Study of the Annealing Effects of Sputtered $\text{Bi}_2\text{Te}_3$ Thin Films with Full Thermoelectric Figure of Merit Characterization

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Micro-thermoelectric (TE) devices have a great potential for future applications in the field of energy harvesting to power autonomous sensors. $\text{Bi}_2\text{Te}_3$ sputtered at elevated substrate temperatures exhibits a high figure of merit ($ZT$) suitable for the fabrication of micro-TE devices. However, a lift-off process that does not allow higher substrate temperatures is often used, and although $\text{Bi}_2\text{Te}_3$ is a well-studied TE material, it lacks full $ZT$ characterization of thin films. Herein, the full TE characterization of sputtered $\text{Bi}_2\text{Te}_3$ thin films is presented, including the charge carrier concentration and mobility, which are deposited at room temperature and postannealed between 150 and 300 °C. The influence of the annealing time and temperature is investigated on a 90 nm-thick $\text{Bi}_2\text{Te}_3$ film. A maximum $ZT$ of 0.20 is found, which results from the increasing crystallinity and reduction of point defects. To investigate the thickness dependency, $\text{Bi}_2\text{Te}_3$ films with thicknesses of 90, 170, 350, and 470 nm are annealed at 250 °C. A maximum $ZT$ value of 0.26 is observed for the 350 nm $\text{Bi}_2\text{Te}_3$ film. Furthermore, it can be shown that with increasing film thickness, the annealing time has to be increased to maximize $ZT$.

1. Introduction

Thermoelectric (TE) materials have been investigated for more than a century because of their promising applications in energy conversion, such as refrigeration and power generation, based on the direct conversion of heat into electricity or vice versa.¹⁻² The figure of merit $ZT = S^2 \sigma / k$ is a measure of the efficiency of a TE material, where $S$ is the Seebeck coefficient, $\sigma$ the electrical conductivity, $T$ the absolute temperature, and $k$ the total thermal conductivity, which has lattice $k_{\text{lat}}$ and electronic contributions $k_e$.³ The enhancement of $ZT$ is challenging due to the charge carrier interrelationship of the transport properties.⁴⁻⁵ Studies to improve $ZT$ are focused on optimizing the power factor $(PF = S^2 \sigma)$ and the suppression of the lattice thermal conductivity, for example, by nanostructuring, phonon engineering, or band structure engineering.⁶⁻⁸ For applications at room temperature (RT), bismuth telluride ($\text{Bi}_2\text{Te}_3$) is the mostly frequently used material due to its high TE efficiency in this temperature range.⁹ $\text{Bi}_2\text{Te}_3$ has a rhombohedral crystal structure with weak van der Waals bonding in the c-axis,¹⁰ which leads to strong anisotropy of the electrical and the thermal transport properties.¹¹

With the increasing demand of autonomous sensors for the Internet of Things (IoT), wearable electronics, and microelectronic cooling, the interest on micro-TE devices has recently increased.¹²⁻¹⁴ For these applications, micro-TE generators and coolers with high TE performance around RT are required. Even with the recent promising results of for example, sputtered Cu₃Te¹⁵ or flexible $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ membranes,¹⁶ up to today, $\text{Bi}_2\text{Te}_3$ is still one of the most frequently used materials for micro-TE devices. These materials are typically deposited by electrochemical deposition (ECD)¹⁷⁻¹⁸ or physical vapor deposition (PVD).¹⁹⁻²⁰ To optimize the TE performance of the micro-TE devices, it is essential to understand the transport properties of the materials; therefore, a full $ZT$ characterization of the deposited thin films is required. Various deposition techniques have been investigated for the deposition of $\text{Bi}_2\text{Te}_3$ thin films, including chemical vapor deposition (CVD),²¹⁻²⁴ ECD,²⁵⁻²⁶ and PVD.²⁷⁻³¹ Due to their high TE efficiency compared with ECD materials, sputtered $\text{Bi}_2\text{Te}_3$ films are often used for the fabrication of micro-TE devices.¹⁹⁻²⁰ However, the as-deposited thin
films typically have a predominantly amorphous state with poor crystallinity and therefore low $ZT$.\textsuperscript{12,13} To improve the TE properties of the deposited Bi$_2$Te$_3$ films, postannealing processes have been widely studied.\textsuperscript{14–37} However, often only the PF or thermal conductivity of the annealed Bi$_2$Te$_3$ films was investigated individually, often in different transport directions, and there is a lack of full TE characterization of one and the same sample in the same transport direction.

