**Epitaxial growth and improved electronic properties of
(Bi_{1-x}Sb_x)₂Te₃ thin films grown on sapphire (0001) substrates:
the influence of Sb content and the annealing**

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Abstract

In this research, we report on the epitaxial growth of basal plane-oriented $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films ($0 \leq x \leq 1$) on sapphire (0001) substrates through Molecular Beam Epitaxy (MBE) and demonstrate the influence of composition, crystal orientation and post-annealing process on their electronic properties. The as-grown $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films change gradually from a strong n -type to a strong p -type conduction when the Sb content increases from 0 to 1, which is attributed to the charge carrier compensation between the n -type Te_{Bi} and p -type Sb_{Te} antisite defects. The crossover between the n - and p -type conduction is found for x between 0.6 ~ 0.7. We also find that post-annealing (at 580 K) is beneficial for the electronic properties of the p -type $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films: they attain improved carrier mobility and significantly increased hole density. However, annealing plays a negative role in the electronic properties of the n -type structures leading to an enhanced resistivity as well as a reduced Seebeck coefficient. The most plausible explanation for such annealing effects is an introduction of p -type defects in both the n -type and p -type $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films. The as-grown Bi_2Te_3 film possesses the largest thermoelectric power factor among all n -type films, reaching 4.1 and 2.5 $\text{mWm}^{-1}\text{K}^{-2}$ at 122 and 300 K respectively, due to the high carrier mobility and proper carrier doping. In contrast, a remarkably improved power factor in p -type $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films is achieved upon annealing at 580 K for 1 h. The highest power factor in p -type $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ and Sb_2Te_3 films is obtained at around 150 K and it increases from 0.2 $\text{mWm}^{-1}\text{K}^{-2}$ ($\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$) and 1.8 $\text{mWm}^{-1}\text{K}^{-2}$ (Sb_2Te_3) for the as-grown films to 3.5 $\text{mWm}^{-1}\text{K}^{-2}$, respectively 3.7 $\text{mWm}^{-1}\text{K}^{-2}$ for the annealed films. The highly crystalline nature of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films grown by MBE assures excellent carrier mobility and is a contributing factor to their outstanding power factors.

Keywords:

$(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ thin films, Molecular Beam Epitaxy, Point defects, Film orientation, Electronic properties, Post-annealing

1. Introduction

Bi₂Te₃-based materials are the best choice for thermoelectric power generation and cooling applications at around room temperature, due to their high dimensionless thermoelectric figure of merit $ZT \geq 1.0$ at 300 K [1-3]. The figure of merit is defined as $ZT = (\alpha^2/\rho)T/\kappa$, where α is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity of the materials, and T is the absolute temperature. The Bi₂Te₃ family of materials crystallizes in the rhombohedral crystal structure (space group $R\bar{3}m$), which is featured by the stacking of hexagonal cells perpendicular to the basal plane, implying a strong anisotropy in the electronic and thermal properties [1]. Studies of Bi₂Te₃-based thin films generated much excitement in the last two decades on account of the predicted large enhancement in ZT in lower dimensional structures due to quantum confinement and phonon scattering effects [4] and the high ZT of 2.4 was reported for Bi₂Te₃/Sb₂Te₃ superlattices [5]. Searching for high performance Bi₂Te₃-based thin films using a reliable synthesis process was also inspired by their potential applications in cooling of chips, optoelectronic and bio-devices in which the performance was highly temperature dependent [6-7]. An additional impetus for the study of Bi₂Te₃ thin films in the past five years came from the realization that such structures represent one of the best forms of a three-dimensional topological insulator [8-11]. Various methods proved effective in the preparation of Bi₂Te₃-based thin films with improved properties, including thermal co-evaporation [12], laser ablation deposition [13], flash evaporation [14], molecular beam epitaxy (MBE) [15,16], electro-chemical deposition [17] and metal organic chemical vapor deposition (MOCVD) [5] among others. Significant efforts focused on the growth of highly ordered structures with optimized carrier transport properties.

