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Thermoelectric properties of bismuth antimony tellurium thin films through bilayer annealing prepared by ion beam sputtering deposition

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ABSTRACT

Bismuth antimony tellurium is one of the most important tellurium-based materials for high-efficient thermoelectric application. In this paper, ion beam sputtering was used to deposit Bi_2Te_3 and Sb_2Te_3 bilayer thin films on borosilicate substrates at room-temperature. Then the bismuth antimony tellurium thin films were synthesized via post thermal treatment of the Bi_2Te_3 and Sb_2Te_3 bilayer thin films. The effect of annealing temperature and compositions on the thermoelectric properties of the thin films was investigated. After the thin films were annealed from 150 °C to 350 °C for 1 h in the high vacuum condition, the Seebeck coefficient changed from a negative sign to a positive sign. The X-ray diffraction results showed that the synthesized tellurium-based thermoelectric thin film exhibited various alloys phases, which contributed different thermoelectricity conductivity to the synthesized thin film. The overall Seebeck coefficient of the synthesized thin film changed from negative sign to positive sign, which was due to the change of the primary phase of the tellurium-based materials at different annealing conditions. Similarly, the thermoelectric properties of the films were also associated with the grown phase. High-quality thin film with the Seebeck coefficient of 240 $\mu V\ K^{-1}$ and the power factor of $2.67 \times 10^{-3}\ Wm^{-1}\ K^{-2}$ showed a single $Bi_{0.5}Sb_{1.5}Te_3$ phase when the Sb/Te thin film sputtering time was 40 min.

1. Introduction

Thermoelectric materials are eco-friendly materials, which can interconvert heat and electric energy directly [1]. Thermo-electric generator based on thermoelectric materials is widely used as a clean, reliable and sustainable energy source [2]. The performance of thermoelectric material is determined by a parameter which is defined as a dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S, σ, T, κ are the Seebeck coefficient, electric conductivity, absolute temperature and thermal conductivity, respectively [3,4]. Bismuth–Antimony–Tellurium is a well-established thermoelectric material that is used in the temperature range of 200–400 K due to its high Seebeck coefficient, good electric conductivity and low thermal conductivity [5–9]. P-type $Bi_{0.5}Sb_{1.5}Te_3$ and n-type $Bi_{1.4}Sb_{0.6}Te_3$ bulk materials have high power factors of $4.0 \times 10^{-3}\ Wm^{-1}\ K^{-2}$, $1.9 \times 10^{-3}\ Wm^{-1}\ K^{-2}$ and ZT of 1.4, 0.3 at room-temperature, respectively. Thin film technique is a good method to improve the thermoelectric properties of thermoelectric materials due to its stronger quantum confinement effect [10,11]. Many studies have been done to fabricate the bismuth antimony tellurium thin film using techniques such as physical vapor deposition or chemical vapor deposition techniques [12–14]. However, neither the Seebeck coefficients nor the conductivity of the thin films prepared by vacuum sputtering method is as good as their bulk material. This is mainly due to the high vapor pressure of Te and the re-evaporation of Te during the preparation [15]. Compared with other techniques, ion beam sputtering deposition (IBSD) is a very attractive technique since it combines a high deposition rate with great versatility in the deposition of thin films by adjusting the target composition and controlling the sputtering energy. In addition, stoichiometric Sb_2Te_3 and Bi_2Te_3 alloy thin films have been obtained by IBSD with fan-shape target in our previous work [16,17]. The quality of the thin films fabricated by IBSD is great and comparable with the best results reported in literature for the same material prepared by other sputtering technologies. In this work, Bi/Te and Sb/Te bilayer thin films were deposited at room temperature by IBSD and P-type $Bi_{0.5}Sb_{1.5}Te_3$ compound thin film was obtained via post thermal treatment of the bilayer. The influence of thermal treatment parameters on fabricating $Bi_{0.5}Sb_{1.5}Te_3$ thin films was studied. The dependence of preparing parameters on the thermoelectric properties of the annealed bismuth antimony tellurium thin films was also investigated.

