Cross-plane thermal conductivity of highly oriented nanocrystalline bismuth antimony telluride thin films

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Abstract

The cross-plane thermal conductivity of highly oriented nanocrystalline bismuth antimony telluride thin films is investigated. The thin film was deposited by a flash evaporation method. The resulting film was oriented with the c-axis to the substrate, and was composed of fine grains with an average grain size of 150 nm. The cross-plane thermal conductivity of the film was measured by a 3ω method at room temperature, and was determined to be 0.6 $W \cdot m^{-1} \cdot K^{-1}$. Compared to the single crystal bulk alloy of nearly the same composition and carrier concentration, the thin film exhibited a 20% reduction in

the thermal conductivity.

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1. Introduction

Nanostructured materials have recently garnered significant attention because of their attractive properties, which can differ from those of the corresponding bulk materials. Such differences are especially desirable for thermoelectric materials, since it is possible to enhance the performance of thermoelectric materials by nanostructuring them, owing to a reduction in their thermal conductivities [1]. The performance of thermoelectric materials is characterized by the dimensionless figure-of-merit ZT, defined as $ZT= S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature and κ is the thermal conductivity. The product $S^2\sigma$ is defined as the thermoelectric power factor. The thermoelectric power factor needs to be maximized and the thermal conductivity needs to be minimized in order to obtain thermoelectric materials with high performance. Recent reports have shown that high-performance thermoelectric materials are achieved by employing superlattice structures [2-4]. In these superlattices, key factors for high thermoelectric performance include a nano-scale structure, high crystal orientation and high crystalline quality. However, the production cost becomes very high because the deposition equipment and the starting materials are expensive.

In order to provide the thin films with high thermoelectric performance without employing superlattices, our strategy was to fabricate thin films with nano-scale structure, high crystal orientation and high crystalline quality by using a simple deposition system

with low cost starting materials. Highly-oriented nanocrystalline thin films with high crystalline quality have the potential to satisfy these structure requirements and yield high thermoelectric properties. In thermoelectric materials, bismuth-telluride-based alloys are known to have high anisotropy and excellent thermoelectric properties at or around room temperature. We have previously fabricated highly oriented nanocrystalline bismuth-telluride-based thin films with high crystalline quality by a flash evaporation method, and have shown a high thermoelectric power factor in the in-plane direction [5]. The next step was to determine the thermal conductivity of the thin films, especially the thermal conductivity in the cross-plane direction, because the superlattices have been extensively investigated for cross-plane thermal conductivity, and it would be useful to compare the cross-plane thermal conductivity of the thin films with that of superlattices [6-8].

In this letter, we report an experimental study on the cross-plane thermal conductivity of highly-oriented nanocrystalline bismuth antimony telluride thin films with high crystalline quality using a 3ω method. The thermal conductivity of the thin film will be discussed, comparing it with that of the corresponding single crystal bulk alloy and superlattices with approximately the same atomic composition.

2. Experimental

Bismuth antimony telluride thin films were fabricated on a glass substrate (size: 50 mm×50 mm, 1.1 mm thick) using a flash evaporation method. The detailed experimental setup has been described elsewhere [5,9]. The starting material for the flash evaporation was $Bi_{0.4}Te_{3.0}Sb_{1.6}$ spherical-shaped powder with an average powder size of 200 μm prepared by a centrifugal atomization method [10]. Inside the flash evaporation chamber, the distance between the tungsten boat and the substrate was 200 mm. When the chamber was evacuated to 1.4×10^{-3} Pa, a current of 80 A was applied to the tungsten boat until the substrate temperature reached 200°C. Next, a hydrogen annealing step was carried out. The sample was placed in an electric furnace that was evacuated to 1.0 Pa, which was purged five times with high-purity (99.999%) argon gas. The furnace was then filled with hydrogen gas at atmospheric pressure, with the hydrogen gas flow rate maintained at 0.3 SLM throughout the annealing process. The temperature was increased steadily at a rate of 5 K/min to 300 ^{o}C, and the sample was then annealed at this temperature for 60 min. The annealing temperature of 300^{o}C was chosen because it yielded the best performance of the thermoelectric power factor in our previous study [5]. After annealing, the sample was cooled naturally to room temperature. Finally, the adhesion of the sample was checked by a tape delamination test in order to confirm that the thin film was in good contact with the substrate.