In this study, we present the full in-plane TE characterization of sputtered Bi$_2$Te$_3$ thin films, including the charge carrier concentration and mobility, with thicknesses between 90 nm and 450 nm on the same sample. The samples were deposited by radio frequency (RF) sputtering without substrate heating and postannealed between 150 and 300 °C. The influence of the annealing time and temperature was investigated on a 90 nm-thick Bi$_2$Te$_3$ film. To investigate the thickness dependence, Bi$_2$Te$_3$ film with thicknesses of 90, 170, 350, and 470 nm were annealed at 250 °C for 4 h and the transport properties characterized. The influences of the annealing time and temperature on the transport properties were discussed together with the structural and chemical composition changes of the material, which were characterized by X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDX).

2. Results and Discussion

2.1. Structural Analysis

Figure 1a-f shows the scanning electron microscope (SEM) images of the surface and cross section of a sputtered Bi$_2$Te$_3$ film with thickness of 90 nm, which was annealed at b) 150 °C, c) 200 °C, d) 250 °C, e) 300 °C, and f) 350 °C for 4 h in each case. With increasing annealing temperatures up to 250 °C, the average grain size increased, while the grain size distribution became narrower. With further increased annealing temperature of up to 350 °C, the film showed a morphological change toward more sintered grains with less defined boundaries and the formation of holes. Figure 1f shows the grain size and grain size distribution of the as-deposited and annealed films, obtained by image analysis of the SEM images. The average grain size of 15 nm was obtained for the as-deposited film, which increased to 17 nm for the film annealed at 250 °C and further increased to 20 nm for the film annealed at 300 °C. In addition, the grain size distribution of the sample first narrows up to an annealing temperature of 250 °C and becomes significantly wider again at 300 °C, which is related to less pronounced grain boundaries, which also made the image analysis less reliable. The chemical composition was measured with EDX. The amount of tellurium
started to decrease at annealing temperatures above 200 °C from 66 at% for the as-deposited sample to 63 at% at an annealing temperature of 250 °C and 48 at% at an annealing temperature of 350 °C, as shown in Figure 1g. In addition, the chemical composition change was measured by EDX on 170 nm, 350 nm, and 470 nm-thick films, which were annealed at 250 °C for 4 h (s. Table 1). A decrease in tellurium of 4.5%, 2%, 1.5%, and 4.1% was observed for the 90, 170, 350, and 470 nm-thick samples, respectively.

Figure 2 shows the grazing-incidence XRD (GIXRD) patterns of the Bi$_2$Te$_3$ films annealed at different temperatures (from as deposited to 300 °C). In Figure 2a the GIXRD patterns of the 90 nm Bi$_2$Te$_3$ film directly after deposition, annealed at 150, 200, 250, and 300 °C, are shown. The as-deposited sample revealed an amorphous state with only slightly pronounced (015) and (1010) peaks of Bi$_2$Te$_3$. After annealing the sample at 200 °C, (006), (0111), and (0015) peaks appeared. As the annealing temperature further increased, the peaks became sharper and their width decreased, which indicates increasing crystallinity from the predominantly amorphous state to the polycrystalline rhombohedral crystal structure of Bi$_2$Te$_3$. The sample annealed at 250 °C showed a main orientation in the (1010) plane, closely followed by the (015) and the (006) plane, while at 300 °C, the ratio between (015) and (006) slightly changed toward (006) orientation. The Bi$_2$Te$_3$ films with higher thicknesses of 170, 350, and 470 nm show higher crystallinity with a preferred (015) orientation (Figure S2b-d, Supporting Information) in the as-deposited state. After annealing at 250 °C for 4 h, a preferred (015) orientation was observed for all three samples (Figure 2b).

