Evaluation of Thermoelectric Performance of Bi$_2$Te$_3$ Films as a Function of Temperature Increase Rate during Heat Treatment

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Abstract: Thin film thermoelectric generators are expected to be applied as power supplies for various Internet of Thing devices owing to their small size and flexible structure. However, the primary challenges of thin film thermoelectric generators are to improve their thermoelectric performance and reduce their manufacturing cost. Hence, Bi$_2$Te$_3$ thin films were deposited using direct current magnetron sputtering, followed by heat treatment at 573 K with different temperature increase rates ranging from 4 to 16 K/min. The in-plane Seebeck coefficient and electrical conductivity were measured at approximately 293 K. The in-plane thermal conductivity was calculated using the models to determine the power factor (PF) and dimensionless figure of merit (ZT). The temperature increase rate clearly affected the atomic composition, crystal orientation, and lattice strains, but not the crystallite size. The PF and dimensionless ZT increased as the temperature increase rate increased. The highest PF of 17.5 μW/(cm·K$^2$) and ZT of 0.48 were achieved at a temperature increase rate of 16 K/min, while the unannealed thin film exhibited the lowest PF of 0.7 μW/(cm·K$^2$) and ZT of 0.05. Therefore, this study demonstrated a method to enhance the thermoelectric performance of Bi$_2$Te$_3$ thin films by heat treatment at the appropriate temperature increase rate.

Keywords: Bi$_2$Te$_3$; temperature-increase rate; DC magnetron sputtering; atomic composition; crystal orientation; thermoelectric

1. Introduction

Thermoelectric materials can convert thermal energy to electric energy, referred to as “thermoelectric generation”, and vice versa by converting electricity to heat, referred to as “Peltier cooling”. To date, the main topic in the research of thermoelectric materials is improving thermoelectric performance by exploring new materials and incorporating nanostructures [1–5]. Thermoelectric performance is defined as the dimensionless figure of merit (ZT), which is expressed as Equation (1),

$$ZT = \frac{\sigma S^2}{\kappa} T,$$

where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the absolute temperature, and $\kappa$ is the thermal conductivity comprising electronic and lattice thermal conductivities. The power factor (PF), defined as $\sigma S^2$, is frequently used as a substitute to ZT for performance estimation.

Recently, there has been growing research on material flexibility for thermoelectric generators used for energy harvesting technology due to the applicability of flexible thermoelectric generators in various places [6–10], such as small areas and bent surfaces. For these conditions, thin film thermoelectric generators are highly suitable. Moreover, they are expected to be applied as power supplies for Internet of Thing (IoT) applications, including wireless sensor nodes and wearable sensors [11–14].

To widely utilize thin film thermoelectric generators as power supplies for IoT applications, their conversion efficiency should be improved while their manufacturing cost...
should be reduced. The conversion efficiency of generators is highly linked with the thermoelectric performance of the thin films. Meanwhile, to decrease the manufacturing cost of the generators, conventional deposition methods, including sputtering [15–18], electrodeposition [19–22], vacuum evaporation [23–26], and printing [27–29], should be used. Among these, sputtering can deposit thin films with high adhesion on various substrates. However, sputtering frequently causes deviations in the composition of the alloyed thin films when the substrate is heated during deposition [30]. To decrease the composition deviation and enhance the thermoelectric characteristics of thin films, post processing treatments, such as heat treatment, laser annealing, and homogeneous electron-beam irradiation, are widely utilized [31–35]. Particularly, heat treatment is one of the most effective among these methods. In addition, the relationship between the annealing temperatures and film characteristics has been well investigated [36–39]. In particular, the heat treatment temperature of the process strongly influences crystallite size [40,41]. However, the effects of the temperature increase rate in heat treatment have been rarely investigated in thermoelectric materials [42], while its effectiveness has been confirmed with other materials [43–46].