3. Results and discussion

The crystalline quality and orientation of the bismuth antimony telluride thin films were analyzed by x-ray diffraction (XRD). The surface and cross-sectional structure of the thin films were investigated using scanning electron microscopy (SEM). Finally, the atomic composition was investigated by means of Energy Dispersive X-ray Spectroscopy (EDX).

The cross-plane thermal conductivity was determined at room temperature by the 3ω method with an accuracy of ±10% [11]. Details of the thermal conductivity measurement and the sample fabrication process for the 3ω method are described elsewhere [12-15]. Figure 1 shows an optical micrograph of a completed sample, the in-plane structure and the cross-plane structure for the thermal conductivity measurement. An SiO_2 film (0.7 μm thick) was deposited on the bismuth antimony telluride thin film with a low deposition rate (0.12 nm/sec) using a sputtering method. A thin aluminum wire, used as a heater, was deposited on the sample by electron beam evaporation through shadow masks. The aluminum wire was 20 μm wide and 0.3 μm thick, and the length of the heating part was 2 mm. Since the bismuth antimony telluride thin film and the SiO_2 film are significantly thinner than the width of the aluminum wire, the direction of heat flow can be considered to be perpendicular to the thin film. We also fabricated a reference sample without the bismuth antimony telluride thin film but that was otherwise

identical to the primary sample.

For measurement of the thermal conductivity, the thin aluminum wire (heater) on the bismuth antimony telluride thin film and the reference sample were driven with an ac electrical current at a sweeping frequency ω. The resulting third-harmonic voltage, at 3ω, was measured across the heater as a function of ω and was then converted into an ac temperature rise amplitude for the heater. The difference between the sample with the thin film and the reference sample was equated to the temperature drop across the thin film and was used to calculate its cross-plane thermal conductivity.

The crystalline quality and orientation of the bismuth antimony telluride thin films were investigated by XRD, shown in Fig. 2. The XRD peaks show a highly diffracted intensity and a narrow width, indicating that the thin film possessed high crystalline quality. We also estimated the average crystal grain size of the thin film from the full-width at half maximum of the XRD peaks using Scherrer's equation. The average crystal grain size was thus estimated to be 150 nm. With regard to the crystal orientation of the thin film, almost all the XRD patterns of the thin film were found to exhibit c-axis oriented peaks. The diffracted intensity ratio of the sum of all of the c-axis oriented peaks, $\Sigma\{0\ 0\ 1\}$, to the sum of all of the peaks, $\Sigma\{h\ k\ l\}$, was estimated to be 0.99. This result indicates that the thin film is highly oriented along the c-axis. We thus note that the cross-plane direction is identical to the c-axis.

The surface and cross-sectional structure of the thin film were examined using SEM (Fig. 3). The surface image shows that the thin film is highly-crystallized and is composed of various sized crystalline grains all in the sub-micron range. Also, no voids were observed at the grain boundaries. In the cross-sectional image, cleavage facets were observed in the thin film, indicating that the film is highly crystallized with high orientation, and again, no voids were observed. No cracks were seen at the interface between the thin film and substrate, indicating that the thin film is well-bonded to the substrate, which is consistent with the results of the tape delamination test. The thickness of the thin film was approximately 200 nm.

EDX yielded the atomic composition of the bismuth antimony telluride thin film. The ratio of the atomic composition of the thin film was Bi : Sb : Te = 8 : 30 : 62, which is mostly stoichiometric.

Figure 4 shows experimentally measured temperature amplitudes experienced by a 20 μm wide heater on both the reference sample and the bismuth antimony telluride thin film sample. The inset in Fig. 4 shows the sample configuration for the thermal conductivity measurement by the 3ω method. The thermal conductivity of the thin film was extracted from curve fitting of the measured temperature difference [16-18]. The cross-plane thermal conductivity of the thin film was determined to be 0.6 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature.

In order to compare the thermal conductivity of the nanocrystalline bismuth antimony telluride thin film to that of other morphologies of nearly the same composition, the cross-plane thermal conductivity of the single crystal bulk alloys and superlattices is presented in table 1. We employ the cross-plane thermal conductivity of 0.75 $W \cdot m^{-1} \cdot K^{-1}$ as the reference data of the single crystal bulk alloy because we consider that the carrier concentration of the bulk alloy is the nearly same value of the thin film [19]. The cross-plane thermal conductivity of the thin film is 20% smaller than the corresponding single crystal bulk alloy. On the other hand, the cross-plane thermal conductivity of the thin film is still 50% larger than its Bi_2Te_3 (3 nm) / Sb_2Te_3 (3 nm) superlattice [6].