Table 1. Chemical composition, grain size, dislocation density, internal strain, and lattice parameters of 4 Bi$_2$Te$_3$ films with increasing thickness from 90 nm to 470 nm.

| Sample | Bi [at%] As dep./250 °C | Te [at%] As dep./250 °C | $d_{\text{crystal}}$ [nm] As dep./250 °C | $\delta$ [10$^{-1}$ [nm]$^{-1}$] As dep./250 °C | $\epsilon$ [10$^{-1}$] As dep./250 °C | $c/a$ |
|--------|------------------------|------------------------|---------------------------------|---------------------------------|-----------------|--------|
| 90 nm  | 34/37                  | 66/63                  | 7.84/14.31                      | 9.22/3.32                      | 38.66/23.20     | 6.9508 |
| 170 nm | 33.0/35.2              | 67.0/65.6              | 7.87/12.37                      | 12.77/6.47                     | 45.49/32.54     | 6.9573 |
| 350 nm | 34.4/35.4              | 65.6/64.6              | 9.93/12.91                      | 10.5/5.27                      | 41.25/29.23     | 6.9769 |
| 470 nm | 35.2/35.7              | 64.8/64.3              | 9.74/17.69                      | 7.28/2.85                      | 34.34/21.48     | 6.9712 |

Figure 2. GIXRD patterns of Bi$_2$Te$_3$ thin films annealed at different temperatures for 4 h. a) 90 nm-thick film annealed at 150, 200, 250, and 300 °C and b) 90, 170, 350, and 470 nm-thick film annealed at 250 °C.
Lotgering factor was observed after the annealing at 250 °C, but the orientation was less pronounced with increasing film thickness, giving a Lotgering factor of 0.12, 0.04, and almost 0 for the 170, 350, and 470 nm-thick film, respectively.

To quantify the grain size, the XRD data was analyzed using Scherrer’s equation. For the as-deposited 90 nm film, a grain size of 7.8 nm was found which increased with increasing annealing temperatures. For the sample annealed at 150, 200, 250, and 300 °C, the grain size increased to 8.1, 10.6, 14.3, and 15.9 nm, respectively, which were slightly lower than the SEM values, but showed the same trend. In addition, from the GIXRD patterns of the 90 nm film annealed at 250 °C, the lattice constants $a$ and $c$ of the pseudohexagonal structure were calculated\cite{38} to be 0.4316 and 3.0588 nm, respectively. Further, the dislocation density was calculated using Williamson and Smallman’s formula and the internal strain was calculated by $e = \beta/4 \cos(\theta)$, where $\beta$ is the full width at half maximum (FWHM) of the (015) peak.\cite{39} The dislocation density decreased from $9.2 \times 10^{15}$ m$^{-2}$ for the as-deposited sample to $6.6 \times 10^{15}$, $4.7 \times 10^{15}$, $3.3 \times 10^{15}$, and $3.1 \times 10^{15}$ m$^{-2}$ for the sample annealed at 150, 200, 250, and 300 °C, respectively, revealing higher crystallinity at higher annealing temperatures. This is in agreement with the reduced internal strain from 38.7 for the as-deposited sample to 32.6, 27.5, 23.2, and 22 for the samples annealed at 150, 200, 250, and 300 °C, respectively.

### 2.2. Thermal and Electrical Properties

#### 2.2.1. Time-Dependent Annealing Effect

The effect of the annealing time on the transport properties was studied in situ on a sputtered 90 nm Bi$_2$Te$_3$ film (Figure 3). The transport properties were characterized using a thin-film analyzer from Linseis, which enables a full in-plane TE characterization including the Hall coefficient during heating, annealing, and cooling of one and the same sample. Figure 3a shows the electrical conductivity ($\sigma$) depending on the temperature of the 90 nm Bi$_2$Te$_3$ film. The sample was heated in a first cycle from RT up to 200 °C (red) and then annealed for 4 h at 200 °C (black) and cooled (blue) back to RT, followed by a second cycle with an annealing time of 5 h, as indicated by the arrows in Figure 2a. In the first heating cycle, $\sigma$ initially decreased with temperature from 444 S cm$^{-1}$ to a minimum of 384 S cm$^{-1}$ at 100 °C and then increased again to 474 S cm$^{-1}$ at 300 °C. The temperature dependency with a kink was related to the change of the predominantly amorphous state toward crystal formation of the film, which was observed in XRD. During annealing at 200 °C for 4 h, $\sigma$ increased further to 487 S cm$^{-1}$ (Figure 3g). After annealing, the sample showed semiconducting behavior. $\sigma$ increased with decreasing temperature, with an activation energy of 4 meV. In the second cycle, $\sigma$ was only slightly increased to 494 S cm$^{-1}$ during annealing.

