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Surface characterization of BiSbTe thermoelectric films electrodeposited from chlorides aqueous solutions and choline chloride based ionic liquids

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ABSTRACT

Investigations of obtaining BiSb, BiTe, SbTe and BiSbTe films in concentrated chloride aqueous solution (5 M NaCl + 1 M HCl) or in ionic liquid based on choline chloride + malonic acid mixture were reported. The concentrations of Bi, Sb, Te, existing as complex anions due to high Cl^- concentration, were within 10–90 mM. The measurements were carried out at room temperature for aqueous medium and 85 °C for ionic liquid. Cyclic voltammetry and electrochemical impedance spectroscopy using Pt electrode were used for investigating the interface process in both electrolytes. The morphology and chemical composition of films deposited on Cu in chloride aqueous solution using current pulses or potential pulses were determined by AFM and SEM microscopy. For BiSb, the effects of change from unipolar to reverse pulses and increase in cathodic current were shown as favorable. SEM images for BiSbTe confirmed the morphology modification by increasing the current pulses, while energy dispersive spectroscopy analyses indicate a dramatic change of composition.

1. Introduction

The preparation of BiSbTe ternary compound as well as BiTe and SbTe binary compounds has attracted considerable interest, being ideally suited to thermoelectric applications including waste heat recovery from power plants, in automobile industry and coolers for microelectronics or computer processors. BiSb (n-type semiconductor) is most useful for thermoelectric refrigeration at low temperature around liquid nitrogen [1] whereas Bi_2Te_3 and $Bi_{2-x}Sb_xTe_3$ (p-type semiconductor) have been considered among the best thermoelectric materials for room temperature applications [1,2]. Sb_2Te_3 is widely utilized in micro-thermoelectric generators and coolers as well as in optoelectronics and biomedical fields [3,4].

A rapid and inexpensive technique for film synthesis of these compounds is the electrodeposition using aqueous solutions with hydrochloric acid [5,6] or nitric acid [7–9], providing an alternative to classical methods (MOCVD or metallurgical). Although in recent years room temperature ionic liquids are increasingly applied for electrochemical co-deposition of numerous metals on various substrates [10], only few investigations on the preparation of such thermoelectric films were reported, employing imidazolium salts [11,12] or molten chloroaluminates [13], as ionic liquid media. Pulse plating was seen to have most beneficial effect on the properties of deposits, as leading to improve a microstructure, in terms of crystallinity and stoichiometry. In addition, the advantage of pulse plating procedure is to afford multiple additional variables in the electrolyte system, i.e. current of electrolysis, pulse length and frequency, simple periodic or more sophisticated profile of delivered current.

In the present work it is investigated comparatively the co-deposition of Bi, Sb, and Te as binary and ternary compound films using either a moderate acid aqueous solution (5 M NaCl + 1 M HCl) or a ionic liquid consisted in a mixture of choline chloride (2 hydroxy-ethyl-trimethyl-ammonium chloride, ChCl) and malonic acid (MA). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were chosen as electrochemical techniques in order to evidence the interface processes. BiSb, BiTe, SbTe and BiSbTe films were obtained on Cu substrate by pulse plating and their surface was characterized.

2. Experimental

The supporting aqueous electrolyte was 5 M NaCl + 1 M HCl solution prepared using Millipore Milli-Q water. Bi_2O_3 and Sb_2O_3 oxides were dissolved as precursors for Bi and Sb ionic species whereas Te ions were obtained by dissolution of TeO_2 in 1 M NaOH solution, followed by neutralization and pH adjusting with concentrated hydrochloric acid solution. The ionic liquid was prepared by heating the mixture (1:1 mol) of ChCl + MA at above 90 °C for 30 min; $BiCl_3$, $SbCl_3$ and TeO_2 were the precursors of Bi, Sb and Te ions, respectively, and their molarities in solution were calculated using a density value of 1.2103 g cm^{-3} at 85 °C working temperature. CV

