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Electrodeposition of Sb, Bi, Te, and their alloys in AlCl₃–NaCl–KCl molten salt

Hirofumi Ebe, Mikito Ueda*, Toshiaki Ohtsuka

Graduate School of Engineering, Hokkaido University, 060-8628 Sapporo, Japan Received 2 December 2005; received in revised form 2 March 2007; accepted 2 March 2007 Available online 12 March 2007

Abstract

The Electrochemistry of Sb, Bi, and Te in AlCl₃–NaCl–KCl molten salt containing SbCl₃, BiCl₃, and/or TeCl₄ at 423 K was investigated by voltammetry, and electrodeposition of the three metals was performed under constant potential control in the melt. The voltammogram on a glassy carbon (GC) electrode in a melt containing $0.025 \text{ mol dm}^{-3}$ [M] SbCl₃ showed a couple of redox peak corresponding to the Sb/Sb(III) redox reaction, and a stable layer of pure Sb was deposited under the constant potential control. The voltammograms in the melt containing 0.025 M BiCl₃ or 0.025 M TeCl₄ showed several redox couples. Stable deposit layers of pure Bi and Te were not obtained under the constant potential control, as the deposited layers detached from the electrode and immediately dissolved into the molten salt. Binary alloy deposition was possible in a melt containing BiCl₃ and SbCl₃, and also with BiCl₃ and TeCl₄. A stable Bi–Sb alloy deposit of metallic Sb and Bi–Sb solid solution was obtained at 0.8 and 0.9 V versus Al/Al(III) in the melt containing BiCl₃ and SbCl₃. The atomic ratio of Bi in the deposited Bi–Te alloy deposit was also obtained with the molten salt containing BiCl₃ and TeCl₄. The deposited Bi–Te alloy consisted of a mixture of Bi₂Te₃, BiTe, and Bi₂Te. The alloy deposit had good crystallinity and the preferential orientation was the (110) plane.

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1. Introduction

Compound semiconductors such as bismuth telluride (Bi_2Te_3) , lead telluride (PbTe) and silicon germanium (SiGe) have the properties of thermoelectric cooling (Peltier effect) and thermoelectric generation (Seebeck effect). When used in thermoelectric cooling applications they are called Peltier devices and have attracted attention, as they have been applied in economical and convenient cooling systems. Especially, Bi_2Te_3 has been widely employed in thermoelectric devices operating at room temperature such as the cooling systems of refrigerator, Freon-free air conditioners, and wine cellars.

Bi₂Te₃ intermetallic compound behaves as a semiconductor, and its type depends on the composition and doping species [1]. A stoichiometric excess of Bi and doping of Sb makes it a ptype semiconductor and an excess of Te and doping of Se makes

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it an n-type semiconductor. Further, these dopants have been suggested to increase the service life of the devices.

Several methods for preparing Bi2Te3 have been reported, including directional crystallization [2,3], vacuum evaporation [4,5], mechanical alloying [6], and spark plasma sintering [7]. Electrodeposition has also been reported for the preparation of Bi₂Te₃ [8–13]. The electrochemical method has a number of advantages over the other methods: (1) easy control of the composition by the applied potential, (2) easy control of film thickness by the applied electricity, (3) low cost, and (4) simple manufacturing procedure. Okido and Ichino reported that stoichiometric Bi₂Te₃ with needle-like morphology was prepared from acidic aqueous solutions containing Bi₂(SO₄)₃ and K_2 TeO₃ [8]. Stein and co-workers reported that the detailed composition of Bi2Te3 film which was electrodeposited in nitric acid solutions containing Bi³⁺ and HTeO₂⁺ depended on the potential, electrolyte concentration during the deposition [9]. There have been few reports on electrodeposition of Bi₂Te₃ using molten salts. We suppose that the crystallinity of deposits is more enhanced by molten salt electrolysis at temperature of

^{*} Corresponding author. Tel.: +81 11 706 7813; fax: +81 11 706 7813. *E-mail address:* mikito@eng.hokudai.ac.jp (M. Ueda).

about 420 K than by the electrolysis in aqueous solutions at room temperature. In the present paper, we report electrochemical behavior in AlCl₃–NaCl–KCl molten salt containing SbCl₃, BiCl₃, and/or TeCl₄ and examine the electrodeposition of Sb, Bi, and Te and their binary alloys.