2. Experimental details

As source materials, two composite targets which were fan-shaped with high purity Sb (99.99%)/Te (99.99%) and Bi (99.99%)/Te (99.99%)

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were fixed in the sputtering sites of the IBSD. The ratio of Sb to Te and Bi to Te was controlled by adjusting the area ratios of the corresponding target plates. The detailed parameters for preparing stoichiometric Sb_2Te_3 and Bi_2Te_3 thin films had been report elsewhere [16,17]. Square soda-lime glasses with a length of 30 mm and thickness of 1.5 mm were used as substrates and were cleaned in acetone, alcohol and deionized water, each for 10 min respectively. The background pressure was 7.0×10^{-4} Pa and the work pressure was 6.1×10^{-2} Pa. A 15 min sputtering cleaning process with a low energy ion beam was performed to remove the contaminants on both the targets and the substrate surfaces prior to film deposition. Plasma energy of 700 keV and beam current of 10 mA were used for sputtering. Firstly, Bi/Te alloy thin films were deposited on the substrates at room-temperature and the deposition time was 30 min. Secondly, the Sb/Te alloy thin films are deposited on the Bi/Te films with the sputtering time of 30 min. Based on our previous research, it had an advantage of improving the thermoelectric properties because the richer Te can be eliminated during the annealing process in vacuum. So the samples were annealed from 150 °C to 350 °C in vacuum for 1 h. The chamber pressure for annealing was less than 8.0×10^{-4} Pa. The effects of the annealing temperature on the properties were investigated. The film annealed at 300 °C has better thermoelectric properties than the others, therefore, all the films with various compositions were prepared with the same annealing temperature of 300 °C. The compositions of the samples were controlled by changing the sputtering time of the Sb/Te thin film while fixing the sputtering time of the Bi/Te thin film to 30 min. The sputtering time of Sb/Te thin film had been set to 10 min, 20 min, 30 min, 40 min and 50 min, respectively. Then the properties of the thin films were studied.

The structure of the thin films was characterized by X-ray diffraction (XRD) technique (D/max2500 Rigaku Corporation) with the conventional θ-2θ mode of the CuK_α radiation ($\lambda = 0.154056$ nm). The thin film thickness was obtained by using a DEKTAK^3 ST surface-profile measurement system. The sheet resistance R_s was determined from a four-point method with a Keithley 2400 current–voltage measurement unit (Keithley Corporation). Electrical conductivity was obtained using $\sigma = (R_s d)^{-1}$. The Seebeck coefficient was measured at room-temperature by a Seebeck coefficient measurement system (SDFP-). The composition ratio and the cross-section view of the thin films were determined by using an energy dispersive X-ray spectroscopy (EDS) microanalysis system (S-4700 Hitachi Corporation).

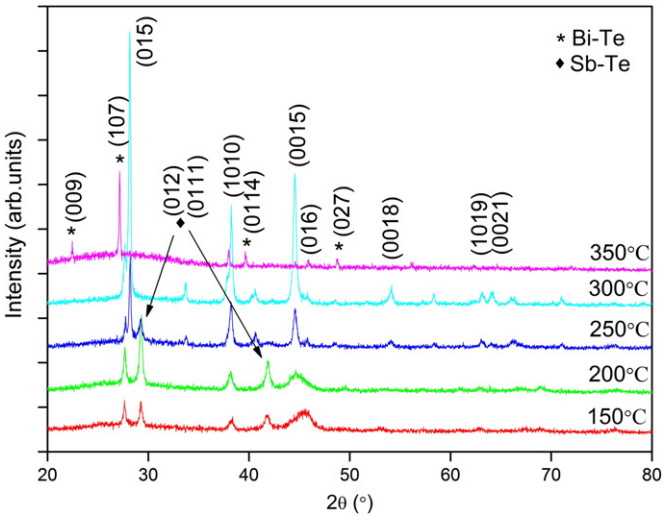

Fig. 1. The XRD patterns of bismuth antimony tellurium thin films as a function of annealing temperature. (Sputtering time: Bi/Te 30 min, Sb/Te 30 min.)