![Figure 3](https://www.advancedsciencenews.com/doi/10.1002/pssr.202100533)

**Figure 3.** In situ transport characterization of a 90 nm Bi$_2$Te$_3$ film annealed at 200 °C for 9 h. Shown are the heating (red), annealing (black), and cooling (blue) sequences in the temperature range from 20 to 200 °C for two cycles, when first H and first C indicate the first and heating and cooling cycle and second H and second C indicate the second heating and cooling. In the first cycle step, the sample was annealed for 4 h, followed by a second cycle with 5 h annealing time. Temperature-dependent a) electrical conductivity, b) charge carrier concentration, c) mobility, d) Seebeck coefficient, e) total thermal conductivity, and f) figure of merit. Dependency of the annealing time on the g) electrical conductivity, h) Seebeck coefficient, and i) PF.
(Figure 3g) and showed a reduced activation energy of 2 meV in the cooling step. The weak temperature dependency of $\sigma$ could be related to strong contributions from grain boundary scattering that do not depend on temperature.

The charge carrier concentration ($n$) and Hall mobility ($\mu$) were obtained from the measured Hall coefficient ($R_H$), assuming single-band transport with $n = (R_H e)^{-1}$ and $\mu = e n \mu$ ($e$ is the elementary charge). In the first heating cycle from 20 to 200 °C, during the crystal formation from the amorphous state, $n$ exponential decreased from $10.5 \times 10^{20}$ to $1.3 \times 10^{18}$ cm$^{-3}$ (Figure 3b), while $\mu$ increased from 2.6 to 13.2 cm$^2$V$^{-1}$s$^{-1}$ (Figure 3c). As a result of further annealing at 200 °C, $n$ decreased slightly from $2.2 \times 10^{20}$ to $1.3 \times 10^{18}$ cm$^{-3}$, which is related to the increased crystallinity and the reduction of $T_{gb}$ point defects.$^{[40,41]}$ During cooling, a semiconducting behavior was observed, analogous to electrical conductivity. In contrast, $\mu$ increased during annealing at 200 °C. After annealing, an increased grain size was observed, which led to less grain boundary scattering and in combination with reduced point defects and increased crystallinity to an increased $\mu$. In the cooling cycle, $\mu$ increased with a temperature dependency close to $T^{-1/2}$, indicating optical phonon scattering, which contrasts with previous findings where acoustic phonon scattering with $T^{-3/2}$ was found, which again might be related to grain boundary scattering.

The temperature-dependent Seebeck coefficient ($S$) is shown in Figure 3d). A negative $S$ was found, showing n-type semiconducting behavior with electrons as main charge carriers. The absolute $S$ at RT increased from 53 to 92 $\mu$V K$^{-1}$ after thermal treatment. The relation between $S$ and $n$ can be expressed by$^{[42]}

$$S = \frac{k_B}{e} \left( s + \frac{5}{2} + \ln \left( \frac{2\pi m^* k_B}{nh^2} \right) \right)^{1/2}$$

(2)

$$S = \frac{k_B}{e} (s - \ln n) + C$$

(3)

where $k_B$ is the Boltzmann constant, $h$ is the Planck constant, $m^*$ is the effective mass, $s$ is the scattering parameter, and $C$ is a constant, respectively. Subsequently, the absolute $S$ decreased durinwhile $n$ decreased. In Figure 3h, the absolute Seebeck coefficient is plotted versus the annealing time at 200 °C. In the first 4 h, an increase of $S$ was observed, which then remained almost constant.

The total thermal conductivity ($\kappa$) is shown in Figure 3e. In the first heating step, $\kappa$ shows a minimum at around 100 °C, analogous to the temperature dependency of $\sigma$. $\kappa$ increased from 0.8 at RT to 1.1 W m$^{-1}$ K$^{-1}$ at 200 °C during heating. During annealing at 200 °C, $\kappa$ showed no significant change. Cooling $\kappa$ showed only a weak temperature dependency with a minimum of 0.9 W m$^{-1}$ K$^{-1}$ at 120 °C. The RT value of $\kappa$ increased from 0.8 W m$^{-1}$ K$^{-1}$ for the as-deposited sample to 1.1 W m$^{-1}$ K$^{-1}$ after the first heating cycle. In general, the total thermal conductivity consists of contributions from the electronic ($\kappa_e$) and lattice ($\kappa_{ph}$) thermal conductivities ($\kappa = \kappa_e + \kappa_{ph}$). Hence, $\kappa_e$ increased with the increased $\sigma$. In addition, as the crystallinity of the material improves, the phonon scattering decreases, which leads to increased $\kappa_{ph}$. In the following cycle, no further changes were observed.