2. Experimental

Sodium chloride (NaCl, Wako, 99.5% pure), potassium chloride (KCl, Wako, 99.5% pure), anhydrous antimony chloride (SbCl₃, Aldrich, 99.999% pure), anhydrous bismuth chloride (BiCl₄, Alfa, 99.9% pure), and anhydrous tellurium chloride (TeCl₄, Aldrich, 99.999% pure) were used as received. Aluminum chloride (AlCl₃, Fluka, 99.0% pure) was purified by a sublimation-condensation process to remove impurities. A Pyrex glass cell was used for the electrochemical measurements and electrodeposition [14]. In the cell, AlCl₃, NaCl, and KCl in a molar ratio of 61:26:13 with 50 ml volume were mixed and melted at 423 K. Any of SbCl₃, BiCl₃, and/or TeCl₄ was added to the melt. A glassy carbon plate (GC, Tokai carbon, GC-20SS) or a pure platinum plate (Pt, Tanaka-kikinzoku, 99.999%) was used as the working electrode and a GC plate as a counter electrode. Pure aluminum wire (Niraco, 99.98%, $\varphi = 0.5$ mm) placed in small Pyrex glass tube was immersed in AlCl₃-NaCl-KCl molten salt and used as a reference electrode. To maintain electrical contact between the electrolyte melt and the reference electrode, a small hole was made by insertion of asbestos fibers at the bottom of the tube. Electrochemical measurements were performed with a Hokuto-Denko HAG-5010 potentiostat in an Ar gas atmosphere at 423 K.

The composition, the assignment of crystal structure, and the morphology of the deposits were analyzed by fluorescence X-ray spectroscopy (JEOL JSX-3220, Rh target), X-ray diffraction (XRD, JEOL JDX-3500, Cu K α radiation), and scanning electron microscopy (SEM, JEOL JXA-8900M), respectively.

3. Results

In the AlCl₃–NaCl–KCl melt, the deposition potential of Al and chlorine evolution takes place at potentials lower than 0.0 V versus Al/Al(III) and at potentials higher than 1.8 V, respectively. The cathodic deposition of Sb, Bi, and Te is expected to take place in the 0.7–0.9 V potential region where these metals can be deposited without co-deposition of Al.

3.1. Pure metals deposition

3.1.1. Voltammograms

To establish the deposition potentials of Sb, Bi, and Te, we evaluated electrochemical behaviors of these ions in the AlCl₃–NaCl–KCl molten salt containing SbCl₃, BiCl₃, or TeCl₄ by voltammetry. The voltammograms recorded on GC electrode are shown Fig. 1(a)–(c); the potential sweep was at a rate of 0.01 V s^{-1} from 1.8 to 0.0 V in the cathodic direction and the reverse from 0.0 V in the anodic direction.

Fig. 1(a) shows a voltammogram for the molten salt containing 0.025 M [mol (dm³ melt of AlCl₃–NaCl–KCl)⁻¹] SbCl₃.



Fig. 1. Voltammograms on the GC electrode in AlCl₃–NaCl–KCl molten salt containing (a) 0.025 M SbCl₃, (b) 0.025 M BiCl₃, and (c) 0.025 M TeCl₄. The scan rate was 0.01 V s⁻¹.

The voltammogram shows a couple of redox peak at around 0.9 V. The cathodic current starts to increase from 0.9 V from where the surface color gradually changed to metallic. The anodic current corresponding to the dissolution of the electrode-posit was observed at potentials higher than 1.0 V during the following anodic potential scan from 0.0 V.