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and EIS investigations were conducted at room temperature in NaCl + HCl aqueous solutions with Zahner elektrik IM 6e potentiostat. An AUTOLAB PGSTAT 12 Eco-Chemie potentiostat was used for measurements at 85 °C in ChCl + MA ionic liquid. The potential scan rates for recording cyclic voltammograms were 100 mV s^{-1} in aqueous solution and 5 mV s^{-1} in ionic liquid, respectively, while for EIS spectra in both media the ac frequency range was 0.05 Hz–100 kHz with a 10 mV perturbation signal. The cell contained Pt foil (0.5 cm^2) as stationary working electrode and a platinum cylindrical mesh as auxiliary electrode. The reference electrodes were Ag/AgCl for aqueous media and a Pt wire immersed in the experimented ionic liquid representing a quasi-reference electrode for ionic liquid media.

The electrolyses for films deposition were also carried out using copper sheets in aerated solutions without stirring. The cathode with an exposed area of 8–20 cm^2 was located vertically and parallel Pt sheets were anodes. Pulse plating was performed using either a home-made pulse current generator or a potentiostat. The copper substrate surface was hand-polished using emery paper, then degreased with acetone, etched in a HNO_3 solution and rinsed with Milli Q water. After plating the samples were again rinsed with water and dried. A maximum of three or four deposition runs were performed using the same bath solution to avoid changes in the bath composition. Film morphology was studied using AFM microscope (Quesant Scope-350) and micrographs and results of chemical analyses were obtained using scanning electron microscope (Philips ESEM XL-30) provided with energy dispersive spectrometer (EDS equipment).

3. Results and discussion

3.1. CV and EIS investigations on the electrochemical behaviour of Bi, Sb and Te ions at Pt/electrolyte interface

CV and EIS carried out on Pt electrode both in aqueous medium at room temperature (25 °C) and in ionic liquid medium at 85 °C allowed the selection of the appropriate potential ranges for electrodeposition of binary or ternary compounds. Typical CVs recorded at 100 mV s^{-1} scan rate showing the electrochemical behaviour of Bi, Sb and Te ions in aqueous chloride solution are presented in Figs. 1 and 2. In Fig. 1 all cathodic branches exhibit a main reduction peak (at −0.39 V for Bi, −0.3 V for Sb and −0.4 V for BiSb) followed by a series of less pronounced peaks or waves within a large potential range (−0.4 V to −0.7 V). During further cathodic exploration, the current increases continuously due to hydrogen evolution as a supplementary process.

The behaviour in the less negative cathodic region supports reports in literature [14,15] about consecutive processes of underpotential deposition (UPD) of Bi or Sb before the massive deposition. Both location and amplitude of series of peaks are also very similar with those reported by others using aqueous solutions and Au, Pt or C electrodes [6,7].

We noticed that the solubility of bismuth or antimony precursors is increased due to the presence of a complexating agent, which is Cl$^-$ anion. Consequently, $BiCl_4{}^-$ and $SbCl_4{}^-$ are present as ionic complex species when participate at cathodic process. The voltammetric curve for BiSb appears to be identical in shape to Bi curve; we assume for the formation of BiSb alloy a direct co-reduction:

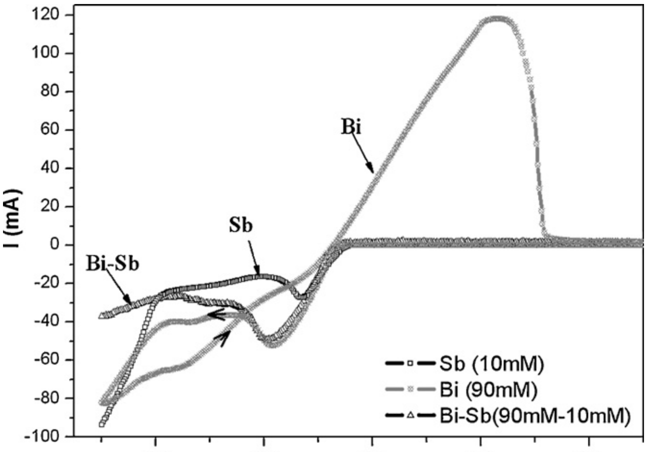

Fig. 1. CVs for Bi, Sb and BiSb deposition on Pt from 5 M NaCl + 1 M HCl aqueous electrolyte, 25 °C; for all three curves: c_{Bi} = 90 mM, c_{Sb} = 10 mM; scan rate 100 mV s^{-1}.