$ZT$ was calculated from the measured $S$, $\sigma$, and $\kappa$ (Figure 3f). The $ZT$ value increased from 0.04 to 0.12 in the first heating cycle. During annealing at 200 °C, $ZT$ increased further to 0.18. Cooling $ZT$ decreased with decreasing temperature to 0.09. In the second heating cycle, $ZT$ only slightly increased, resulting in a maximum $ZT$ value of 0.19 and PF of 0.45 mW m$^{-1}$ K$^{-1}$ (Figure 3i) at 200 °C for the 90 nm Bi$_2$Te$_3$ film annealed at 200 °C for 9 h.

$\sigma$, $S$, and PF as a function of annealing time are shown in Figure 3g-i. Relatively large changes were found in the first 4 h, and after 4 h the material properties did not change significantly. Therefore, we chose an annealing time of 4 h to investigate the influence of the annealing temperature on a second 90 nm-thick Bi$_2$Te$_3$ film.

2.2.2. Temperature-Dependent Annealing Effect

The dependency of the annealing temperature was investigated on another sputtered 90 nm Bi$_2$Te$_3$ film. The sample was sequentially annealed at 150, 200, 250, and 300 °C for 4 h in each case. The annealing at 150, 200, and 250 °C was done in the measurement setup with in situ characterization of the transport properties (Figure 4). For annealing at 300 °C, a vacuum furnace was used due to the limitations of the measurement setup (max. 250 °C) and the transport properties were characterized after annealing.

Figure 4a shows $\sigma$ in dependency of the temperature. $\sigma$ at RT increased from 372 to 530 S cm$^{-1}$ by sequential annealing the sample at 150 and 200 °C for 4 h. The sample showed a semiconducting temperature behavior with a thermal activation energy of 0.013 eV for 150 °C and 0.006 eV for 200 °C. At 250 °C, the temperature dependency changed from semiconducting behavior to metallic. When the annealing temperature was further increased to 300 °C, $\sigma$ decreased to 361 S cm$^{-1}$ and showed again a thermally activated transport behavior with an activation energy of 0.016 eV. This large decrease of $\sigma$ is most likely related to evaporation of Te, which decreased from 66 at% in the as-deposited state to 57 at% during annealing at 300 °C (Figure 1h).

$n$ obtained from the Hall coefficient depending on the temperature is shown in Figure 4b. The decreased $n$ is related to increased crystallinity, the evaporation of Te, and with that the reduction of Te$_{gb}$ antides defects in the polycrystalline film.$^{[40]}$ The carrier concentration at RT decreased from $10 \times 10^{20}$ to 0.4 $\times 10^{20}$ cm$^{-3}$ after annealing at 300 °C and decreased exponentially with decreasing temperature. $\mu$ in dependency of the temperature is shown in Figure 4c. A large increase in $\mu$ up to 250 °C was observed due to the increase in crystallinity, reduction of point defects, and grain size growth.$^{[43]}$ However, from 250 to 300 °C, the mobility did not increase significantly, which could be related to grain boundary scattering due to the fact that the grain size did not change significantly in this temperature range anymore. In the cooling cycle, $\mu$ increased with a temperature showing a dependency of $T^{-0.4}$, $T^{-0.7}$, $T^{-1.3}$, and $T^{-1.1}$ for the sample annealed at 150, 200, 250, and 300 °C, respectively, indicating a transition from optical phonon scattering toward acoustic phonon scattering.
The temperature-dependent $S$ is shown in Figure 4d. The absolute $S$ at RT gradually increased from 56 to 124 $\mu$V K$^{-1}$ after annealing at 300 °C. From the temperature-dependent $S$, the thermal bandgap was evaluated using the relation $E_g = 2 e |S_{\text{max}}|/T_{\text{max}}$ from Goldsmid and Sharp. We obtained a bandgap of 0.029, 0.045, 0.047, and 0.048 eV for the sample annealed at 150, 200, 250, and 300 °C, respectively.

The temperature dependence of $\kappa$ while annealing the sample at 150, 200, 250, and 300 °C is shown in Figure 5a. $\kappa$ at RT increased from 0.7 to 1.2 W m$^{-1}$ K$^{-1}$ during annealing up to 250 °C, while no further change was observed during annealing above 250 °C.

