

# Fabrication and characterization of $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$ compounds thin films by flash evaporated deposition

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## Abstract

$(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films on glass substrates are fabricated by a flash evaporated deposition method. In order to enhance the performance of the thin films, annealing in an argon atmosphere is carried out for 1 hour in the temperature range from 200 to 400 °C. The structure of the thin films, in terms of homogeneity and crystalline quality, is investigated by means of x-ray mapping and x-ray diffraction pattern respectively. The cross-sectional microstructure is examined using scanning electron microscopy. We confirm that as-grown  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin film has mostly homogeneous structure except the portion of sticking particles. The crystalline quality of the thin films is improved and the size of crystal grains is grown up to the same size of the film thickness as higher annealing temperature. The transport properties of the thin films, in terms of the electrical resistivity, Seebeck coefficient and thermoelectric power factor are determined at room temperature. By optimization of annealing conditions, it is possible to obtain the high-performed thin film with a thermoelectric power factor of  $12.2 \mu\text{W cm}^{-1} \text{K}^{-2}$ . We consider that the performance of the thin films are enhanced for optimized annealing because electrons can pass through smoothly in the thin films for the grain growing as well as the reduction of crystal boundaries.

## 1. Introduction

Bismuth telluride based alloys have been an attractive thermoelectric material widely used in cooling devices and proposed for energy conversion applications around room temperature. These thermoelectric devices can be almost maintenance free and downsizing because of no moving parts. It is possible to extend the applications of thermoelectric devices for their feature of downsizing. Micro-thermoelectric cooling is a suitable technique for the local cooling of micro-sensors and devices as it can be microelectronically integrated [1,2]. Micro-thermoelectric generating can supply small electric power to low power devices and actually have been equipped into wrist watches [3].

The primary candidate technology for downsizing of thermoelectric devices is to apply semiconductor-processing technologies including thin film fabrication. The key

issue of micro-thermoelectric devices is how to fabricate thin films with high performance. The performance of thermoelectric materials depends on the thermoelectric figure-of-merit of the material,  $ZT$ , which is defined as  $ZT = S^2T/\rho\kappa$ , where  $S$  is the Seebeck coefficient,  $\rho$  is the electrical resistivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature. The product  $S^2/\rho$  is defined as the power factor. The power factor should be maximized while the thermal conductivity should be reduced in order to achieve high efficiency thermoelectric materials. Recently, progress has been made in improving the figure-of-merit of thin film thermoelectric materials and a significant improvement in thermoelectric figure-of-merit may also be achieved by employing superlattice or quantum well structures [4,5].

There are presented many deposition techniques such as flash evaporated deposition [6-8], co-sputtering [9,10], pulsed laser deposition [11,12], metal organic chemical vapor deposition (MOCVD) [13,14] and molecular beam epitaxy (MBE) [15-17]. Thus, although there are many deposition techniques, sufficient results for the stage of practical use have not been achieved yet because of higher production cost for expensive equipments or inadequate thin film properties. In these deposition methods, we employ the flash evaporated deposition method as the fabrication of bismuth telluride based alloys thin films. This deposition method has a possibility of low production cost because of the simple system that only includes vacuum chamber with particles holder, tungsten heater for evaporation and substrate holder. On the other hand, the performance of the thin films is relatively low without annealing. In fact, annealing processes are known to enhance the transport properties [18,19]. However, there are few reports of linking a structural feature by the effect of annealing and that of transport properties on the thin films fabricated by flash evaporated deposition.

In this study, the structure and transport properties of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films on glass substrates and their dependence of various annealing conditions are reported.  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films are deposited by flash evaporated deposition method. The powders for the thin film deposition are polycrystalline spherical shape with averaged size of  $20\mu\text{m}$ .

## 2. Experiment

$(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films are prepared by flash evaporated deposition method. A schematic of our experimental flash evaporated deposition setup (ULVAC VPC-260) is illustrated in Fig. 1. The vacuum chamber is mainly composed of powder vessel with guide, tungsten heater for evaporation and substrate holder. The distance between tungsten heater and substrate is 30mm. The tungsten heater is made a

slight depression (50mm length, 10mm width, 2mm depth) to protect powders spilling out from the heater. The guide is made from stainless steel and covered with Teflon thin film for powders passing through smoothly to the heater. We prepare spherical powders averaged size of 20 $\mu$ m to control their flow precisely. The powders are confirmed to be stoichiometry by EDX (Energy-dispersive x-ray spectroscopy). Figure 2 shows the surface morphology of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds powders by SEM (secondary ion mass-spectroscopy). There are many lines on the surface and it reveals that the powders are polycrystalline. First, we set 5g of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds powders in the vessel and glass substrate (Cornig 7059, 55mm length, 25mm width, 1.1mm thick) on the holder then vacuum the chamber up to  $1.4 \times 10^{-3}$  Pa. Second, 80A of current is pass through the heater and wait until the substrate temperature reaches at 200°C. Third, the powders are led on the heater then evaporated them on the glass substrate. The thickness of the completed thin film is 0.5  $\mu$ m.

