

Electrodeposition of Bi-Sb Alloy Using Cu Electrodes

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ABSTRACT

Bi-Sb alloys were grown by means of an electrodeposition method using Cu electrodes. The alloys were studied with the help of an x-ray diffractometer and an electron probe microanalysis. The both investigations have shown no trace of Cu in the obtained alloys. It can be concluded that Cu electrodes can be used for the deposition of Bi-Sb alloys; which results in an advantage of availability of the electrode.

Keywords: Electrodeposition; EPMA; XRD; Compound Semiconductors; Thermal Electric Generation

1. Introduction

Thermoelectric power generation is attractive from an environment-friendly aspect. Nowadays the solar battery and the wind electric power generation are well accepted and spread out as a clean generation method. For the practical applications of thermoelectric power generation, it is necessary to develop new materials to pursue better effectiveness. At the same time, thermoelectric materials can be applied to electronic cooling and heating devices on the other hand.

Among various materials, Bi₂Te₃ has been best known and studied as well as a Bi-(Te,Se) alloy. Because of a large thermoelectric figure of merit around $3 \times 10^{-3} \text{ K}^{-1}$ at room temperature [1], the Bi₂Te₃ system has been deeply investigated so far. On the basis of its crystal structure, the system shows a large asymmetry in resistivity, Hall coefficient, magnetic resistance and thermal conductivity. Researchers reported the existence of the second conduction band [2,3], the asymmetry of relaxation time of carriers [4], and the determination of the scattering coefficient of carriers [5]. In addition, anisotropic galvanomagnetic and thermoelectric properties have been studied [6]. In recent years several group reported that a superlattice structure enhances thermoelectric figure of merit [7,8]. This is actually an excellent idea though forming superlattice requires high-cost manufacturing methods such as a molecular beam epitaxy.

The Bi-Sb alloy is another good candidate for a thermoelectric material in a room temperature range. Further, the Bi-Sb alloy conveniently has the maximum figure of merit at room temperature. V. D. Das *et al.* reported [9]

the dependence of resistance on temperature, in a Bi-Sb alloy film deposited by a vacuum deposition method. R. Tolutis *et al.* [10] observed negative magneto-resistance in a Bi-Sb alloy film. In addition, superlattice nanowire arrays of Bi and Sb was recently demonstrated by means of a pulsed electrodeposition method [11]. While the Bi-Sb system has been widely studied, a Bi-Sb alloy film was deposited by an electrodeposition method [12]. This method only needs a container of electrolyte, where soaked a substrate and a counter electrode connected with an electric power supply. It is why this method actually has an advantage of low cost for the deposition. An electrode made of Bi-Sb alloy has been usually used for the deposition. We tried to use a Cu electrode for the deposition for the purpose of better availability of the electrode and analyzed the obtained Bi-Sb alloy films.

2. Experimental

Electrolyte consisted of the mixture of BiCl₃ (12 g) and SbCl₃ (1.5 g) dissolved in aqueous HCl (50 ml) diluted with water (100 ml). The amount of SbCl₃ was quite small because of its hard solubility. A substrate electrode and a counter electrode were situated in the electrolyte at a distance of 1.5 cm to each other. Both electrodes were made of Cu plates masked with polymer films where the square (1 × 1 cm) area was exposed to the electrolyte. A direct current-constant power supply (40 mA) was connected to the substrate as a cathode and the counter electrode as an anode. The deposition was performed continuously for 20 hours. The voltage appeared across the electrodes was 0.11 V at the beginning of the deposition.

The amount of the Bi-Sb alloy deposited on the substrate was about 1.8 g.

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The obtained samples were investigated with an x-ray diffraction (XRD) apparatus (RAD-IIA by Rigaku), a scanning electron microscopy (SEM: S-570 by Hitachi) equipped with an electron probe micro analysis (EPMA: EMAX-5770 by Horiba). The main issue of the investigations is elemental constitution of the obtained material.

The surfaces of grown Bi-Sb alloy samples were too rough to measure x-ray diffraction pattern. The grown Bi-Sb alloy samples were cleaved off from the Cu substrate and then the interface to the substrate was analyzed. The grounded powder of Bi-Sb alloy in the surface region is also measured. As for an EPMA measurement, the cross sections of the Bi-Sb alloy samples were studied for a depth profile.

3. Results and Discussion

The SEM photos of the cleaved interface and the surface of a BiSb sample are shown in **Figures 1(a)** and **(b)**, respectively. The obtained BiSb evidently consisted of polycrystals. The grain size at the interface was under 10 μm but that at the surface was several ten μm . The fact argues that the crystal grows gradually as the film was deposited thicker.