To analyze the electronic and lattice contributions to the thermal conductivity, $\kappa_{\text{ph}}$ was calculated from $\kappa_{\text{ph}} = \kappa - \kappa_e$, where $\kappa_e$ using the Wiedemann–Franz law, $\kappa_e = L_0 \sigma T$, where $L_0$ is the Lorenz number. $L_0$ shown in the inset of Figure 5b, was obtained from $S$, assuming a single parabolic band model. $L_0$ decreased from $2.1 \times 10^{-8}$ to $1.8 \times 10^{-8}$ W $\Omega$ K$^{-2}$ with increasing annealing temperature. The temperature-dependent $\kappa_{\text{ph}}$, shown in Figure 5b increased with increasing annealing temperature, which corresponds to the increasing crystallinity of the sample and thus reduced phonon scattering, from 0.6 to 0.9 W m$^{-1}$ K$^{-1}$ at RT. The lattice contribution to $\kappa$ increased from 70% to 82% for the sample annealed at 150 and 300 °C, showing dominating phonon transport in the Bi$_2$Te$_3$ film. $\kappa_e$ is shown in Figure 5c. $\kappa_e$ first increased from 0.25 to 0.41 W m$^{-1}$ K$^{-1}$ for the sample annealed from 150 to 250 °C and then decreased to 0.2 W m$^{-1}$ K$^{-1}$ after the film was annealed at 300 °C. First, $\kappa_e$ increased with increasing $\mu$ up to an annealing temperature of 250 °C. No further increase in $\mu$ was observed at an annealing temperature of 300 °C, but $\kappa_e$ decreased drastically, resulting in a decreased $\kappa_e$. The electronic contribution to $\kappa$ accordingly decreased from 30% at 250 °C to 20% at 300 °C, although the value of $\kappa_e$ did not change significantly between annealing at 250 and 300 °C.

The ZT value increased with increasing annealing temperature up to 250 °C and decreased again during annealing at 300 °C (Figure 5d). The 90 nm-thick Bi$_2$Te$_3$ film showed its highest ZT value of 0.2, after annealing the sample at 250 °C. For the sample annealed at 150, 200, 250, and 300 °C, a maximum ZT value of 0.1, 0.17, 0.2, and 0.17, respectively, was observed.

In the following sections, we chose an annealing temperature of 250 °C and an annealing time of 4 h to investigate the influence of the sample thickness.

### 2.2.3. Thickness-Dependent Annealing Effect

To investigate the thickness dependency, we annealed four Bi$_2$Te$_3$ films with thicknesses of 90, 170, 350, and 470 nm sequentially at 150, 200, and 250 °C, each for 4 h (Figure S2–S4, Supporting Information), and analyzed their transport properties after the last annealing step (Figure 6). $\sigma$ of the as-deposited films did not show...
a clear thickness dependency; we obtained 379, 404, 356, and 381 S cm$^{-1}$ for a thickness of 90, 170, 350, and 470 nm, respectively. The temperature-dependent $\sigma$ of the films after annealing is shown in Figure 6a. $\sigma$ increased for the 90 nm film to 717 S cm$^{-1}$ and for the 170 nm film to 649 S cm$^{-1}$ at RT, showing a semiconducting temperature dependency. With further increasing thickness, we obtained lower $\sigma$ RT values of 579 S cm$^{-1}$ for 350 nm and 475 S cm$^{-1}$ for 470 nm and the samples showed a metallic temperature dependency. This is in contrast to the expected thickness dependency that would result from surface and grain boundary scattering, which is typically the predominant transport mechanism in thin films. However, we did not find clear dependency on the grain size and film thickness as expected from classical size theory. One possible explanation for our results is the change of the crystalline orientation that we observed in XRD, as Bi$_2$Te$_3$ is known to have highly anisotropic transport properties.$^{[48,49]}$ The thinnest sample did show a stronger $c$-axis orientation, while at 170 nm, a clear preferred (015) orientation was observed, which was even more pronounced in the samples with 350 and 470 nm.