Fig. 1(b) shows a voltammogram for the molten salt containing 0.025 M of BiCl₃. Three redox couples appear in the voltammogram. At a first reduction wave c_1 at 1.1 V, a reddish brown fog was generated from the GC electrode surface spreading into the molten salt. At the second reduction wave c_2 around 0.9 V, this fog reacted with the electrode to form a gel-like film on the electrode. This film was, however, very unstable and immediately dissolved into the melt. As the potentials were scanned to the more negative, the small cathodic peak c_3 appeared at 0.5 V at which a black deposit was observed. During the reverse sweep to the positive direction, the black electrodeposit detached from the electrode and then dissolved into the melt in the potential region from peaks a_1 to a_2 .

Fig. 1(c) shows a voltammogram for the molten salt containing 0.025 M of TeCl₄. At the wave c_1 around 1.4 V during the cathodic scan, a purple fog was generated from the GC electrode. From 0.9 V, cathodic current increased and exhibited the second wave c_2 at about 0.8 V. The purple fog disappeared around the electrode at the wave c_2 , at which a metallic deposit was formed. The metallic deposit changed the color to black with the scan to the more negative potentials. With the increase in cathodic current there was a wave c_3 , at 0.4 V, and the deposit developed into a dendrite shape. During the positive reverse potential sweep, the deposit detached from the GC electrode and dissolved into the melt around the wave a_1 at 1.1 V. The color of the melt after the positive sweep turned pale purple.

To examine the influence of electrode differences on the electrodeposition, we measured the voltammogram on a Pt electrode in a melt containing 0.025 M BiCl₃. This voltammogram is shown in Fig. 2, where the voltammogram on GC electrode is also plotted for comparison. The voltammograms of the Pt and GC electrodes were not different except for an anodic peak at 1.4 V on the Pt electrode. This peak may correspond to the dissolution of Pt and Bi from the Bi–Pt alloy which was formed during the cathodic sweep.

3.1.2. Deposition under constant potential control

From the observation of the electrode surface during the CV measurements, the deposition potentials of the three metals were assumed to be about 0.9 V. A constant potential electrolysis on the Pt electrode was carried out to confirm the deposition of pure



Fig. 2. Voltammogram on the Pt electrode in AlCl₃–NaCl–KCl molten salt containing 0.025 M BiCl₃. The voltammogram on GC electrode is plotted for comparison.

Sb, Bi, and Te, and Table 1 summarizes the electrodeposit of the three metals as a function of the potential.

The Sb layer was electrodeposited at potentials from 0.9 to 0.5 V, at potentials lower than 0.7 V, the deposits grew in dendrite shape, and at potentials higher than 0.7 V the deposits exhibited good adhesion and formed a flat homogeneous layer. The deposits formed at 0.7 V, contained of 3.5 at.% aluminum, while the deposit at 0.8 and 0.9 V was composed of pure Sb without any trace of aluminum.

No stable pure Bi deposit was obtained by the constant potential electrolysis from 0.9 to 0.5 V. There was no deposit at 0.9 and 0.8 V, while a gel-like film was observed at 0.5 V. This film, however, dissolved into the melt immediately after the formation. After the dissolution of the gel-like film, a thin white-gray film remained on the Pt electrode and was identified to be Bi_2Pt by XRD.

No stable pure Te layer was obtained and needle-like deposits grew at potentials lower than 1.0 V. The deposit dissolved immediately to form a purple fog around the electrode.

3.2. Binary metal deposition

For Sb–Bi and Bi–Te alloy deposition, the electrodeposition was carried out with a constant electric charge of $40 \text{ C} \text{ cm}^{-2}$ on the Pt electrode at potentials lower than 0.9 V.

Table 1

Morphology of electrodeposition of Sb, Bi, and Te at electrolysis potential from 0.5 to 0.9 V.

Potential E (V)	Sb	Bi	Те
0.9	Flat homogeneous deposit	No deposit	Needle-like deposit
0.8	Flat homogeneous deposit	No deposit	Needle-like deposit
0.7	Flat homogeneous deposit containing Al	_	Needle-like deposit
0.5	Dendrite	Gel-like deposit	Black deposit containing Al



Fig. 3. Optical photograph of electrodeposit from the melt containing 0.025 M SbCl₃ and 0.025 M BiCl₃ at 0.9 V.