The electronic properties of Bi₂Te₃-based materials are strongly anisotropic. The carrier mobility is much larger along the basal plane than perpendicular to it (i.e., along the c -axis) by a factor of 2.8 ~ 6.3 [1,18-19]. Moreover, the Seebeck coefficient

of *n*-type materials in the basal plane is also larger than that along the *c*-axis [20,21]. Thin films of Bi₂Te₃-based materials grow exclusively with their basal plane parallel to the substrate, i.e., the layers stack along the *c*-axis. This is due to the van der Waals bonding and the minimization of the energy. This, however, does not mean that the films are truly single crystalline as one often encounters 60 degree relative orientation of the quintuple-layer stacks associated with a very weak van der Waals bonding and very small energy differences between the two orientations. The films typically show excellent electronic properties that can be further tuned by doping [12,14-16]. An example of impressive thermoelectric properties achieved with such films is the power factor ($PF = \alpha^2/\rho$) of $\sim 3.8 \text{ mWm}^{-1}\text{K}^{-2}$ measured on *p*-type (Bi_{0.15}Sb_{0.85})₂Te₃ films [22]. Recent research also indicates that the carrier density and mobility can be manipulated by heat treatment in the range of 500 - 600 K [12,14-17,22-24]. It is believed that such annealing modifies the density of intrinsic point defects as well as improves the overall atomic layer orientation. Although impressive, the power factor of Bi₂Te₃-based thin films is till now still somewhat lower than those reported for bulk single crystals ($\sim 5.0 \text{ mWm}^{-1}\text{K}^{-2}$) [1,25]. The reasons include a less than perfect lattice ordering and the carrier doping that has not been optimized in thin films. **In this study, we focus on the adjustment of carrier doping by annealing the MBE-grown single crystal-like (Bi_{1-x}Sb_x)₂Te₃ films in order to achieve improved electronic properties.**

The MBE technique is an out-of-equilibrium deposition process with the most significant advantage being its precise control of the flux rate of the constituent elements **and preferred orientation of Bi₂Te₃ based films**, regardless of the choice of substrates [7,12,14-16]. In order to tune the carrier density in both *n*-type and *p*-type films, a series of (Bi_{1-x}Sb_x)₂Te₃ ($0 \leq x \leq 1$) films was grown by MBE on sapphire (0001) substrates using the optimized synthesis parameters [26]. We investigated the influence of the content of Sb and of the annealing treatment on the carrier transport which *de facto* meant that we were able to effectively alter and tune the carrier concentration in both *n*-type and *p*-type films. The highest power factors of ~ 4.1 and $3.7 \text{ mWm}^{-1}\text{K}^{-2}$ were achieved in these near-single crystalline *n*-type and *p*-type (Bi_{1-x}Sb_x)₂Te₃ films, respectively.

2. Experimental Procedure

Basal plane-oriented $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films with the thickness of ~ 200 nm were epitaxially grown on sapphire (0001) substrates in an MBE chamber using high purity 6N Bi, Sb_2Te_3 and Te sources. The Sb content in $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films was determined from the flux rate ratio between Bi and the Sb_2Te_3 , relying on calibrations from the actual growth rates of binary Bi_2Te_3 and Sb_2Te_3 at the same growth temperature. The growth rate of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films was adjusted and maintained at $\sim 1 \text{ nm min}^{-1}$. The substrate temperature was held at 500 K under a slight excess of Te flux in order to achieve high quality $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films. The optimized temperature of post-annealing was selected at 580 K. Annealing at lower temperatures was not as effective in its influence on transport properties while attempts to anneal at yet higher temperature resulted in a serious re-evaporation of films from the substrate [26].

Clear sinusoidal oscillations in the intensity of Reflection High-Energy Electron Diffraction (RHEED) patterns were *in-situ* monitored via a RHEED (KSA 400) apparatus, see also Ref. [26]. Such patterns and oscillations manifest the basal plane orientation and the layer-by-layer growth mode of these $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films. The crystal quality of these films was *ex-situ* examined by x-ray diffraction (XRD) measurements, using a Scintag X1 powder diffractometer and a Rigaku Ultima IV x-ray diffractometer with Cu K_α ($\lambda = 1.5406 \text{ \AA}$) radiation. The actual thickness of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films was determined using a Veeco Dimension Icon Atomic Force Microscope (AFM). The Hall coefficient and resistivity of the films were measured from 10 K to 300 K in a Quantum-Design Magnetic Property Measurement System (MPMS) using a modified probe. The Seebeck coefficient and electrical resistivity were measured using a longitudinal steady-state technique in a home-made cryostat [27,28]. The current was along the basal plane for all measurements, while the magnetic field for Hall effect measurements was perpendicular to the basal plane. The uncertainty of the Hall coefficient, electrical resistivity and Seebeck coefficient measurements was estimated to be $\pm 5\%$, $\pm 3\%$, and $\pm 2\%$, respectively.