Hence, this study explored the influences of the temperature increase rate in heat treatment on the structural and thermoelectric characteristics of bismuth telluride (Bi$_2$Te$_3$) thin films. Bi$_2$Te$_3$ exhibits the highest thermoelectric characteristics at approximately 293 K [47–49]. The highest ZT value of 2.4 was achieved using a Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattice via a metalorganic chemical vapor deposition [1]. The Bi$_2$Te$_3$ has rhombohedral tetradymite-type crystal structure with hexagonal unit cells. The lattice parameter along the c-axis is approximately seven times larger than that along the a- or b-axis, which contributes to the material’s remarkable anisotropy of transport properties [50–52]. For instance, the electrical conductivity along the a,b-plane is approximately three times larger than that along the c-axis [53]. The films were prepared through DC magnetron sputtering without substrate heating, followed by heat treatment with different temperature increase rates. The structural and thermoelectric characteristics of the formed Bi$_2$Te$_3$ thin films were analyzed and the effect of the structural characteristics on the thermoelectric characteristics were examined.

2. Materials and Methods

The Bi$_2$Te$_3$ thin films were deposited on a 25 × 30 mm$^2$ polished alumina substrate (Kyocera Co., Ltd., Kyoto, Japan) by DC magnetron sputtering (CFS-8EP, Tokuda) without substrate heating. A bismuth-telluride target (99.9%, Chemiston Ltd., Hiki, Japan) with a composition of 32 at.% Bi and 68 at.% Te was used. The diameter of the target was 127 mm and the distance between the target and substrate was set to 140 mm. After placing the substrates on the holder, argon gas (purity: 99.995%) at a pressure of 1 Pa was fed to the chamber when the pressure reached 2.5 × 10$^{-4}$ Pa. Sputtering was carried out at a DC power of 200 W for 40 min, with the film thickness controlled at approximately 1 µm.

Next, for film deposition, the samples were heat treated in an electric tubular furnace. A small amount of hydrogen gas (5%) was added to argon gas (95%) in the carrier gas (purity: 99.995%) at a pressure of 1 Pa was fed to the chamber when the pressure reached 2.5 × 10$^{-4}$ Pa. Sputtering was carried out at a DC power of 200 W for 40 min, with the film thickness controlled at approximately 1 µm.

The surface configurations of the Bi$_2$Te$_3$ thin films were analyzed by scanning electron microscopy (SEM; S-4800, Hitachi, Tokyo, Japan) operating at an electron accelerating voltage of 3 kV. The atomic compositions of the thin films were measured via an electron probe microanalyzer (EPMA; EPMA-1610, Shimadzu, Kyoto, Japan), whereas the compositions were calibrated using the ZAF4 program equipped in EPMA-1610. The crystal structures of the thin films were determined by X-ray diffraction (XRD; Mini Flex II, Rigaku, Tokyo, Japan).
Japan) using Cu-Kα radiation (λ = 0.154 nm at 2θ range of 7° to 80°). The crystal orientation, average crystallite size, and lattice strains were calculated from the XRD patterns using Rietveld refinement [54].

The in-plane Seebeck coefficient, S, was measured at approximately 293 K using the basic measurement procedure described in the previous report [55]. One end of the film was put on a heat sink, while the other end was put on a heater. Two K-type thermocouples (diameter of 0.1 mm) were held on the middles of the films with a gap of 10 mm between them. The temperature difference between the thermocouples was controlled, from 1 to 5 K, while the thermoelectric power was measured at every 1 K. The Seebeck coefficient, S, was acquired from the linear approximation of voltage–temperature slope. The in-plane electrical conductivity, σ, of the Bi₂Te₃ thin films was measured at approximately 293 K via a four-point probe method (RT-70V, Napson, Tokyo, Japan). The in-plane PF σS² was derived from the experimentally measured Seebeck coefficient and electrical conductivity.

There are a few measurement methods in obtaining the thermal conductivities of thin films in the in-plane direction. Here, we calculated the in-plane total thermal conductivity, κ, of the films, which was sum of the electronic and lattice thermal conductivities based on the previous report [30]. The electronic thermal conductivity was acquired from the experimentally measured electrical conductivity combined with the Wiedemann–Franz law. The lattice thermal conductivity was acquired using models on the basis of effects of the crystallite size and crystal orientation. The dimensionless ZT was determined from the experimentally measured PF and the calculated thermal conductivity.