We have previously reported the dependence of the lattice thermal conductivity on grain size of Bi_2Te_3 thin films based on experimental results and the theory of phonon scattering on grain boundaries [15]. This report indicated that enhanced phonon scattering due to the nanocrystalline structure of the film was responsible for the observed reduction in thermal conductivity. From the theoretical curve grain size vs lattice thermal conductivity, the ratio between the lattice thermal conductivity parallel to the c-axis at the grain size of 150 nm and 100 μm whose grain size of thermal conductivity was nearly the same as its single crystal was approximately 0.75. Assuming that the ratio between the lattice thermal conductivity and the electronic thermal conductivity is constant without depending on the grain size because the measured thermal conductivity in this study is sum

of the lattice thermal conductivity and the electronic thermal conductivity, our experimental results in this study are consistent with the theory of phonon scattering on grain boundaries. However, the lattice thermal conductivity of superlattice (Bi_2Te_3 (3 nm) / Sb_2Te_3 (3 nm)) does not match the theoretical curve. This may be because the lattice thermal conductivity of superlattice can not apply to the theoretical model of phonon scattering on grain boundaries.

Therefore, we confirmed that cross-plane thermal conductivity can be reduced by employing a highly oriented nanocrystalline thin film with high crystalline quality. For further improvements in the thin film performance, it is necessary to reduce the size of the crystalline grains while maintaining the high orientation and crystalline quality.

4. Conclusion

In summary, we prepared highly oriented nanocrystalline bismuth antimony telluride thin films with high crystalline quality, with an average crystal grain size of 150 nm. We experimentally measured the cross-plane thermal conductivity, using the 3ω method at room temperature, to be 0.6 $W \cdot m^{-1} \cdot K^{-1}$. The cross-plane thermal conductivity of the thin film was 20% smaller than the corresponding single crystal bulk alloy, and 50% larger than that of superlattices of nearly the same composition. We confirm the reduction of the thermal conductivity by the theoretical model of phonon scattering on

grain boundaries, and then consider that the thermal conductivity can be reduced by employing highly oriented nanocrystalline thin films with high crystalline quality. It is more important to reduce the size of the crystal grains while maintaining high orientation and crystalline quality in order to catch up to the thermal conductivity of superlattices.

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Table

Table 1. Cross-plane thermal conductivity of bismuth antimony telluride thin film and related materials.

Materials	Orientation	κ ($W \cdot m^{-1} \cdot K^{-1}$)	References
Nanocrystalline BiSbTe thin film	c-axis (cross-plane)	0.6	This work
Single crystal BiSbTe bulk alloys	c-axis	0.75	ref. 19
Bi_2Te_3/Sb_2Te_3 superlattices	c-axis	0.4	ref. 6

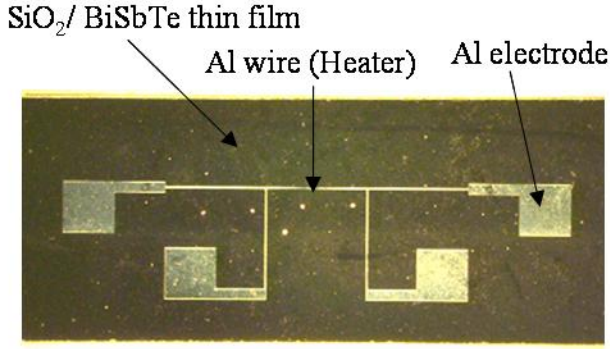
Figure caption

Fig. 1. Schematic structure and image of the sample used for the measurement of the thermal conductivity using 3ω the method. (a) Surface SEM micrograph, (b) in-plane structure, and (c) cross-plane structure.