3. Results and discussion

Figure 1 displays XRD patterns of the as-grown (a) and the annealed (b) $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ thin films. Except for the peaks belonging to the sapphire substrate (marked by arrows) and the K_β diffraction of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ (shown in diamond-shaped symbols), the strong peaks were indexed to the (00 l) diffractions, confirming that $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films were grown epitaxially along the c -axis of the sapphire (0001) substrate in the MBE process. Besides the (00 l) patterns, weak peaks with lattice indices of (015) and (110) were also observed in these as-grown films, which was not evident in the films with thickness of 30 nm or smaller in our previous study [26]. This indicates the change of the growth mode from a layer-by-layer growth at the beginning of the deposition to the growth of multi-domains in thicker films. After annealing at 540 K or 580 K for 1 h, the crystal **quality** of the films was improved as compared to the as-grown films, as documented by the elimination of the (015) and (110) weak reflections, see Fig. 1(b).

RHEED reflections of the as-grown $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films are shown in Figs. 2(a-c) and the annealed films in Figs. 2(d-e). The streaks pointed out by the white arrows represent the characteristic RHEED patterns of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ along the azimuthal direction of $[1\bar{1}00]$, **while the streaks and spots pointed out by red arrows belong to the reflections from domains rotated by 30° , i.e. the azimuthal $[11\bar{2}0]$ orientation. Although the films have excellent c -axis stacking, the in-plane misorientation of domains by a multiple of 30° is typical of the growth of these tetradymite-type structures due to the weak van der Waals bonding. As Figs. 2(d-f) indicate, the structural quality improves dramatically upon annealing with the $[11\bar{2}0]$ reflections substantially suppressed.** Also noted in Fig. 2, the intensity of the Kikuchi lines increased after the annealing treatment, attesting to the improved crystallinity of the films.

The carrier transport in Bi_2Te_3 -based materials was mainly dominated by intrinsic antisite point defects with a general formula of A_B (element A occupying the lattice

site of element B). The type of defects and their concentration depend on the composition deviation from stoichiometry as well as on the temperature [1]. In Bi_2Te_3 and Sb_2Te_3 , the carrier transport is substantially controlled by antisite defects of the type Bi_{Te} , Te_{Bi} and Sb_{Te} , which determine the n -type (by Te_{Bi}) and p -type (by Bi_{Te} and Sb_{Te}) conduction [29-34]. Transport parameters of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films are listed in Table 1. The sign of the Hall coefficient was negative in the as-grown Bi_2Te_3 and positive in the as-grown Sb_2Te_3 films, respectively, implying the dominance of the n -type antisite defects Te_{Bi} respectively p -type antisite defects Sb_{Te} in the above two binary compounds. Mixing Bi_2Te_3 and Sb_2Te_3 to obtain ternary $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films should lead to the corresponding modification of the carrier density (n or $p = \pm 1/eR_H$, with e the elementary charge, and R_H the Hall coefficient) and the dominant carrier type with the content of x , and the concomitant tuning of the Fermi level position as the n -type defects (Te_{Bi}) compete with p -type defects (Sb_{Te}). As schematically shown in the inset of Fig. 3(a), the Fermi level moves down from the conduction band into the bandgap and then eventually into the valence band with increasing x . The magnitude and the sign of R_H is consistent with such a shift of the Fermi level. Clearly, pure Bi_2Te_3 and Sb_2Te_3 show very weak temperature dependence over the whole measured temperature range, indicating their near-degenerate conduction. The alloys, due to their much lower carrier density, display a significant temperature dependence of R_H and a much larger magnitude. In this process, A nearly full compensation was achieved at $x = 0.6 \sim 0.7$, different from the literature value $x \approx 0.96$ as reported by Zhang et al. [35], where a different Te flux rate was used.