3. Results

3.1. Structural Characteristics of the Bi₂Te₃ Thin Films

Figure 1 shows the surface configuration of the Bi₂Te₃ thin films formed with different temperature increase rates during heat treatment. The film formed without heat treatment was composed of numerous fine grains with an average size of 100 nm (Figure 1a). For the sample that underwent heat treatment at a temperature increase rate of 4 K/min, there were considerable changes in the surface configuration compared to the films without heat treatment (Figure 1b). Particularly, the fine grains seemingly melted and formed irregularly shaped large agglomerations with an average size of 1 µm. With further increase in the temperature increase rate to more than 8 K/min, the tips of grains became rounded, with adjacent grains adhered together owing to their partial melting (Figure 1c–e). Therefore, the surface configuration of the thin films was affected by the low temperature increase rate during heat treatment. The mechanism of this phenomenon is not yet clear. However, a possible mechanism can be explained based on the theory of recovery and recrystallization of plastically deformed metals [56]. The as-deposited Bi₂Te₃ thin films obtain relatively high lattice strain [30], which is a similar trend in plastically deformed metals. According to the above-mentioned theory, firstly, a recovery occurs at lower temperature, and subsequently, recrystallization occurs at higher temperature. When the temperature increase rate was low, the recrystallization was accelerated and the recrystallization temperature lowered since the incubation period of nucleation, i.e., period of recovery, was passed at a lower temperature. By working the mechanism in this study, the grain size of the Bi₂Te₃ film became large at a lower temperature increase rate.
Figure 1. SEM images of the surface configurations of the Bi$_2$Te$_3$ thin films (a) without heat treatment, and heat treatment at a temperature increase rate of (b) 4 K/min, (c) 8 K/min, (d) 12 K/min, and (e) 16 K/min.

The atomic composition ratios, $\text{Bi}/(\text{Bi} + \text{Te})$, of the Bi$_2$Te$_3$ thin films formed under different temperature increase rates are as shown in Figure 2. The thin film formed without heat treatment has an atomic composition ratio of approximately 0.38, that is marginally lower than the stoichiometric proportion of 0.40. An atomic composition ratio of 0.43 was observed for the thin film with heat treatment performed at a temperature increase rate of 4 K/min. The atomic composition ratio decreases, approaching the stoichiometric proportion as the temperature increase rate increases. Particularly, at a temperature increase rate of 16 K/min, the thin film has an atomic composition ratio of 0.41 due to the higher evaporation rate of Te than Bi and the easier atomic evaporation of Te at a low temperature increase rate.
The XRD patterns of the Bi$_2$Te$_3$ thin films formed under different temperature increase rates are as shown in Figure 3. All films display the identical peaks of the rhombohedral Bi$_2$Te$_3$ phase (JCPDS 15-0863) and alumina phase of the substrate. In the film without heat treatment, the XRD peaks coinciding with the (015), (1010), and $c$-axis-oriented peaks of (00l) were distinctly observed. These peaks have broad widths due to their low crystallinity. Furthermore, the $c$-axis-oriented peaks of the film move to angles higher than the standard peaks (JCPDS 15-0863), indicating the decrease in the lattice constant of the $c$-axis. When heat treatment was implemented at different temperature increase rates, the XRD peaks of the films became sharper owing to their high crystallinity. At the diffraction angles $2\theta$ of $7^\circ$–$80^\circ$, the thin films that underwent heat treatment with different temperature increase rates are nearly similar.