In the melt containing 0.025 M SbCl₃ and 0.025 M BiCl₃, electrodeposits of Sb-Bi were obtained at the potentials of 0.9 and 0.8 V. The electrodeposit was silver gray and had a smooth texture, as shown in Fig. 3. The fluorescence X-ray spectroscopy revealed that the atomic ratios of Bi-Sb were 37-63 and 57-43 at 0.9 and 0.8 V, respectively. The XRD pattern of the 37Bi-63Sb deposit at 0.9 V is shown in Fig. 4, which indicates that the deposit is composed of metallic Sb single phase [15] and a solid solution of Bi-Sb [16]. The SEM photograph (Fig. 5) showed that this deposit had a homogeneous surface consisting of fine granules with $1-3 \mu m$ diameter. The grain size became larger with the lower electrodeposition potentials. The deposits obtained at 0.7 and 0.6 V showed dendric growth and immediately detached from the Pt electrode. Under the detached dendrite layer there was a silver-gray layer which was assigned to be Bi₂Pt by XRD.

No stable electrodeposits of Bi–Te could be obtained from the melt containing 0.025 M BiCl₃ and 0.025 M TeCl₄, since



Fig. 4. XRD pattern of electrodeposit from the melt containing 0.025 M SbCl_3 and 0.025 M BiCl_3 at 0.9 V.



Fig. 5. SEM photograph of electrodeposit from the melt containing 0.025 M SbCl₃ and 0.025 M BiCl₃ at 0.9 V.

a high current density for the deposit growth induced dendric shape of the deposit and this was immediately detached. Stable deposits were obtained at 0.9 and 0.85 V, when the concentrations of BiCl₃ and TeCl₄ were lower, at 0.015 and 0.0075 M, respectively. The electrodeposit obtained at 0.9 V had a relatively homogeneous surface, as shown in Fig. 6, it exhibited a black-gray color and the atomic ratio of Bi–Te was found to be 60–40 by the fluorescence X-ray spectroscopy. The XRD pattern of the 60Bi–40Te deposit at 0.9 V is shown in Fig. 7. Since the compounds of Bi₂Te₃ [17], BiTe [18], and Bi₂Te [19] could not be distinguished from the XRD peak positions, and it was not possible to assign a specific composition of the Bi–Te deposits, however, the XRD pattern showed that the deposit had the preferential orientation of (1 1 0). The SEM photograph of the Bi–Te



Fig. 6. Optical photograph of the electrodeposit from the melt containing 0.015 M BiCl₃ and 0.0075 M TeCl₄ at 0.9 V.



Fig. 7. XRD pattern of the electrodeposit from the melt containing 0.015 M BiCl₃ and 0.0075 M TeCl₄ at 0.9 V.



Fig. 8. SEM image of the electrodeposit from the melt containing 0.015 M BiCl₃ and 0.0075 M TeCl₄ at 0.9 V.

deposit is shown in Fig. 8. The deposited consisted of needle like crystals with relatively large crystal size from 10 to $20 \,\mu$ m.

4. Discussion

Verdieck and Yntema reported the deposition potential of various metals in AlCl₃–NaCl–KCl eutectic melt at 429 K [20]. There, the potential for the redox couple of Sb(III)/Sb(0) was reported to be 0.95 V versus Al/Al(III). From the voltammogram in Fig. 1(a) and analysis of electrodeposit, the deposition potential evaluated in this study was in good agreement with their value.

The electrochemistry of Bi is more complicated than that of Sb. We observed three couples of redox waves on the voltammogram in Fig. 1(b). Verdieck and Yntema proposed that the Bi reduction took place by two steps [20]; the first step is a reaction from Bi(III) ions to lower valence Bi ions, probably Bi(I), at 1.1 V and the second is a reaction of electrodeposition

to Bi metal at 0.51 V. Torsi and Mamantov [21] and Izvekov and Chovnyk [22] investigated the forms of Bi ions in AlCl₃–NaCl or AlCl₃–NaCl–KCl molten salt. The deposition potentials by Torsi and Mamantov and Izvekov and Chovnyk are very different from the potential by Verdieck and Yntema, because of the difficulty in preparing the stable deposit and the complicated forms of dissolved Bi ions in the melt. In our experiment, we assume that the Bi(III)/Bi(I) redox reaction occurs at about 1.1 V (wave c_1) on the voltammogram in Fig. 1(b). In the potential range around 0.9 V (wave c_2), although Bi metal is electrodeposited, it immediately dissolves into the melt. At the potentials lower than that for wave c_2 , Bi forms a black alloy deposit containing Al.