$n$ in dependency of temperature is shown in Figure 6b. We did not observe a significant thickness dependency. RT values of $0.9 \times 10^{20}$, $1.1 \times 10^{20}$, $1.0 \times 10^{20}$, and $1.1 \times 10^{20}$ cm$^{-3}$ were observed for thickness of 90, 170, 350, and 470 nm, respectively, while during heating, $n$ increased exponentially for all samples. A stronger thickness dependency was found for $\mu$, which decreased with increasing film thickness. At RT, the samples with a thickness of 90, 170, 350, and 470 nm showed $\mu$ of 47, 38, 30, and 28 cm$^2$V$^{-1}$s$^{-1}$, respectively, which again is most likely related to the change of the crystal orientation. From the results, it can be seen that for the samples with 90 and 170 nm, the temperature dependency of $\sigma$ is dominated by $\mu$, while for the samples with 350 and 470 nm, the temperature-dependent $\sigma$ follows $n$.

The normalized electrical conductivity ($\sigma/\sigma_0$), the normalized charge carrier concentration ($n/n_0$), and the normalized mobility ($\mu/\mu_0$) depending on the annealing time at 250°C are shown in Figure 6d–f. $\sigma/\sigma_0$ of the 90 nm film reached a maximum of 4% after 1 h of annealing. With increasing film thickness, the annealing time to reach the maximum increased (Figure 6d). For the samples with 350 and 470 nm thickness, the maximum was not reached in the annealing time of 4 h. A similar behavior was observed for $n/n_0$ and $\mu/\mu_0$, which showed a decrease of 10% for $n$ and an increase of roughly 16% for $\mu$.

The temperature-dependent $S$ is shown in Figure 6g. For the samples with 90 nm, 170 nm, 350 nm, and 470 nm, we obtained $S$ of $-98.9$, $-99.6$, $-102.4$, and $-99.2$ $\mu$V K$^{-1}$ at RT, respectively. The highest $S$ was observed for the 350 nm-thick Bi$_2$Te$_3$ film. $x$ in dependency of the temperature is shown in Figure 6h. The samples with the 350 nm Bi$_2$Te$_3$ film showed the lowest $\kappa$ of $0.7$ W m$^{-1}$K$^{-1}$ at RT, while for the thinnest sample with...
90 nm, the $\kappa$ of 1.3 W m$^{-1}$ K$^{-1}$ was obtained, which is related to increasing $\mu$ with decreasing film thickness. The ZT value for the different film thicknesses depending on the temperature is shown in Figure 6i. The highest ZT value of 0.26 was observed at 190 °C for the 350 nm-thick Bi$_2$Te$_3$ film, closely followed by the 470 nm with 0.24 at 200 °C. The films with a thickness of 170 and 90 nm showed slightly lower ZT values of 0.23 and 0.20.

In Figure 6j–l, the normalized Seebeck coefficient ($S/S_0$), the normalized thermal conductivity ($\kappa/\kappa_0$), and the normalized ZT ($ZT/ZT_0$) depending on the annealing temperature are shown. $S/S_0$ showed a gradual increase with increasing annealing time, except for the sample with 170 nm, which did not show any significant change. In a similar way, $\kappa/\kappa_0$ increased gradually with the annealing time. With increasing film thickness, the annealing time until the maximum was reached increased, as seen before for $\sigma/\sigma_0$ (Figure 6d). Here, again the maximum was not reached in the annealing time of 4 h for the samples with 350 and 470 nm. ZT/ZT$_0$ in Figure 6l) showed a gradual increase with annealing time, which leads to an improvement in ZT of 8% for the 90, 350, and 470 nm films. The samples with 350 and 470 nm have not yet reached their maximum and can possibly be increased further.