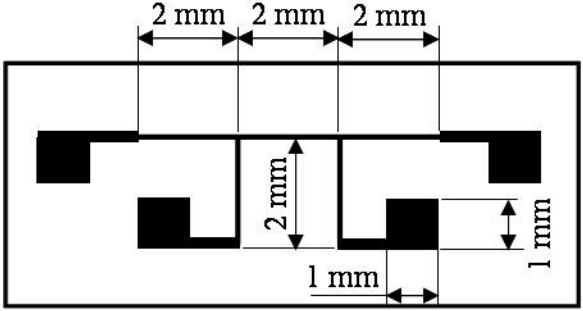
Fig. 2. XRD pattern of the bismuth antimony telluride thin film.

Fig. 3. Surface (a) and cross-sectional structure (b) of the bismuth antimony telluride thin film obtained using SEM.

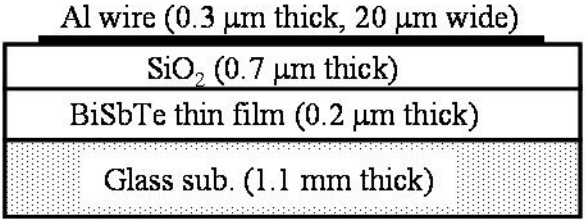
Fig. 4. The temperature amplitudes experienced by 20 μm wide heaters deposited onto the reference and the bismuth antimony telluride thin film.


SiO_2/ BiSbTe thin film
Al wire (Heater)
Al electrode

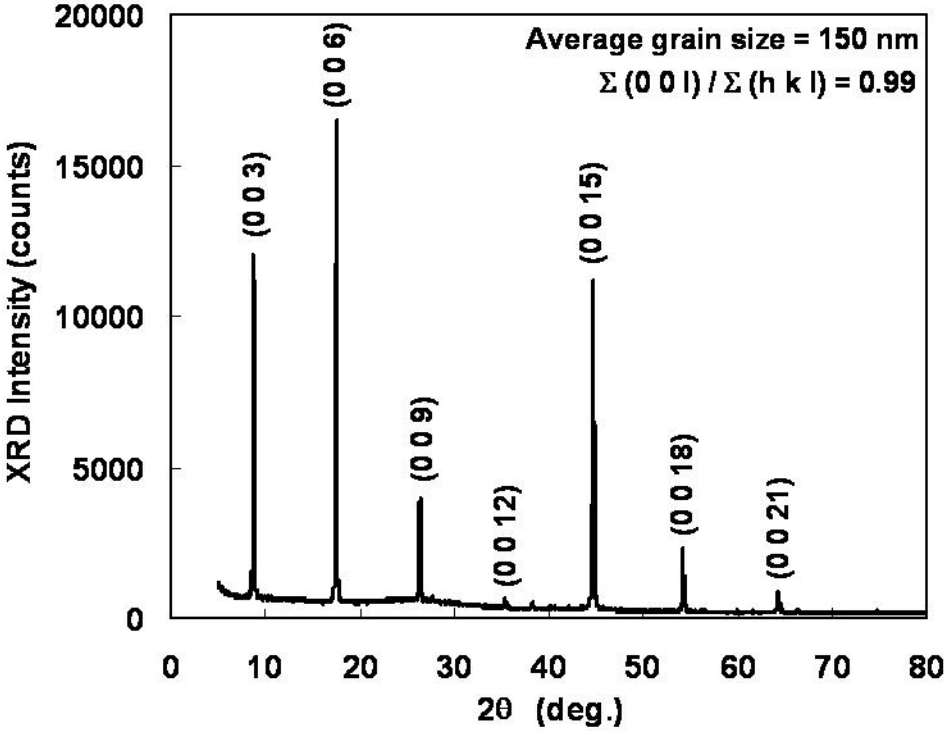
(a)

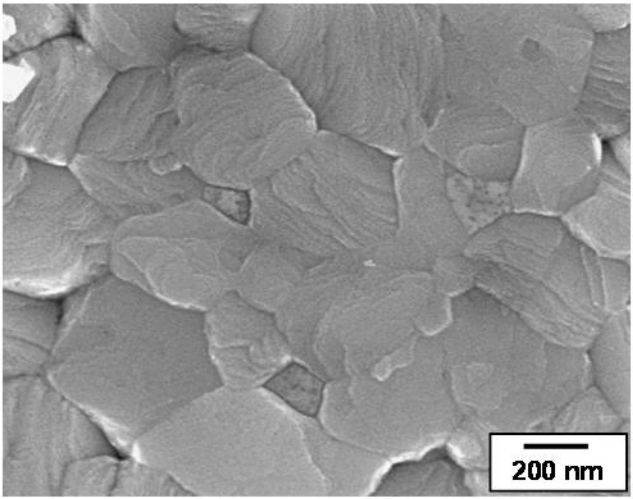

2 mm
2 mm
2 mm
2 mm
1 mm
1 mm

(b)

