Effect of thermal annealing on the structural and thermoelectric properties of electrodeposited antimony telluride thin films

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A B S T R A C T

We investigated the effect of thermal annealing on structural and thermoelectric properties of p-type antimony telluride (Sb_2Te_3) thin films fabricated on a stainless steel (SUS304) substrate by electrodeposition. Antimony telluride thin films were annealed for 1 h at temperatures between 200 and 400 °C. We observed that the as-deposited thin film and thin films annealed at temperatures less than 250 °C possessed a stoichiometric atomic composition (Sb:Te = 40:60) with no impurities from the substrate. At the annealing temperature of 300 °C, we observed a certain amount of impurities (Fe, Cr, Ni) in the thin film. The Seebeck coefficient was decreased but the electrical conductivity was increased for films treated at 300 °C. As a result, the thin film exhibited a maximum power factor of 13.6 $\mu W/(cm \cdot K^2)$. On further increasing the annealing temperature to 400 °C, the film structure and thermoelectric properties were drastically changed. The impurity concentration in the thin film reached approximately 50 at.%. The crystal structure of Sb_2Te_3 completely disappeared, and instead, other chemical compounds formed by alloying the elements of the thin film and the substrate were observed.

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1. Introduction

Recently, thermoelectric materials have attracted considerable interest because of developments in energy harvesting technology. These materials are able to covert thermal energy into electric energy, and vice versa convert electricity into heat. In particular, thermoelectric generators produce electric power from thermal energy for a variety of uses for mobile and wireless electronics [1—3]. Commercial applications of thermoelectric generators require high energy conversion efficiency, miniaturization, and low manufacturing costs.

The energy conversion efficiency, i.e., thermoelectric performance, is dependent on a dimensionless figure of merit (ZT), which is defined as $ZT = \sigma S^2 T/\kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient, T is the absolute temperature, and κ is the thermal conductivity. To improve the thermoelectric performance, the power factor, σS^2, should be maximized and the thermal conductivity should be minimized. Regarding the chemical composition of thermoelectric materials, bismuth telluride (Bi_2Te_3) and similarly structured materials with the $R3m - D_{3d}^5$ space group,

such as antimony telluride (Sb_2Te_3) and bismuth selenium (Bi_2Se_3), are the most suitable materials [4]. This is because these materials exhibit the highest ZT near room temperature (RT), providing many energy harvesting applications. In general, thermoelectric generators consist of n-type (e.g. bismuth telluride) and p-type (e.g. antimony telluride) thermoelectric materials.

Thin film technology is beneficial from the viewpoint of miniaturization as well as the low manufacturing cost of thermoelectric generators. The advantage of thin film technology is that it allows for deposition of thin films over a large area at once and fabrication of fine structures. In addition, this technology makes it relatively easy to control the crystal growth and atomic composition of the materials. To date, there are many reports of thin film thermoelectric generators produced using various conventional deposition methods, including evaporation [5—7], sputtering [8—10], and electrodeposition [11—13]. Among these deposition methods, electrodeposition is one of the most favorable because it is very cost effective; this is because of its easy scalability, high deposition rate, and the fact that it involves operation at low temperature with no requirement for vacuum conditions.

Electrodeposited bismuth telluride-based alloy thin films were first fabricated by Takahashi et al. [14]. They fabricated the thin films using an aqueous solution of pH 0.9 containing various $Bi(NO_3)_3$ concentrations and a constant TeO_2 concentration

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(1.50 mM) on a Ti sheet. Martin-Gonzalez et al. performed a systematic investigation of the electrochemical reactions and compositional changes as a function of applied potential [15]. Since then, research in bismuth telluride-based alloy thin films formed by electrodeposition has received much attention owing to the improvement in thermoelectric properties under the established experimental conditions [16–18]. To further improve the thermoelectric performance, deposited films must be subjected to additional treatment such as thermal annealing [9,19], electron beam irradiation [20–22], and pulsed laser annealing [23,24]. In particular, thermal annealing is well investigated in bismuth telluride-based alloy thin films, and has been demonstrated to greatly improve thermoelectric properties [25–27]. However, not much is known about the effects of thermal annealing for electrodeposited bismuth telluride-based alloy thin films, especially p-type thin films [28–30]. Additionally, impurity diffusion from the substrate into the deposited film during thermal annealing has not been well investigated [31].

In this study, we investigated the effect of thermal annealing on structural and thermoelectric properties of p-type antimony telluride thin films prepared by electrodeposition. The thin films were formed on stainless steel (SUS304) substrates, followed by thermal annealing under an inert gas atmosphere. The structural properties of the treated thin films were characterized in terms of their surface morphology, atomic composition, and crystallographic structure. The in-plane thermoelectric properties were measured at RT. Finally, we discuss the relationship between annealing temperature and the various film properties, and the impurities in the thin films.

2. Experimental section

Prior to the electrodeposition, cyclic voltammetry (CV) was performed with a standard three-electrode cell (HSV-110; HOKUTO) in an unstirred electrolyte solution consisting of 1.3 mM SbF$_3$, 1.6 mM TeO$_2$, and 0.39 M hydrochloric acid diluted by deionized water. The electrolyte temperature was maintained at RT. The CV scan rate was fixed at 5 mV/s. The working electrode (electrode area: 1.5 cm^2) was a stainless steel (SUS304) substrate with 80 μm thickness, chosen because of its excellent corrosion resistance. A platinum-coated titanium mesh on a titanium plate was used as the counter electrode (electrode area: 1.5 cm^2). A Ag/AgCl (saturated KCl) electrode was used as the reference electrode.