To analyze the XRD patterns in detail, the crystallographic features of the Bi$_2$Te$_3$ thin films were derived from the measured XRD patterns via Rietveld refinement, as shown in Figure 4. Figure 4a presents the relationship between the temperature increase rate and crystal orientation of the Bi$_2$Te$_3$ thin films. The crystal orientation was calculated from the Lotgering factor, $F$, calculated using Equation (2) [57–59]:

$$F = \frac{P - P_0}{1 - P_0},$$

where $P_0 = \Sigma I_0(00l)/\Sigma I_0(hkl)$ and $P = \Sigma I(00l)/\Sigma I(hkl)$. $I_0$ and $I$ indicate the peak intensities in the XRD patterns of the standard (JCPDS 15-0863) and those of the Bi$_2$Te$_3$ films measured experimentally, respectively. When the $F$ value is close to 1.0, the crystals are oriented along the $c$-axis direction. At a temperature increase rate of 4 K/min, the film has an $F$ value of 0.46, which is lower than that of the unannealed film ($F$ value = 0.58). This phenomenon is related to the grain agglomerations observed in Figure 1a, in which the grains grew in various directions during heat treatment. At a temperature increase rate of 8 K/min, the $F$ value increases to 0.61. With further increase in the temperature increase rate, the $F$ value gradually decreases. This phenomenon can also be explained using the theory of recovery and recrystallization of plastically deformed metals [56]. In general, the surface energy of the crystal plane affects the orientation when the recrystallization is in progress in the thin films. In the Bi$_2$Te$_3$ material, the lowest surface energy was exhibited at a (00l) plane [60]. Therefore, when the temperature increase rate decreased from 16 to 8 K/min, the recrystallization progressed and the atoms tended to move easily on the surface. As a result, the film was orientated to the (00l) direction, increasing the $F$ value. To further decrease the temperature increase rate to 4 K/min, the $F$ value decreased. This phenomenon might occur since the (015) peak increased as the random crystal growth...
progressed, due to the decrease in the recrystallization temperature and partially melting the thin film [61,62].

Figure 3. XRD patterns of the Bi$_2$Te$_3$ thin films without and with heat treatment at different temperature increase rates.

The average crystallite size of the Bi$_2$Te$_3$ thin films is shown in Figure 4b. The average crystallite size was estimated by the Scherrer equation using the highest XRD peak for each film. The average crystallite size indicates the average diameter of the respective crystal orientations existing in a polycrystalline material. Without heat treatment, the thin film had a crystallite size of 8 nm. When heat treatment was performed, the crystallite size of the thin films significantly increased to 45–50 nm for all investigated temperature increase rates. Therefore, the crystallite size is not highly dependent on the temperature increase rate. It is to be noted that the trend between the grain size of the film at 4 K/min in Figure 1b and crystallite size of the corresponding film in Figure 4b seemed to be different. This difference occurred because the average crystallite size determined from the XRD peaks using the Scherrer equation referred to the average diameter of the individual crystal orientations found in polycrystalline materials. Therefore, it was considered that the polycrystalline grains observed in Figure 1b became large, but the average diameter of the individual crystal orientations (crystallite size) was not changed much.
Figure 4. Crystallographic properties of the various Bi$_2$Te$_3$ thin films determined from the XRD analysis: (a) Lotgering factor $F$, (b) crystallite size, and (c) lattice constants.

Figure 4c presents the lattice strains of the Bi$_2$Te$_3$ thin films. The lattice strain $\varepsilon_l$ is described as the ratio of the lattice parameter of the thin films to that of the standard data (JCPDS 15-0863) for Bi$_2$Te$_3$. For example, in the $a,b$-axis direction, the lattice strain can be presented as $\varepsilon_l (a,b\text{-axis}) = (a-a_0)/a_0$, where $a$ is the $a$-axis lattice parameter of the samples and $a_0$ is that referred by the standard data. Compressive and tensile strain is denoted by a negative and positive value, respectively. The thin film that did not undergo heat treatment obtained large strains of 1.6% in the $a,b$-axis direction and $-6.2\%$ in the $c$-axis direction. Although heat treatment has relaxed the strain of the thin film, the residual strain is still dependent on the temperature increase rate. With a temperature increase rate of 4 K/min, the lowest strains of 0.03% (tensile strain) in the $a,b$-axis and $-0.16\%$
(compressive strain) in the c-axis directions were noted. When the temperature increase rate was increased, the strain in the a,b-axis direction further increased, while that in the c-axis direction decreased. This can be attributed to the gradual relaxation of the large strains obtained in the unannealed thin film as the temperature increase rate decreases.