The electrochemical behavior of Te in the melt is also complicated, as shown in Fig. 1(c). It was reported that the dissolved Te ions in molten salt comprised Te(IV), Te(II) and Te₄²⁺ [23]. It is, however, difficult to identify the redox potentials corresponding to each redox reaction. We believe that the purple fog observed during the voltammetry is an ionic species of Te. A reaction from Te(IV) to Te ions with lower valences may, therefore, occur at the first reduction wave c₁ in Fig. 1(c). Te metal deposit was apparently observed during electrolysis at the potentials lower than 1.0 V. Although this metal deposit is unstable in this melt in the same manner as Bi metal deposit, the rate of dissolution was observed to be lower than that of Bi. For third reduction wave c₃ in Fig. 1(c), Te is possibly deposited as an Al–Te alloy as the similar way to Bi.

When comparing the redox reactions of these three metals, it is seen that the electrodeposition potentials were not very different and much more positive than that of pure Al. The alloy deposit of Bi–Sb–Te can, therefore, be done without any influence of Al deposit in the melt of AlCl₃–NaCl–KCl melt containing the individual salts.

For the electrodeposition of Bi–Sb binary alloys, electrodeposits were obtained only at 0.9 V and 0.8 V, where the current densities were approximately between 3 and 4 mA cm⁻². However, the current density of electrodeposition at 0.7 V increased dramatically and a stable deposit was not obtained due to dendrite shaped deposits which easily detached. It should be noted that a stable deposit of Bi could not be obtained as possible as pure metal but it could be electrodeposited by alloying with Sb.

The Bi-Te alloys were obtained from the melt containing 0.015 M BiCl₃ and 0.0075 M TeCl₄. In this melt with lower concentrations of Bi and Te ions, the current density was relatively small, preventing the dendrite growth of the deposit. The XRD analysis in Fig. 7 suggests that three types of Bi-Te compounds, Bi₂Te₃, BiTe, and Bi₂Te, co-exist. From the fluorescence Xray spectroscopy, the ratio of Bi and Te was 60:40, which also suggests that the deposit consists of a mixture of the various types of Bi-Te compounds. The diffraction patterns of the compounds show the hexagonal structure corresponding to the three Bi-Te compounds, however, the main compound is assumed to be a Bi2Te3 intermetallic compound from the needle-kike surface morphology in the SEM photograph, as shown in Fig. 8. It has been suggested that, when the $(1 \ 1 \ 0)$ plane in Bi₂Te₃ is the preferential orientation, the Bi2Te3 works as a thermoelectric devices with high efficiency [1]. A preferential orientation in the (1 1 0) plane was observed in Fig. 7 and crystallites on the deposit surface were of a similar size as shown in the SEM photograph of Fig. 8. From the orientation and crystallites, molten salt electrolysis may be an efficient and easy method to produce Bi_2Te_3 .

5. Conclusions

The electrodeposition of Sb, Bi, Te and alloys of the three was examined in AlCl₃–NaCl–KCl molten salt containing the individual metal ions at 423 K:

- (1) It was possible to electrodeposit Sb as a pure metal, however, stable pure Bi and Te could not be electrodeposited from the molten salt, as the electrodeposited Bi and Te layers were detached and dissolved into the melt immediately after formation.
- (2) Alloys of Bi and Sb and also of Te and Bi could be deposited. The deposited Bi–Sb alloy consisted of metallic Sb and a solid solution of Sb–Bi. The deposited Bi–Te alloy consisted of intermetallic compounds of Bi₂Te₃, which was probably mixed with BiTe and Bi₂Te. The deposited Bi–Te alloy had a preferential orientation of (1 1 0) plane.

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