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Section 10: Special Topics

MAGNETO-THERMOELECTRIC ALLOYS OBTAINED BY ELECTRODEPOSITION

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When a magnetic field is applied on a narrow gap semiconductor with high hole mobility, a substantial rise in the figure of merit can be observed due to Ethinghausen effect. The most important proof of this effect was achieved by using Bi-Sb alloys. The present paper is devoted to performance of the electrochemical synthesis of Bi-Sb alloys from acid aqueous solutions and to the investigations of physico-chemical properties of these alloys. Thick films of Bi-Sb alloy were electrodeposited from both chloride and perchlorate solutions.The electrodeposited films obtained from perclorate solutions are thicker, more compact and more uniform. The Bi/Sb ratio in the solution bulk was found to be approximately the same to the Bi/Sb ratio in the electrodeposited alloy. The Hall effect was measured by a home-made apparatus. The range of the magnetic field (B) determined by a standard induction coil was 0.05-1 T. Carrier concentration, n is 10^{18} cm^{-3} and increases slow in the choosen magnetic range.

Keywords: Thermoelectricity, Magneto-thermoelectric alloy, Electrodeposition

1. Introduction

Electrodeposition of semiconductor nanostructures, having unique physico-chemical properties, is one of the most common applications of electrochemical synthesis of inorganic semiconductors. As they are electrochemically deposited, these objects may be in the form of quantum dots [1.2], nanocrystallites [3], fibres [4], films [5], multilayers [6] etc.

The electrochemical synthesis of various compounds, such as, CdS, CdSe, CdTe, GaAs, GaSb, $CuInX_2$, MoX_2, Bi_2X_3, X = S, Se, Te,) have been already successfully accomplished [7-12].

As the electrochemical methods are relatively simple, not capital intensive and allowing to deposit the film onto electrodes of various geometry, they are very attractive for depositing semiconductor layers with different characteristics (necessary for various applications): conduction type, band gap, carrier concentration, etc. Electrochemically deposited semiconductor films are mostly polycrystalline films. The drive for increased performance and miniaturization of a wide range of electronic systems requires higher power levels and higher packaging densities. However, thermal management problems are rapidly becoming a major issue for this technological process, as they limit the degree of integration of devices and components. [13]

Despite considerable efforts in the last 10-20 years the figure of merit of the best thermoelectrics could be improved only slightly. Only in few cases Z value with ZT > 1 could be achieved.

Nanochannels with a length-to-diameter aspect ratio 1000:1 and channel densities up to 10^{15} cm^{-2} using Bi electrodeposited wires were already obtained [14], for which significant quantum-enhanced ZT effects can be expected to result.

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The present paper is devoted to performance of the electrochemical synthesis of Bi-Sb alloys from acid aqueous solutions and to investigations of physico-chemical properties of these alloys.

2. Experimental

The electrochemical measurements were performed using a three-electrode cell and a PAR 173 potentiostat/galvanostat connected to a computer through a special interface. A platinum electrode (0.014 cm^2) was used as working electrode (for thick layer deposition a molybdenum sheet was used instead of platinum). A SCE was used as reference electrode (all potentials are referred to SCE). All solutions used for Bi-Sb deposition were prepared using analytical grade reagents and doubly distilled water.

