}conc. = 0.025M.

The most important fact from the technological point of view is the establishing of the potential region for electrochemical co-deposition of all three ions in order to obtain the ternary compound Bi$_{2-x}$Sb$_x$Te$_3$. We can suppose that after occurrence of gaseous H$_2$Te (+0.15 V to + 0.1 V) and the deposition of a tellurium film (between + 0.1 V and –0.15 V) it follows a narow potential region of technological interest, where firstly the binary compound Sb$_2$Te$_3$ (-0.15 V to –0.18 V) and after that the ternary compound Bi-Sb-Te are formed. The co-deposition of all three elements into one well-defined stoichiometric compound takes place until the potential –0.3 V.
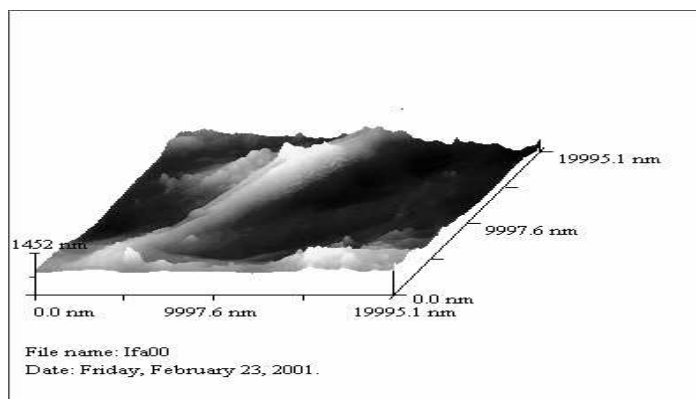

Fig. 6. AFM topographic image of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ film before thermal annealing.

The range may be extended or narrowed according to the composition of solution. At more negative potentials the deposition of single elements predominates.

Fig. 6 shows a picture obtained by atomic force microscopy (AFM) of electrodeposited Bi-Sb-Te alloy, using a bath composition as in Fig. 5. It can be noticed the polycrystalline shape of the surface, with grain size around 1 micrometer.
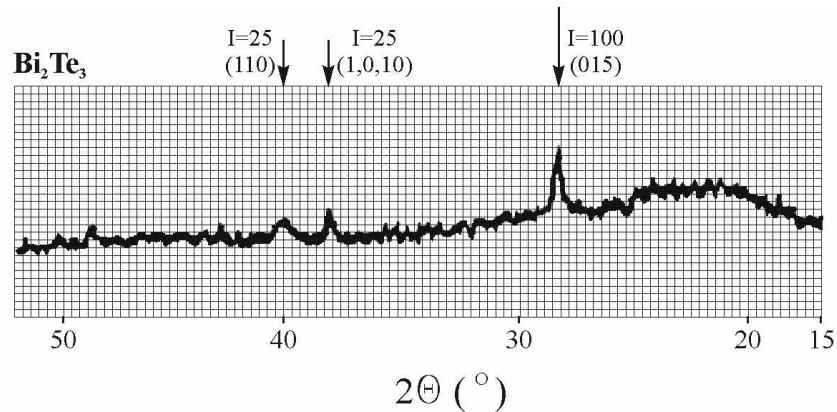
Fig. 7. XRD pattern of Bi$_{2-x}$Sb$_x$Te$_3$ sample recorded on the removed and ground film.

The X-ray diffraction pattern of a typical sample is presented in Fig. 7. Besides an amorphous phase revealed by a large maximum at low diffraction angles, the lines of the rhombohedral Bi$_2$Te$_3$ phase are clearly evidenced.

Our above described investigations constitute a basis for the manufacturing of electronic microdevices, compatible with the techology of integrated circuits. In this sense, we have tried to obtain thermoelectric microstructures using a photolithographic procedure. The results were presented in Fig. 8, demonstrating a good compatibility of our acid aqueous solutions with the positive photoresist used.

The preliminary measurements of thermoelectrical parameters have shown good specific performances (the Seebeck coefficient of around 120-150 μV/K and electrical resistivity of 7-10 mΩcm).
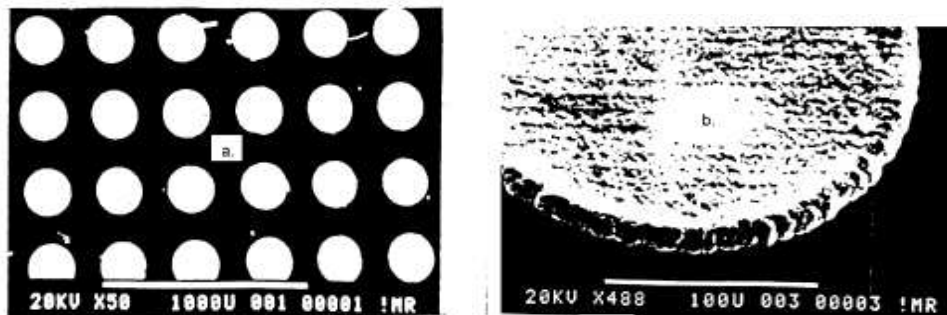

Fig. 8. SEM micrographs of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ film on a Ni substrate using photographic technique Magnification, (a) × 50; (b) × 500.

4. Conclusions

The presented electrochemical method to produce composition modulated Bi$_{2-x}$Sb$_x$Te$_3$ alloys has the advantages to work with high electrodeposition rates, 30-50 μm/h for the films. The electrolyte, which consists in a very concentrated hydrochloric acid solution (HCl 6M) and Bi^{III}, Sb^{III} and Te^{IV} electro-active species, allows the co-deposition of bismuth, antimony and tellurium to be accomplished at room temperature on glassy carbon, platinum or nickel electrode. The corresponding mechanisms of electrodeposition of single, binary and ternary chalcogenides compounds have been proposed on the basis of cyclic voltammograms and polarization curves. It was demonstrated the good compatibility of the proposed working electrolyte with the photo-lithographic technique specific to the fabrication of the integrated circuits.

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