When both electrons (e) and holes (p) contribute to the transport, the Hall coefficient R_H becomes [36],

$$R_H = -\frac{1}{e} \frac{n\mu_e^2 - p\mu_p^2}{(n\mu_e + p\mu_p)^2}$$

where n , p , μ_e , and μ_p stand for the electron density, hole density, electron mobility, and hole mobility, respectively. The carrier mobility μ is calculated from $\mu = R_H/\rho$. It should be clear that the calculation of μ using a single carrier model is not adequate when both electrons and holes contribute to the transport. In our study, the Fermi level

of films with $x = 0.6$ and 0.7 was located within the band gap or near the band edges, as indicated in Fig. 3(a). These films likely had a notable contribution from both electrons and holes, which made the quantitative calculation and comparison of mobilities unreliable. However, the trend in the mobility with the increasing Sb content should be still indicative of the alloy scattering effect **due to the increased lattice disorder by forming $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ alloys**, especially at low temperatures where the minority carriers freeze out. **In this study, the carrier mobility first decreased and then increased with the Sb content. The smallest mobility was reached at $x \approx 0.6$, signaling the strongest scattering of carrier carriers happens at around this composition.**

As shown in Fig. 4(a), the electrical resistivity of the films was strongly composition dependent, possessing a similar trend as the absolute value of R_H . Films with $x \leq 0.2$ and $x = 1$ had a small R_H and metallic resistivity in a wide range of temperatures. In contrast, films with $x = 0.6$ and 0.7 , with electrical transport roughly in the bipolar regime **where n -type and p -type defects nearly fully compensated each other**, showed decreasing resistivity with **increasing** temperature in essentially the whole temperature range studied. Commonly, the magnitude of the Seebeck coefficient follows a similar trend as the resistivity, i.e., as the resistivity decreases so does the magnitude of the Seebeck coefficient and *vice versa* [1,16]. This was also the case with $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$, shown in Fig. 4(b), except for films with $x = 0.6$ and 0.7 . It has been well-known that the minority carriers play a highly detrimental role regarding the magnitude of the Seebeck coefficient, especially when their density is comparable to the density of the majority carriers. Owing to the much higher resistivity of films with $x = 0.6$ and 0.7 , the Seebeck coefficient should have reached much higher values than for the other compositions. The rather low magnitude of the Seebeck coefficient of these two films indicates that both electrons and holes play a role in their charge transport [37]. **The fact that the $x = 0.6$ sample retains its negative Seebeck coefficient while the $x = 0.7$ sample shows a positive Seebeck coefficient is due to the crossover in the conduction behavior between the n -type and p -type dominated transport which takes place for Sb compositions between $x = 0.6$ and $x =$**

0.7. Because of the rather small bandgap of Bi_2Te_3 and its low x alloys (0.015 eV for $x = 0$ [1]), it was expected that the Seebeck coefficient will display a turnaround in its temperature dependence already at temperatures below 300 K as the minority carriers become excited across the band gap in sufficient quantities. This is, indeed, the case with most of the films in this study except for pure Sb_2Te_3 ($x = 1$) with a higher band gap of ~ 0.025 eV and, consequently, the bipolar conduction setting in only above 300 K. The behavior of the Seebeck coefficient and the electrical resistivity is reflected in the trend of the power factor (α^2/ρ) shown in Fig. 4(c). Films with $x = 0$, and $x = 1$ (pure Bi_2Te_3 and Sb_2Te_3 films) have obviously a lower resistivity than the other compositions and still a reasonable magnitude of the Seebeck coefficient and thus possess high power factors. The as-grown Bi_2Te_3 attained the highest power factor of 4.1 (2.5) $\text{mWm}^{-1}\text{K}^{-2}$ at 122 K (300 K) among all $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films, relying on its excellent carrier mobility and carrier doping similar to that in bulk single crystals [1,18].

In our research, the effect of annealing on the transport properties of our films is shown in Figs. 5 and 6, where the Hall coefficient R_H and the carrier mobility μ of several annealed $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films are compared to the data of as-grown (not annealed) films. Transport data for temperatures of 10 K and 300 K are summarized in Table 1. The thermal treatment at high temperatures had a significant effect on the electronic transport of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films. For the n -type Bi_2Te_3 ($x = 0$), annealing at 580 K for 1 h nearly tripled the magnitude of R_H (at 10 K) as compared to that of the as-grown film. In contrast, compared to the as-grown films, the Hall coefficient of annealed p -type $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ ($x = 0.7$) and Sb_2Te_3 ($x = 1$) films decreased dramatically after annealing at 580 K for 1 h by nearly an order of magnitude for the film with $x = 0.7$ and by a factor of two for the pure Sb_2Te_3 film. Similar changes in the carrier density upon thermal treatment of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films were also observed by other researchers [12,14-17,22-26]. We have already stated that antisites are the dominant structural defects in the tetradymite-type structure of Bi_2Te_3 , Sb_2Te_3 and their alloys. Changes in the Hall coefficient of both the n -type and p -type $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films upon annealing reveal the increased density of p -type antisite defects (likely of the type Bi_{Te}