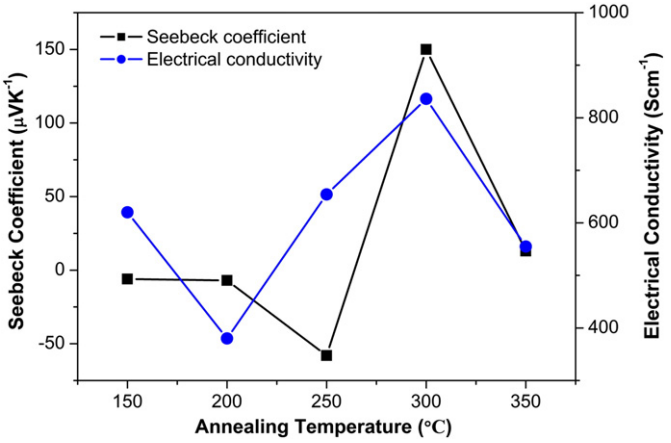

Fig. 2. The Seebeck coefficient and the electrical conductivity of the thin films as a function of the annealing temperature. (Sputtering time: Bi/Te 30 min, Sb/Te 30 min.)

3. Results and discussion

Fig. 1 shows the XRD patterns of bismuth antimony tellurium thin films as a function of annealing temperature. The samples were annealed at 150 °C, 200 °C, 250 °C, 300 °C and 350 °C, respectively. The major diffraction peaks located at 2θ of 28.2°, 38.3° and 44.6° are observed and most peaks of the XRD patterns are related to the $Bi_{0.5}Sb_{1.5}Te_3$ characteristic phase. However, there are also some peaks which are not related to any of the well known bismuth antimony tellurium phase. Instead, they are indexed as Sb–Te and Bi–Te phases at different annealing parameters. When the thin films were annealed at a temperature of 150 °C, the Bi–Te phase is the dominating phase. It is suggested that the Bi–Te compound is easier to be synthesized than other materials containing Sb due to the low melting point of the Bi and Te. The phase transforms to the $Bi_{0.5}Sb_{1.5}Te_3$ and Sb–Te phases when the temperature increased to above 200 °C. With the increase in annealing temperature, the intensity of the peaks related to the $Bi_{0.5}Sb_{1.5}Te_3$ phase, such as (015), (1010) and (0015) which are located at 28.2°, 38.3° and 44.6°, is enhanced and other peaks related to $Bi_{0.5}Sb_{1.5}Te_3$ also increase. Less impurity peaks in the sample can be observed and their intensities are much smaller than the characteristic peaks when the temperature reached 250 °C and 300 °C, which indicates that the $Bi_{0.5}Sb_{1.5}Te_3$ phase is the dominant phase and the thin films have high crystalline quality. However, some peaks related to $Bi_{0.5}Sb_{1.5}Te_3$ disappear when the temperature increases to 350 °C. A phase transition into the Sb–Te + $Bi_{0.5}Sb_{1.5}Te_3$ phase happened and the Sb–Te phase is the major grown phase of the thin films as evident from the XRD pattern shown in Fig. 1. It is speculated that the evaporation of Te and the separation of Bi during annealing can result in the loss of Te and Bi, so the Sb–Te can sufficient synthesize at high temperature.

Fig. 2 shows the Seebeck coefficient and the electrical conductivity of the thin films as a function of the annealing temperatures. It can be found that the Seebeck coefficient increases from -6 μV K^{-1} to -58 μV K^{-1} when the temperatures increased from 100 °C to 250 °C. Then the Seebeck coefficient changed from a negative sign to a positive sign

Table. 1
The element content and thin film thickness as a function of sputtering time by SEM and EDS analyzed.

Sputtering time	10 min	20 min	30 min	40 min	50 min
Bi (%)	42.9	36.5	29.7	10.4	3.5
Sb (%)	9.8	13.6	18.2	31.5	37.9
Te (%)	47.3	49.9	52.1	58.1	58.6
Thickness (nm)	410	510	530	670	750