Figure 2(a) shows an XRD pattern obtained from the cleaved interface of Bi-Sb. Eleven sharp peaks marked with open circles in the figure were observed, corresponding to Bi-Sb were observed, with a small peak situated at 43.5 degree in 2θ assigned to (111) reflection by Cu. A relatively strong peak at 67.7 degree was not well assigned yet. **Figure 2(b)** shows a powder XRD pattern from the powder obtained by grinding a part of a surface region only. In this pattern, the same 11 peaks to Bi-Sb were observed with a little shift (from 0.2 to 0.4 degree) in the lower side. It can not be determined that the shift derived from the compositional change or the change in stress caused by the grind to powder. It should be mentioned that the structure at 43.5 degree (Cu) was not seen in the **Figure 2(b)**, which argues the reflection by Cu (111) in **Figure 2(a)** derived from a Cu trace that trans-

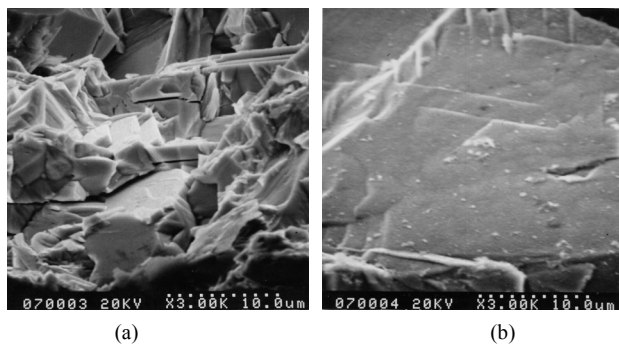


Figure 1. (a) SEM photograph of electrodeposited BiSb; the cleaved interface contacted to a Cu substrate; (b) SEM photograph of electrodeposited surface of BiSb.

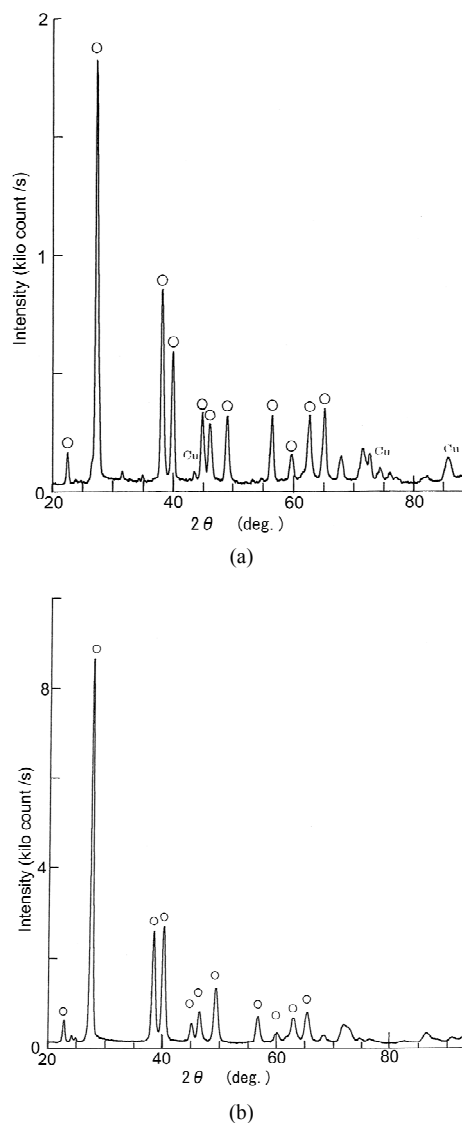
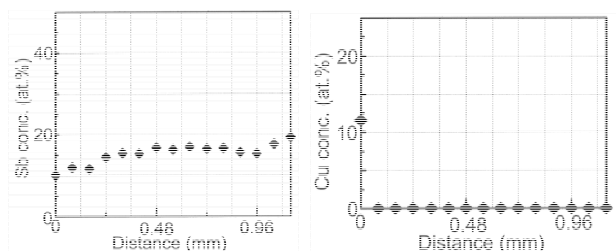


Figure 2. (a) XRD patterns of obtained BiSb: The cleaved plane; (b) XRD patterns of obtained BiSb: The powdered sample taken from only the surface region.

ferred from the Cu substrate to the sample when it was cleaved.

In order to determine the compositional ratio, EPMA measurements were performed. The results of linear analyses on a cross sectional plane are shown in **Figures 3(a)** and **(b)**: the atomic concentration of Cu and Sb as a function of the distance from the substrate, respectively.

Cu was not detected in the grown Bi-Sb region at any distance except for 0 mm. The absence for Cu is consistent with the XRD pattern from the powdered surface region of the grown Bi-Sb. This means that Cu was not precipitated even if Cu was dissolved at the anode. The Sb atomic concentration was 10% at the interface and increased to 20% with the distance. This change probably resulted from the gradual change in solute concentration



Figures 3. The atomic concentration of Cu (top) and Sb (bottom) obtained by means of an EPMA measurement.

in the electrolyte during the growing. The control of concentration in the electrolyte is expected to the precipitation for a constant atomic ratio during the deposition.

It was found that the anode (Cu) was dissolved during the deposition. As a matter of fact the deposited Bi-Sb did not include Cu but the expense of Cu electrodes is not actually recommended. It is better to use other metal that is not dissolved in the electrolyte for a maintenance-free production method.

4. Conclusion

Bi-Sb alloy was electrically deposited in a solution as a low-cost deposition method. When Cu electrodes were used for the electrodeposition, the obtained Bi-Sb alloy film did not contain Cu on the basis of XRD and EPMA measurements. The atomic concentration of Sb became larger with the distance from the interface, which was probably originated from the change of solute concentration in the electrolyte.

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