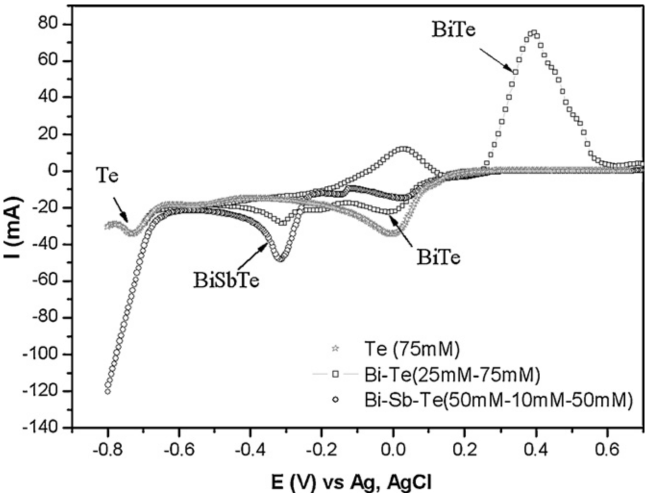

Fig. 2. CVs for Te, BiTe and BiSbTe deposition on Pt from 5 M NaCl + 1 M HCl aqueous electrolyte, 25 °C; Te curve: c_{Te} = 75 mM, BiTe curve: c_{Bi} = 25 mM and c_{Te} = 75 mM, BiSbTe curve: c_{Bi} = 50 mM, c_{Sb} = 10 mM and c_{Te} = 50 mM; scan rate 100 mV s^{-1}.

$$(1-x)BiCl_4{}^- + xSbCl_4{}^- + 3e^- \rightarrow Bi_{1-x}Sb_x + 4Cl^- \qquad (1)$$

The electrochemical process (1) is possible because the complexation brings the reduction potentials of bismuth and antimony ions close to each other, thus allowing co-deposition in spite of differences in the standard potentials scale. An evidence is the shift in peak potential by replacing the solution with antimony chloride with solution containing both bismuth and antimony chlorides. For all curves, a single anodic (stripping) peak at reverse scan (shown in Fig. 1 for Bi curve, only) was observed, corresponding to redissolution of freshly deposited films. A crossover of the direct and reverse scan that occurred sometimes in more negative potential region may be indicative of a nucleation-controlled bulk deposition process, since the formation of thermodynamically stable nuclei requires a potential more negative than that required to reduce ions of bismuth or antimony.

Fig. 2 presents comparatively the deposition processes of elementary Te, BiTe and BiSbTe in the same chloride concentrated electrolyte. The voltammetric curve for singular Te ion reduction on Pt shows a first peak at 0 V, identified as Te UPD reaction. Along the curve it follows a series of small peaks and finally a reduction peak at about −0.73 V, attributed to massive deposition of tellurium. In our work with chloride-rich medium, we suppose that tellurium species may exist in solution as Te_x^{4-x} complex ionic species, most probable as $TeCl_6{}^{2-}$ anion [12]. A direct discharge to elementary Te is expected:

$$TeCl_6{}^{2-} + 4e^- \rightarrow Te + 6Cl^- \qquad (2)$$

The CV curve for BiTe was obtained by keeping the same Te ion concentration in solution and by adding Bi ions. First cathodic peak (at +0 V) may be attributed to Te UPD process, although it is less pronounced that corresponding peak on previous described curve. The voltammogram has a different shape, because after the peak located at 0 V attributed to Te UPD a new occurred reduction peak at −0.3 V was recorded, identified with co-reduction reaction to form Bi_2Te_3 chemical compound:

$$2BiCl_4{}^- + 3TeCl_6{}^{2-} + 18e^- \rightarrow Bi_2Te_3 + 26Cl^- \qquad (3)$$