We confirm the surface morphology and homogeneity of the deposited  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin film by means of SEM and x-ray mapping respectively (Fig. 3). The SEM image shows that several crater-like spots and black spots appear on the as-grown thin film. The cause of the appearance of these spots may due to the arrival of incomplete melted powders from the heater. Some of those powders keep sticking on the substrate, and other those of powders stick on the substrate first and then remove from the substrate. It is necessary to improve the deposition condition for keeping the thin film with surface cleanness in the future. X-ray maps are obtained to determine the distribution of different elements in the thin film. These maps are obtained from same regions, as shown in the SEM image. Figure 3 illustrates the presence of the elements bismuth, tellurium, and antimony in the thin film. It is noted that all elements in the thin film are mostly obtained homogeneous distribution except the crater-like spots.

In order to examine the effect of annealing condition precisely, we choose a thin film sample with uniform thickness and properties in the thin film, and then cut it into small fragments (25mm length, 4mm wide). The annealing conditions are that temperatures range from 200 °C to 400 °C for 1 hour in argon ambient. The structure of the thin films, in terms of microstructure and crystalline quality, is investigated by means of SEM and x-ray diffraction pattern respectively. The transport properties of the thin films, in terms of the electrical resistivity, Seebeck coefficient and thermoelectric power factor, are determined at room temperature. The electrical resistivity is determined by a 4 point-probe method. The Seebeck coefficient is measured by applying a temperature gradient along the in-plane direction, while monitoring the

resulting Seebeck voltage.

### 3. Results and discussion

The structure of annealed  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films, in terms of cross-section and surface microstructure, is investigated by means of SEM (Fig. 4). The SEM micrographs clearly show the grain size differences. The as-grown thin film is not observed grains on this magnification of the micrograph. It is noted that the thin films fabricated by flash evaporated deposition technique are laid on substrates rapidly so that there is no time to re-crystallize sufficiently at the substrate temperature of 200 °C. At annealing temperature of 200 °C, we confirm the grains where the size is approximately 50 ~100 nm. As annealing temperatures increase, the grain size of the thin films is enhanced. Finally, the grain size of the thin film reaches the same as the film thickness at annealing temperature of 400 °C. However, the thin film at annealing temperature of 400 °C deteriorates and is porosity. We consider that some elements in the thin film are evaporated during the excessive annealing condition.

X-ray diffraction (XRD) patterns of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films are shown in Fig. 5. The diffraction patterns of the thin films clearly reveal the effect of annealing condition. The as-grown thin film has weak and broad diffraction peaks that imply small grain size. The averaged grain size estimated as 5.5 nm by Scherrer's equation. The diffraction peaks of the thin films are enhanced but the crystal orientation still remain random as annealing temperature increase. However, the diffraction peaks at annealing temperature of 400 °C are smaller than those of 350 °C. This is because there are many porous in the thin film at annealing temperature of 400 °C so that the intensity of x-ray diffraction becomes weak.

The transport properties, in terms of electrical resistivity, Seebeck coefficient and power factor, of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films are estimated at room temperature. Figure 6 shows annealing temperature dependence of transport properties on  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films. We insert the data of the transport properties of as-grown thin film on the same temperature at annealing temperature of 200 °C. This is because the substrate temperature on the thin film deposition is fixed at 200 °C. By treatment of annealing at temperature of 200 °C, the electrical resistivity significantly reduces by 45% compared to that of as-grown thin film. The electrical resistivity of the thin films further reduces as annealing temperature increases, and it reaches 1.84 mΩ · cm at annealing temperature of 400 °C. On the other hand, Seebeck coefficient of the thin films between as-grown and annealing temperature of 200 ~ 250 °C is approximately same value. As annealing temperatures increase, the Seebeck

coefficient of the thin films improves and it reaches 218.2  $\mu\text{V/K}$  at annealing temperature of 300  $^{\circ}\text{C}$ . However, the Seebeck coefficient of the thin films decreases at annealing temperature over 350  $^{\circ}\text{C}$ . The correlation of the dependence of annealing temperature between the electrical resistivity and Seebeck coefficient is complicated. It is possible to divide into two regions bordering on the annealing temperature of 300  $^{\circ}\text{C}$ . The electrical resistivity  $\rho$  is given as  $\rho=1/(qn\mu)$ , where  $n$  is the carrier concentration,  $\mu$  is the mobility. Seebeck coefficient is expressed as,

$$S = (k/q)[r + 2 + \ln(N/n)], \quad (1)$$

where  $k$  is the Boltzmann's constant,  $r$  is the scattering parameter,  $N$  is the density of states[20]. In the presence of impurities, the scattering parameter is equal to 2, while  $r = 0$  for the atomic lattice. In the region of annealing temperature under 300  $^{\circ}\text{C}$ , the electrical resistivity of the thin films reduces but Seebeck coefficient mostly keeps constant. It is possibly shown that the mobility is enhanced for reducing the carrier scattering on the grain boundaries while the carrier concentration and impurities mostly keep constant. In another region of annealing temperature over 300  $^{\circ}\text{C}$ , the electrical resistivity of the thin films still reduces when Seebeck coefficient decreases. It is possibly noted that the mobility is still enhanced for the large scale of the grains of the thin films. However, the carrier concentration increases for the evaporation of some elements in the thin film then Seebeck coefficient decreases. This phenomenon is consistent with the SEM image at annealing temperature of 400  $^{\circ}\text{C}$ . Finally, the thermoelectric power factor reaches 12.2  $\mu\text{W cm}^{-1} \text{K}^{-2}$  at annealing temperature of 300  $^{\circ}\text{C}$ .