3. Conclusion

We investigated the transport properties, including the in-plane ZT characterization, charge carrier concentration, and mobility of RF-sputtered Bi$_2$Te$_3$ films, depending on the annealing time, annealing temperature, and film thickness. The dependency of annealing time was studied on a 90 nm-thick Bi$_2$Te$_3$ film, which was annealed at 200 °C for 9 h and the transport properties were characterized in situ. We observed an increase in the electrical conductivity, absolute Seebeck coefficient, and thermal conductivity, which led to an increased maximum ZT. The increase could be attributed to the crystal formation from the almost-amorphous state of the as-deposited sample, the further increased crystallinity with annealing time, and the reduction of Te$_{\text{Bi}}$ point defects in addition to grain growth. Moreover, we found that the electrical conductivity, the Seebeck coefficient, and the PF increased only in
the first 4 h of annealing at 200 °C but did not show significant changes by further annealing. The influence of the annealing temperature was investigated on a second 90 nm-thick Bi₂Te₃ film. The sample was sequentially annealed at 150, 200, 250, and 300 °C for 4 h. The highest ZT of 0.2 was observed at an annealing temperature of 250 °C. When the sample was further annealed at 300 °C, a decrease in ZT was observed, which could be attributed to the evaporation of tellurium and a strong reduction of Te₂Bi₃ point defects, which decreased the charge carrier concentration and the electrical conductivity, while the lattice thermal conductivity increased due to increased crystallinity. To investigate the thickness dependency, we annealed Bi₂Te₃ films with thicknesses of 90, 170, 350, and 470 nm at 250 °C for 4 h. A maximum ZT value of 0.26 was observed for the 350 nm-thick Bi₂Te₃ film. In contrast to the expected increase of the electrical conductivity with increasing film thickness, due to classical size effects, we observed a decrease, which could be attributed to the change in the crystal orientation with increasing film thickness. Furthermore, it could be shown that with increasing film thickness the annealing time has to be increased to achieve maximum ZT.

4. Experimental Section

Bi₂Te₃ thin films with thicknesses 90, 170, 350, and 470 nm were deposited on the prestructured measurement chip[10] (ZT chip) using a shadow mask and additionally on a Si substrate with 300 nm SiO₂ by RF magnetron sputtering (TORR International Services LLC) from a Bi₂Te₃ target (99.9999%) (EVOCHEM Advanced Materials). Before the deposition, the sputtering chamber was evacuated for 60 min, resulting in a vacuum below 10⁻⁵ mbar. The vacuum level during deposition was held at 1 x 10⁻² mbar with an Ar flow rate of 15 sccm. The target was sputter cleaned for 15 min at 20 W before deposition. The RF sputtering power for Bi₂Te₃ was kept constant at 20 W without substrate heating, and the deposition rate was 2.4 Å s⁻¹. After deposition, the film thickness was measured with a surface profilometer (DekTak 150).

The in-plane electrical conductivity, thermal conductivity, Seebeck, and the Hall coefficient were measured with a Linseis Thin Film Analyzer in the temperature range from 20 to 250 °C[10]. The electrical conductivity was measured using the van der Pauw (VdP) method with accuracy of ±6%.[11] In addition, for Hall characterization, an external magnetic field of ±1 T was applied. The thermal conductivity was measured with the 3-omega method with an accuracy of ±10%.[12] The accuracy of the Seebeck coefficient measurement was ±7%.[13]

Due to the limitation of the measurement setup to max. 250 °C, the annealing at 300 °C for 4 h was performed in a quartz tube furnace (GSL-1100 K-LD) under high vacuum (8 x 10⁻⁵ mbar). Before annealing, the tube was flushed with Ar.

For structural characterization, GIXRD was performed on a Bruker D8 advance diffractometer with Co Kα radiation with the Bi₂Te₃ thin film on SiO₂ substrate without Fe filter, no rotation, and in the angle 2θ range 15°-60°. The grain size of the samples with 90, 170, 350, and 470 nm was evaluated for the as-deposited sample and after annealing at 250 °C from the (015) peak using Scherrer’s equation

\[ D = \frac{0.94 \lambda}{\beta \cos \theta}, \]

where \( \beta \) is the FWHM and \( \theta \) is the X-ray wavelength (Co Kα, \( \lambda = 1.788974 \)). According to reference card Bi₂Te₃ (ICDD:01-083-5978) from the database, the lattice parameters \( a \) and \( c \) were evaluated from the (006) and (015) peaks assuming a hexagonal system:

\[ \frac{1}{\beta} = \frac{1}{a} + \frac{1}{c}. \]

The SEM and energy-dispersive X-ray (EDX) analysis were carried out on a Sigma 300 from Zeiss.

4. Experimental Section

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The in-plane electrical conductivity, thermal conductivity, Seebeck, and the Hall coefficient were measured with a Linseis Thin Film Analyzer in the temperature range from 20 to 250 °C[10]. The electrical conductivity was measured using the van der Pauw (VdP) method with accuracy of ±6%.[11] In addition, for Hall characterization, an external magnetic field of ±1 T was applied. The thermal conductivity was measured with the 3-omega method with an accuracy of ±10%.[12] The accuracy of the Seebeck coefficient measurement was ±7%.[13]

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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