and Sb_{Te}) as temperature increases. This is reminiscent of the distinctly *p*-type conduction in single crystals of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ grown with the nominally stoichiometric composition at much higher temperatures (> 850 K) [1]. Annealing at 540 K and 580 K leads to a deficiency of Te due to its highly volatile nature which then favors the formation of the Bi_{Te} and Sb_{Te} antisite defects as they possess the lowest formation energy among all defects [32,33]. In contrast, acceptor-generating vacancies on the Bi and Sb sites are not likely to form upon annealing because re-evaporation of Sb and Bi is not significant at annealing temperatures used in our experiments. The results in Fig. 5(b) indicate that, unlike the case of *n*-type Bi_2Te_3 , annealing seemed to be beneficial for the enhancement of the mobility in *p*-type $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ and Sb_2Te_3 . For *n*-type Bi_2Te_3 , the mobility μ decreased by a factor of nearly 2.5 at 10 K following annealing at 580 K for 1 h.

The effect of heat treatment on R_H and μ directly reflects on other transport properties of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films, as shown in Fig. 6. The temperature dependent resistivity of the annealed $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films is shown in Fig. 6(a). After annealing, the notably increased resistivity of *n*-type Bi_2Te_3 coincided with the enhanced magnitude of R_H as well as the reduced μ . At the same time, the reduced resistivity in *p*-type $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ ($x = 0.7$) and Sb_2Te_3 ($x = 1$) was ascribed to the reduced Hall coefficient and the improved mobility of holes. The most prominent change was observed in *p*-type $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ where the resistivity was lowered by an order of magnitude after annealing at 580 K for 1 h and the nature of conduction changed from that of a semiconductor to a distinctly metallic dependence in the entire range of temperatures up to 300 K. Figure 6(b) shows the temperature dependent Seebeck coefficient of annealed $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films. In *n*-type Bi_2Te_3 , the increased magnitude of R_H following annealing resulted in a decreasing magnitude of the Seebeck coefficient and a much earlier turnaround signaling the onset of bipolar conduction. As we already mentioned, annealing at 580 K favored the formation of *p*-type antisite defects which partly compensated electrons, reducing the overall carrier density and allowing intrinsic excitations to be notable already near 200 K as opposed to 250 K in the as-grown Bi_2Te_3 films. For *p*-type $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films, annealing strongly reduced

the resistivity while it maintained or even enhanced the Seebeck coefficient. Consequently, a greatly enhanced power factor was realized in p -type $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films following annealing, as documented in the Fig. 6(c). The power factors in p -type $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ and Sb_2Te_3 were increased from 0.2 respectively 1.8 to 3.5 respectively $3.7 \text{ mWm}^{-1}\text{K}^{-2}$. Unfortunately, annealing had a negative impact on the power factor of the n -type Bi_2Te_3 due to the increased resistivity and decreased Seebeck coefficient.

As shown in Table 1, $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films possessed exceptionally high carrier mobility on the order of $10^3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 10 K, which was comparable to values measured on bulk single crystals, verifying the very high crystalline quality of films grown by the MBE technique. We also noted that the carrier mobility of binary Bi_2Te_3 and Sb_2Te_3 films reached excellent values of 75.8 and $758 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively, at room temperature, the results comparable to the best reported values of $135 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for n -type Bi_2Te_3 films [38] and $433 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for p -type Sb_2Te_3 films [16] with similar Hall coefficients. While p -type $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films clearly benefited from annealing, a different strategy must be identified to improve the performance of n -type films.