3.2. Electrical Transport Characteristics of the Bi$_2$Te$_3$ Thin Films.

Figure 5 shows the electrical transport characteristics of the Bi$_2$Te$_3$ thin films in the in-plane direction formed at different temperature increase rates during heat treatment. In Figure 5a, the Seebeck coefficients of the Bi$_2$Te$_3$ thin films became more negative as the temperature increase rate increases. The maximum negative Seebeck coefficient of $-178$ $\mu$V/K was noted at a temperature increase rate of 16 K/min, which was more negative than that of the unannealed thin film ($S = -162$ $\mu$V/K). Basically, the higher Seebeck coefficient was exhibited at the lower carrier concentration. Therefore, it was considered that the Seebeck coefficient of the films negatively increased with increase of the temperature increase rate due to the decrease in the carrier concentration; the atomic composition ratio is close to the stoichiometric proportion. In the bulk materials, single-crystalline Bi$_2$Te$_3$ exhibited a Seebeck coefficient of approximately $-200$ $\mu$V/K [63]. As observed in Figure 5b, the unannealed thin film displays a significantly low electrical conductivity owing to its small crystallite size and low crystallinity. On the other hand, the thin film obtained at 4 K/min has an electrical conductivity of 645 S/cm, increasing to 777 S/cm as the temperature increase rate increases to 8 K/min. With further increase in the temperature-increase rate, the electrical conductivity of the thin films decreases. Electrical conductivity depends on various structural characteristics, including crystallite size, crystal orientation, lattice strain, and atomic composition [41,63–65]. In particular, it was considered that the crystal orientation and atomic composition played an important role. The film at 8 K/min exhibited the highest electrical conductivity as the film obtained high mobility due to the high $F$ value and high carrier concentration because of the deviation of atomic composition ratio from the stoichiometric proportion. Figure 5c shows extremely low $PF$ of the unannealed Bi$_2$Te$_3$ thin film owing to its low electrical conductivity. When heat treatment was performed, $PF$ significantly increased because of the increase in the electrical conductivity. Moreover, $PF$ increases as the temperature increase rate increases. The highest $PF$ of 17.5 $\mu$W/(cm·K$^2$) was noted at a temperature increase rate of 16 K/min. Therefore, controlling the temperature increase rate can increase the $PF$ of the Bi$_2$Te$_3$ thin films.
3.3. Thermal Transport Characteristics of the Bi$_2$Te$_3$ Thin Films

Figure 6 shows the calculated thermal transport characteristics of the Bi$_2$Te$_3$ thin films in the in-plane direction formed under different temperature increase rates during heat treatment. The detailed calculation procedure is presented in the previous report [30]. The electronic thermal conductivity, $\kappa_e$, is derived from the experimentally measured electrical conductivities using the Wiedemann–Franz law, given by $\kappa_e = L \sigma T$. The Lorenz number, $L$, is calculated using Equation (3), as follows [66]:

$$L = \left[1.5 + \exp\left(-\frac{|S|}{116 \times 10^{-6}}\right)\right] \times 10^{-8} \quad (3)$$

Electronic thermal conductivity is greatly influenced by the electrical conductivity and slightly affected by the Seebeck coefficient. Thus, the relationship between the electronic thermal conductivity and temperature increase rate, and electrical conductivity and temperature increase rate are similar. The highest electronic thermal conductivity of 0.42 W/(m·K) was recorded with the thin film obtained at a temperature increase rate of 8 K/min. Meanwhile, the lowest value of 0.33 W/(m·K) was noted at the thin film obtained at a temperature increase rate of 16 K/min. The electronic thermal conduc-
tivity of the unannealed film was exceedingly low at 0.01 W/(m·K), owing to the low electrical conductivity.