Antimony telluride thin films were prepared by potentiostatic electrodeposition using a standard three-electrode cell. The conditions of the electrodes were the same as those of the CV analysis. The working and counter electrodes were degreased using a sodium hydroxide and a hydrochloric acid solution, and then washed with deionized water. The thin film deposition was performed while stirring at 200 rpm at RT. The constituents of the electrolyte were the same as that of the CV analysis. The electrode voltage was set at −0.1 V using a potentiostat/galvanostat (HA-151B, Hokuto Denko). We measured the film thickness by two methods, which are cross-section SEM images and mass difference between the initial substrate and the film deposited substrate. We observed that the film thickness was mostly uniform, and the two methods exhibited mostly the same thickness. As a result, the electrochemically deposited films had an average thickness of approximately 300 nm.

To thermally anneal the antimony telluride thin films, the samples were placed in an electric furnace, evacuated to 1.0 Pa and then purged five times with mixed gas (argon 95% and hydrogen 5%). The furnace was then filled with the same mixed gas at atmospheric pressure, under a gas flow rate of 1.0 SLM throughout the thermal annealing process. Temperatures were increased from

200 to 400 °C at a rate of 4 K/min and the samples were maintained at the maximum temperature for 1 h. After thermal annealing, the samples were cooled to RT naturally in the furnace. To avoid complications in analysis due to the electrical conduction of the stainless steel substrate, the film was fixed on a glass plate using an epoxy resin, followed by thin film removal from the substrate.

Surface morphologies of the antimony telluride thin films were examined using a scanning electron microscope (SEM; JSM-6301F, JEOL). Atomic compositions were measured by an electron probe microanalyzer (EPMA; EPMA-1610, Shimadzu). The crystallographic properties were evaluated by X-ray diffraction (XRD; Mini Flex 600, Rigaku) using the Cu-K$_\alpha$ line ($\lambda = 0.154$ nm).

The in-plane Seebeck coefficient, S, of the antimony telluride thin films was measured at RT. One end of the thin film was connected to a heat sink and the other end to a heat source. The Seebeck coefficient was determined as the ratio of the potential difference along the film between the different temperatures. Temperatures were measured with two 0.1 mm diameter K-type thermocouples pressed onto the thin films. The distance between the thermocouples was 13 mm. The in-plane electrical conductivity, σ, of the thin films was also measured at RT by a four-point probe method (RT-70V, NAPSON). The in-plane power factor, $S^2\sigma$, was calculated from the measured Seebeck coefficient and electrical conductivity.

3. Results and discussion

3.1. Cyclic voltammetry analysis

To determine the appropriate potential range for depositing an antimony telluride film, CV analysis using an electrolyte consisting of 1.3 mM SbF$_3$, 1.6 mM TeO$_2$, and 0.39 M hydrochloric acid was performed, as shown in Fig. 1. The cyclic voltammogram revealed two cathodic peaks at potentials of approximately −0.1 and −0.2 V vs Ag/AgCl, which may be attributed to the electrodeposition of Te and Sb, respectively [32]. The overall antimony telluride (Sb$_2$Te$_3$) deposition reaction can be described as follows [33]:

$$2SbO^+ + 3HTeO_2^+ + 13H^+ + 18e^- \rightarrow Sb_2Te_3 + 8H_2O \qquad (1)$$
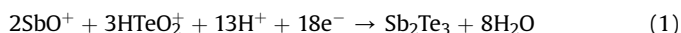
Based on the obtained cyclic voltammogram, it is apparent that the appropriate applied potential for the deposition of antimony telluride thin films is in the range of −0.1 to −0.2 V. We set the
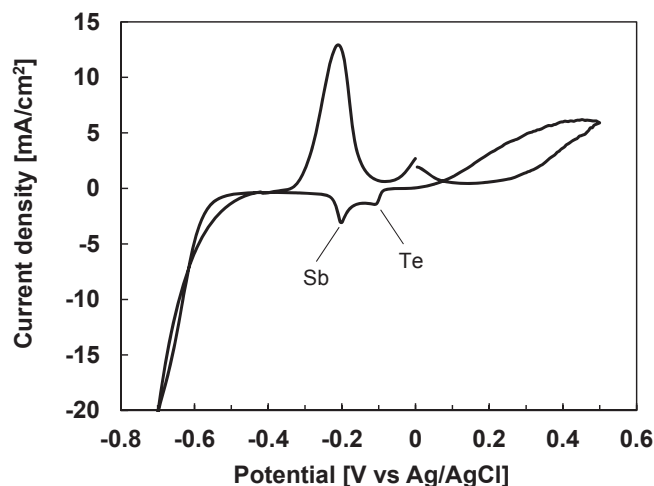

Fig. 1. Cyclic voltammetry scan of the Sb/Te electrolyte recorded at RT and a scan rate of 5 mV/s.