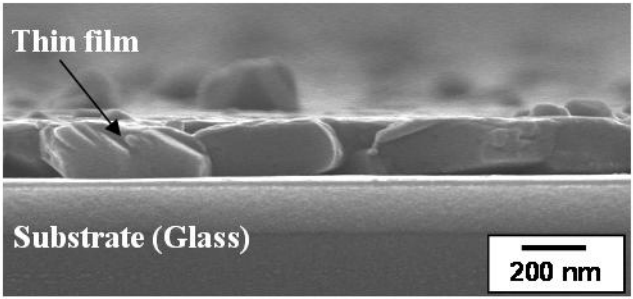

Al wire (0.3 μm thick, 20 μm wide)
SiO_2 (0.7 μm thick)
BiSbTe thin film (0.2 μm thick)
Glass sub. (1.1 mm thick)

(c)

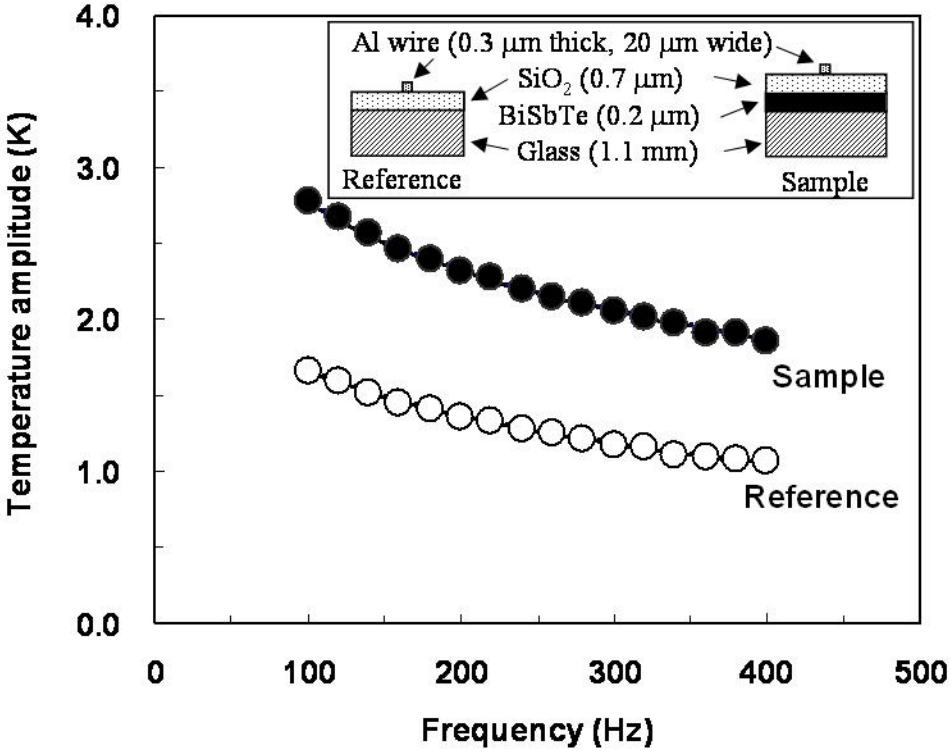

Average grain size = 150 nm
Σ (0 0 l) / Σ (h k l) = 0.99
(0 0 3)
(0 0 6)
(0 0 9)
(0 0 12)
(0 0 15)
(0 0 18)
(0 0 21)
XRD Intensity (counts)
20000
15000
10000
5000
0
0
10
20
30
40
50
60
70
80
2θ (deg.)



(a)



(b)


Al wire (0.3 μm thick, 20 μm wide)
SiO2 (0.7 μm)
BiSbTe (0.2 μm)
Glass (1.1 mm)
Reference
Sample
Sample
Reference
Temperature amplitude (K)
Frequency (Hz)
0.0
1.0
2.0
3.0
4.0
0
100
200
300
400
500