The lattice thermal conductivity was subject to the average crystallite size, crystal orientation, and lattice strain of a material [67–70]. Consequently, the lattice thermal conductivity was determined using the measured crystallite size and the theoretical model presented in the previous report [71]. The effect of the lattice strain could be ignored when the crystallite size was below 100 nm; thus, it was not considered in this calculation. In addition, the lattice thermal conductivity along the in-plane direction was estimated using the measured \( F \) values and the observational model proposed by Kudo et al. [72]. For all films, the lattice thermal conductivities were higher than those of the electronic thermal conductivities. Particularly, for the thermally annealed thin films, the lattice thermal conductivity was nearly constant at 0.74–0.79 W/(m·K), whereas that of the unannealed thin film was 0.40 W/(m·K). The main reason for the small variation of the lattice thermal conductivity of the thermally annealed thin film is that the crystallite size does not highly depend on the temperature increase rate, as shown in Figure 4b. In addition, the lattice thermal conductivity of the thermally annealed thin films was approximately 50% lower than that of the single crystal Bi\(_2\)Te\(_3\) thin films in the \( a, b \)-axis [63].

The total thermal conductivity was calculated by adding the electronic and lattice thermal conductivities. The highest total thermal conductivity of 1.19 W/(m·K) was obtained with a temperature increase rate of 8 K/min, while the lowest value of 1.08 W/(m·K) was obtained at a temperature increase rate of 16 K/min. Meanwhile, the unannealed film displayed a total thermal conductivity of 0.41 W/(m·K). The total thermal conductivities calculated in this study were comparable to those of nanocrystalline bismuth-telluride-based alloy films reported in previous research [73,74].

![Figure 6](image_url)

**Figure 6.** Calculated in-plane thermal transport properties of the prepared Bi\(_2\)Te\(_3\) thin film.

### 3.4. Dimensionless Figure of Merit of the Bi\(_2\)Te\(_3\) Thin Films

The in-plane dimensionless \( ZT \) of the Bi\(_2\)Te\(_3\) thin films, estimated based on the measured \( PF \) and calculated total thermal conductivity, are shown in Figure 7. The unannealed thin film had a \( ZT \) of 0.05. When the heat treatment was performed at a temperature increase rate of 4 K/min, \( ZT \) significantly increased to 0.31, which was approximately six times higher than that of the unannealed thin film. Furthermore, as the temperature increase rate increased, \( ZT \) linearly increased. The thin film at 16 K/min exhibited the highest \( ZT \) of 0.48, which was approximately 1.5 times higher than that of the thin film at 4 K/min. Hence, this study demonstrated that high \( ZT \) values, comparable to those in previous reports [75–77], can be obtained by selecting the appropriate holding temperature and temperature increase rate in the heat treatment.
Hence, this study demonstrated that high ZT values, comparable to those in previous reports [75–77], can be obtained by selecting the appropriate holding temperature and temperature increase rate in the heat treatment. To enhance the thermoelectric performance of the Bi$_2$Te$_3$ thin films by varying the temperature increase rate in the heat treatment, these films were formed via DC magnetron sputtering on alumina substrates. The structural characteristics were analyzed using SEM, EPMA, and XRD. The thermoelectric characteristics in the in-plane direction, including Seebeck coefficient, electrical conductivity, and PF, were measured at approximately 293 K. The in-plane thermal conductivity was derived using the theoretical model, thereby estimating ZT. The temperature increase rate clearly affected the structural characteristics, especially the atomic composition, crystal orientation, and lattice strains. As a result, the Bi$_2$Te$_3$ thin film obtained at a temperature increase rate of 16 K/min displayed the highest PF of 17.5 µW/(cm·K$^2$) and ZT of 0.48, while the unannealed thin film displayed the lowest PF of 0.7 µW/(cm·K$^2$) and ZT of 0.05. Therefore, the thermoelectric performance of the Bi$_2$Te$_3$ thin films were improved by heat treatment at the appropriate temperature increase rate.

**Author Contributions:** O.N. and M.T. gestated the idea and designed the experiments. T.K. fabricated the samples and characterized their thermoelectric properties and microstructures. R.E. analyzed the structural properties of the samples using EPMA. O.N. and M.T. wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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