#### 4. Conclusion

$(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films on glass substrates are fabricated by a flash evaporated deposition method. For the controlling precise powers flow, we prepare spherical powders averaged size of 20 $\mu\text{m}$ . In order to enhance the performance of the thin films, annealing in an argon atmosphere is carried out for 1 hour in the temperature range from 200 to 400  $^{\circ}\text{C}$ . The structural properties of the thin films are investigated using x-ray mapping, SEM micro-morphology and x-ray diffraction pattern. The transport properties of the thin films are estimated by the electrical resistivity, Seebeck coefficient and thermoelectric power factor. It is shown that the grain size of the thin films is enhanced as annealing temperature increases but the excessive annealing condition causes porous thin films for the evaporation of some elements. This deterioration of the thin film at the higher annealing temperature is consistent with the transport properties. It is found to obtain the high-performed thin film with a

thermoelectric power factor of  $12.2 \mu\text{W cm}^{-1} \text{K}^{-2}$  at annealing temperature of  $300^\circ\text{C}$ . For more improving the properties of  $(\text{Bi}_2\text{Te}_3)_{0.2}(\text{Sb}_2\text{Te}_3)_{0.8}$  compounds thin films, it is necessary to optimize the thin film deposition conditions.

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### References

- [1] D. J. Yao, C. J. Kim, G. Chen, J. L. Liu, K. L. Wang, J. Snyder and J. P. Fleurial, Proceedings of the International Conference on Thermoelectrics 20th International Conference on Thermoelectrics, Beijing, China, June 8-11, 2001, p. 401.
- [2] F. Völklein, Gao Min and D. M. Rowe, Sensors and Actuators A 75 (1999) 95.
- [3] M. Kishi, H. Nemoto, T. Hamao, M. Yamamoto, S. Sudou, M. Mandai and S. Yamamoto, Proceedings of the International Conference on Thermoelectrics 18th International Conference on Thermoelectrics, Baltimore, MD, USA, August 29-September 2, 1999, p. 301.
- [4] R. Venkatasubramanian, E. Siivola, T. Colpitts and B. O'Quinn, Nature 413 (2001) 597.
- [5] T. C. Harman, P. J. Taylor, M. P. Walsh and B. E. LaForge, Science 297 (2002) 2229.
- [6] K. Miyazaki, A. Jaquot, T. Shirakawa, M. Kozasa and H. Tsukamoto, Proc. 3rd European Conf. on Thermoelectrics, 開催場所と日, 2005, p.116.
- [7] F. Völklein, V. Baier, U. Dillner and E. Kessler, Thin Solid Films 187 (1990) 253
- [8] A. Foucaran, A. Sackda, A. Giani, F. Pascal-Delannoy and A. Boyer, Materials Science and Engineering B52 (1998) 154.
- [9] H. Böttner, A. Schubert, K.H. Schlereth, D. Eberhard, A. Gavrikov, M. Jägle, G. Kühner, C. Künzel, J. Nurnus and G. Plescher, Journal of Microelectromechanical

systems 13 (2004) 414.

[10] H. Noro, K. Sato and H. Kagechika, *Journal of Applied Physics* 73 (1993) 1252.

[11] J. C. Caylor, A. M. Stacy, R. Gronsky and T. Sands, *Journal of Applied Physics* 89 (2001) 3508.

[12] J. Walachová, R. Zeipl, J. Zelinka, V. Malina, M. Pavelka, M. Jelínek, V. Studnička and P. Lošt'ák, *Appl. Phys. Lett.* 87 (2005) 081902.

[13] R. Venkatasubramanian, T. Colpitts, E. Watko, M. Lamvik and N. El-Masry, *Journal of Crystal Growth* 170 (1997) 817.

[14] A. Al Bayaz, A. Giani, M. Al Khalfoui, A. Foucaran, F. Pascal-Delannoy and A. Boyer, *Journal of Crystal Growth* 258 (2003) 135.

[15] A. Boyer and E. Cisse, *Materials Science and Engineering B* 13 (1992) 103.

[16] S. Cho, Y. Kim, A. DiVenere, G. K. Wong, J. B. Ketterson, J. R. Meyer, *Applied Physics Letters*, *Appl. Phys. Lett.* 75 (1999) 1401.

[17] T. Inoue, K. Miyazaki, *Thermal Science and Engineering* 7 (1999) 95.

[18] Y.Z. Boikov, B.M. Goltsman, V.A. Kusatov, *Sov. Phys. Solid State* 20 (1978) 757.

[19] V. Damorada Das, P. Gopal Ganesan, *Semicond. Sci. Technol.* 12 (1997) 195.

[20] A. F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling*, Infosearch Limited, London, 1957, p.20.