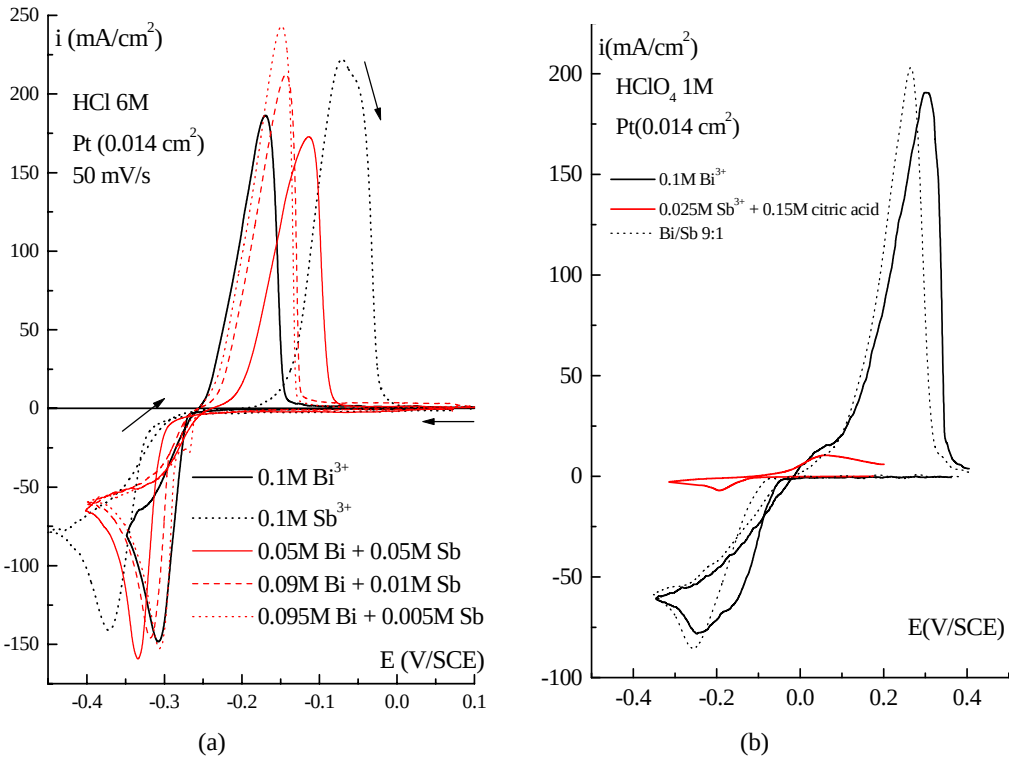

Fig. 1. Cyclic voltammograms for Bi, Sb and Bi-Sb alloy deposition from 6M HCl (a) and 1M $HClO_4$ (b) solutions; sweep rate =50 mV/s.

The cyclic voltammograms for the systems Sb^{3+}/Sb and Bi^{3+}/Bi are shown in Fig.1. A well-defined reduction wave is observed in both cases: for Sb^{3+} at about –0.13V and for Bi^{3+}, at about –0.24 V. The potentiodynamic polarization curves (Fig.2) show that the deposition of bismuth and antimony starts at about –0.05V and –0.07 V respectively. In 6M HCl the deposition potentials are more negative, the reducible species in this case being the complexes $BiCl_4^-$ and $SbCl_4^-$ (that are present in concentrated chloride solutions), rather than BiO^+ and SbO^+.

Thin films of Bi-Sb alloy were electrodeposited from both chloride and perchlorate solutions; the best results were obtained using the perchlorate electrolyte: the electrodeposited films are thicker, more compact and more uniform.

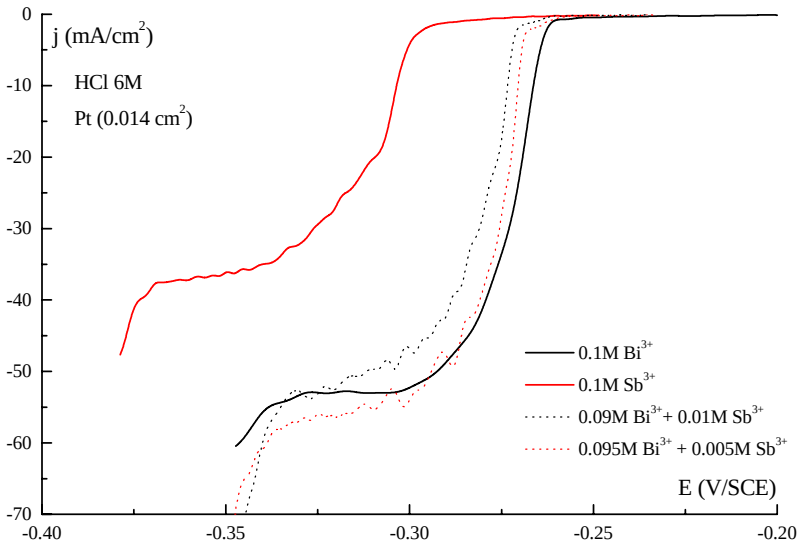

Fig. 2 Polarization curves for Bi, Sb and Bi- Sb alloys electrodeposition obtained from 6M HCl solutions; sweep rate =0.5 mV/s.