4. Conclusion

In this research we demonstrated the tuning of electronic transport properties of the basal plane-orientated $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ ($0 \leq x \leq 1$) films grown by MBE, through the adjustment of Sb content and the post annealing treatment. As indicated by the RHEED and XRD measurements, the crystallinity of the $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films improved with the increased Sb content. Moreover, thermal treatment right after the growth further improved the crystallinity of the films, as indicated by the disappearance of weak spots in the RHEED pattern and the diffraction aside from the dominant (00 l) reflections. Electrical transport measurements implied that the electronic properties of the as-grown $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films were controlled by charge carrier compensation due to the competition of n -type Te_{Bi} and p -type Sb_{Te} antisite defects as one altered the Bi/Sb ratio. The carrier transport evolved gradually from n -type to p -type with the increasing content of Sb and the transition took place at a

composition with $x = 0.6 \sim 0.7$. Annealing of as-grown films at 580 K was shown to effectively increase the density of p -type antisite defects which led to the notably decreased Hall coefficient of p -type films and a concomitant significant enhancement of their power factor. In contrast, annealing had a negative effect on the electronic properties of n -type Bi_2Te_3 films. Benefiting from their preferred oriented crystal lattice, these MBE grown $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films showed excellent electrical properties comparable to the best reported results obtained on thin films. The largest power factor for n -type $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films was found in the as-grown Bi_2Te_3 with a value of $4.1 \text{ mWm}^{-1}\text{K}^{-2}$ at 122 K. While we did not succeed in improving this value upon annealing, the heat treatment carried out at 580 K for an hour had a spectacular effect on p -type forms of films. The highest power factors for p -type $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ and Sb_2Te_3 were achieved at around 150 K. The power factors increased from 0.2 ($\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$) and 1.8 (Sb_2Te_3) for as-grown films to 3.5 and 3.7 $\text{mWm}^{-1}\text{K}^{-2}$ for the annealed films, respectively. Thus, annealing treatments seemed to be highly beneficial for p -type films while they were inefficient and, in fact, counterproductive, in the case of n -type films. This was due to the formation of p -type antisite defects during annealing that tended to compensate electrons in n -type structures while they somewhat enhanced the carrier density in p -type films while a high Seebeck coefficient was maintained.

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Table 1: Transport parameters of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ thin films measured at 10 K and 300 K: Hall coefficient R_H , carrier mobility μ , electrical resistivity ρ , Seebeck coefficient α , power factor PF .

	R_H ($\text{cm}^3 \text{C}^{-1}$)		μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)		ρ @ 300 K	α @ 300 K	PF @ 300 K
	10 K	300 K	10 K	300 K	($10^{-5} \Omega \text{m}$)	($\mu\text{V K}^{-1}$)	($\text{mWm}^{-1} \text{K}^{-2}$)
As-grown films							
$x = 0$	-0.54	-0.12	4367	75.8	1.80	-212.3	2.51
$x = 0.2$	-1.56	-0.13	1364	40.8	4.44	-161.6	0.59
$x = 0.6$	-1.86	-0.18	183.9	32.1	6.81	-111.8	0.18
$x = 0.7$	3.64	0.52	237.1	64.2	8.24	81.9	0.08
$x = 1$	0.33	0.49	1400	551	1.15	141.4	1.74
Annealed films							
$x = 0$; 580 K 1 h	-1.40	-0.08	1221	28.3	3.02	-97.9	0.32
$x = 0.7$; 580 K 1 h	0.51	0.27	1283	90.0	3.16	237.6	1.79
$x = 1$; 540 K 1 h	0.35	0.55	2118	758	0.869	138.0	2.19
$x = 1$; 580 K 1 h	0.16	0.26	1854	459	0.565	123.2	2.69

Figure captions

Figure 1: XRD patterns of (a) as-grown and (b) annealed $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films. The parameter of post annealing was abbreviated in the form of “ANN 580 K 1 h”, indicating the films were annealed (ANN) at 580 K for 1 h. The same abbreviation was applied throughout the paper.

Figure 2: RHEED patterns of $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films. Images (a), (b) and (c) display the patterns obtained from as-grown Bi_2Te_3 , $\text{Bi}_{0.6}\text{Sb}_{1.4}\text{Te}_3$ and Sb_2Te_3 films, respectively and images (d), (e) and (f) show RHEED patterns for annealed films of the same composition (annealed at 580 K for 1 h).

Figure 3: Temperature dependent (a) Hall coefficient and (b) carrier mobility of as-grown $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films. The inset is a schematic diagram depicting changes of the Fermi level with the content of Sb.

Figure 4: Temperature dependent (a) electrical resistivity, (b) Seebeck coefficient, and (c) the power factor of as-grown $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films.

Figure 5: Temperature dependent (a) Hall coefficient and (b) carrier mobility of annealed $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films.

Figure 6: Temperature dependent (a) electrical resistivity, (b) Seebeck coefficient, and (c) the power factor of annealed $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ films.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6