For this reason the perchlorate electrolyte was chosen for the electrodeposition of thicker Bi-Sb alloy films. Higher deposition temperatures allow higher electrodepostion currents, but the deposit quality is not improved. Moreover, for temperatures exceeding 45°C, irreversible precipitation of Sb_2O_3 may occur in the solution bulk. The Bi-Sb alloy films used for further physical characterization were deposited at room temperature (20°C), at constant current density (2 A/dm^2) from $HClO_4$ 1M containing 0.1 M Bi^{3+} and various concentrations of Sb^{3+} (from Bi/Sb ratio of 18:1 to Bi/Sb 6:1). The Bi/Sb ratio in the solution bulk was found to be approximately the same to the Bi/Sb ratio in the electrodeposited alloy.

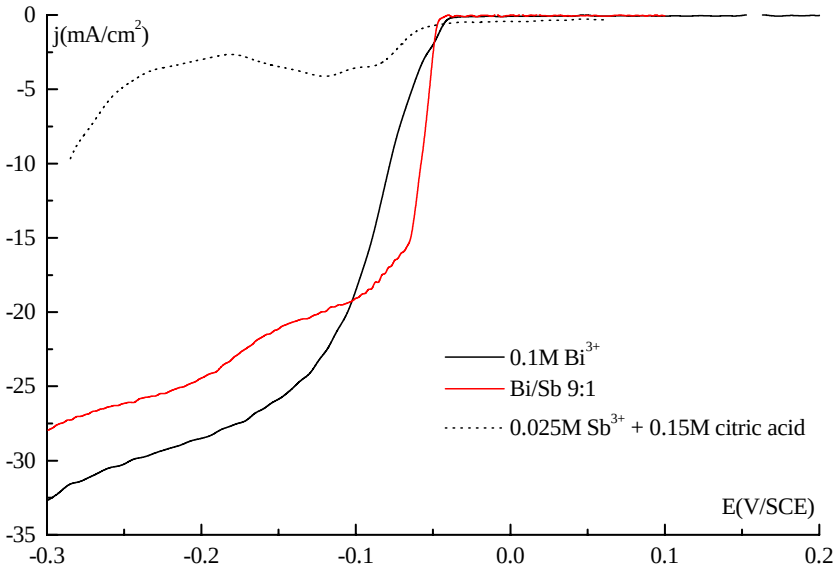

Fig. 3 Polarization curves for Bi, Sb and Bi- Sb alloys electrodeposition obtained from 1M $HClO_4$ solutions; sweep rate =0.5 mV/s.

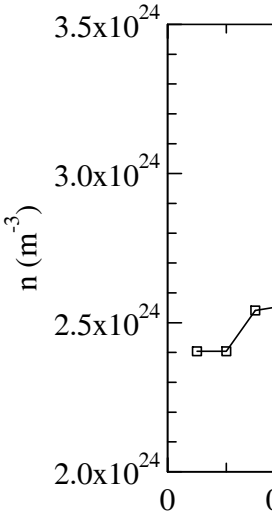

Fig. 4. The dependence of carrier concentration n (m^{-3}) with magnetic field B (T).

The Hall effect was measured by a home-made apparatus. The range of the magnetic field (B) determined by a standard induction coil was 0.05-1 T. From the coefficient Hall formula:

$$R_H\ [m^3/C] = V_H*g/(B*I), \quad (1)$$

where V_H is Hall voltage, g is sample thickness and I is the current intensity, the charge concentration was calculated from

$$n\ [m^{-3}] = -1/\ (n*e), \quad (2)$$

where e is electron charge.

As one seeing on Fig. 4, carrier concentration n is 10^{18} cm^{-3} and increases slow in the choosen magnetic range.This concentration sustain the value of the energy gap (4 meV) calculated from $\sigma(T)$ measurement in 270-320 K range.

3. Conclusions

The potentiodinamic curves show that the deposition of Bi and Sb start at 0,05V and 0,07 V respectively in $HClO_4$ solutions. In 6M HCl the deposition potentials are more negative. Thicker, compact and uniform Bi-Sb alloy films are obtained from perclorate electrolit. We observed that carriers concentration have a value about 10^{18} (cm^{-3}), in good agreement with values for TE materials obtained by classical technology and increases with magnetic field.

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