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Research Article

Annealing Effect on the Thermoelectric Properties of Bi_2Te_3 Thin Films Prepared by Thermal Evaporation Method

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Bismuth telluride-based compounds are known to be the best thermoelectric materials within room temperature region, which exhibit potential applications in cooler or power generation. In this paper, thermal evaporation processes were adopted to fabricate the n-type Bi_2Te_3 thin films on SiO_2/Si substrates. The influence of thermal annealing on the microstructures and thermoelectric properties of Bi_2Te_3 thin films was investigated in temperature range 100–250°C. The crystalline structures and morphologies were characterized by X-ray diffraction and field emission scanning electron microscope analyses. The Seebeck coefficients, electrical conductivity, and power factor were measured at room temperature. The experimental results showed that both the Seebeck coefficient and power factor were enhanced as the annealing temperature increased. When the annealing temperature increased to 250°C for 30 min, the Seebeck coefficient and power factor of n-type Bi_2Te_3-based thin films were found to be about −132.02 μV/K and 6.05 μW/cm·K^2, respectively.

1. Introduction

Because the energy sources, such as petroleum, coal, and coal gas, will exhaust in the near future. Therefore, the problem of energy shortage and greenhouse effect become more and more serious, thus energy saving and reduction of the carbon emission become very important topics. Hence, the green technology is getting more and more attention. Thermoelectric (TE) effect is the simplest technology to convert the temperature difference to electrical energy. It generates electrical energy from the useless heat by thermoelectric effect. Thermoelectric materials can directly convert heat into electricity and vice versa. They have a lot of important applications, such as power generator [1] and cooler [2]. The performance of thermoelectric materials is decided by Seebeck coefficient, electrical conductivity, and thermal conductivity. The energy conversion efficiency of the thermoelectric materials is evaluated by the figure of merit ZT, $ZT = (S^2\sigma/\kappa)T$ (S, Seebeck coefficient; σ, electrical conductivity; T, absolute temperature; and κ, thermal conductivity) [3]. According to the formula, in order to obtain the excellent thermoelectric figure of merit, the materials must exhibit large Seebeck coefficient, high electrical conductivity, and low thermal conductivity. Among, the $S^2\sigma$ is defined as the power factor (PF). Currently, the bismuth telluride (Bi-Te) and antimony telluride- (Sb-Te-) based compounds are found to be the best thermoelectric materials within the room temperature region. Furthermore, Bi-Te- and Sb-Te-based thermoelectric materials show the highest figure of merit ZT and are widely utilized for the commercialized thermoelectric generators and coolers [4].

Generally, the thermoelectric devices are fabricated from blocks of the materials. On the other hand, the low-dimensional materials can improve the thermoelectric properties, such as increasing the density of states of Fermi level and enhancing the phonon scattering [5]. In addition, the bulk sample is difficult to miniaturize the thermoelectric devices. Therefore, for miniaturizing the device and improving thermoelectric properties, some techniques have been reported to grow thin films, such as flash evaporation [6], pulsed laser deposition (PLD) [7, 8], sputtering [9], electrochemical deposition [10], metal organic chemical vapor deposition (MOCVD) [11, 12], and molecular beam epitaxy (MBE) [13–15]. However, some processes need long time to prepare the materials and expensive facilities. Hence, the thermal evaporation method is adopted in this

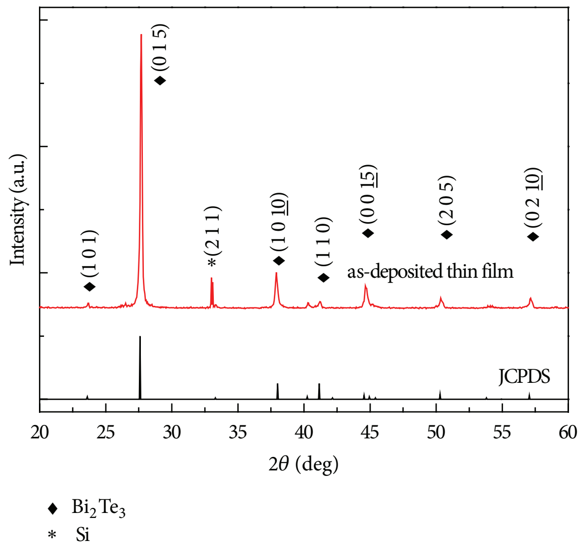


FIGURE 1: XRD patterns of the Bi_2Te_3 thin film deposited at the substrate temperature of 150°C.

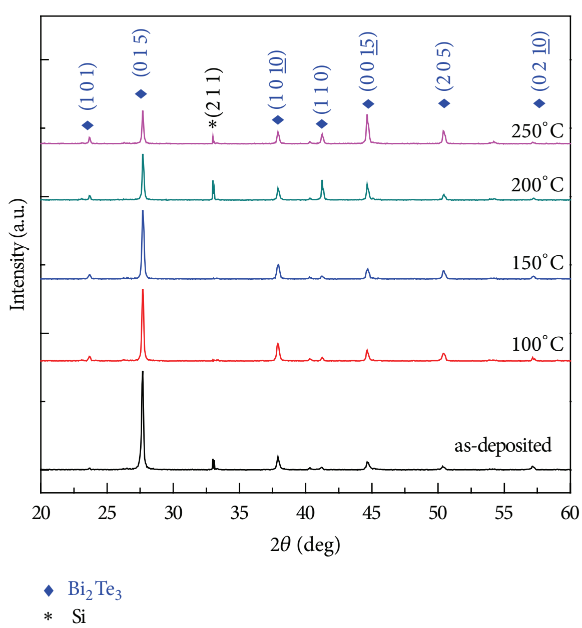


FIGURE 2: XRD patterns of Bi_2Te_3 thin films deposited at the substrate temperature of 150°C and annealed at various temperatures for 30 min in N_2 atmosphere.

study to fabricate BiTe-based thin films, because it is an attractive technology and can offer some advantages, such as lower fabricating expenses and short processing time. In our previous research [16], bismuth telluride thin films were deposited by thermal evaporation, and the effects of evaporation parameters and substrate temperature on the microstructures and thermoelectric properties of thin films were investigated. In order to improve the thermoelectric

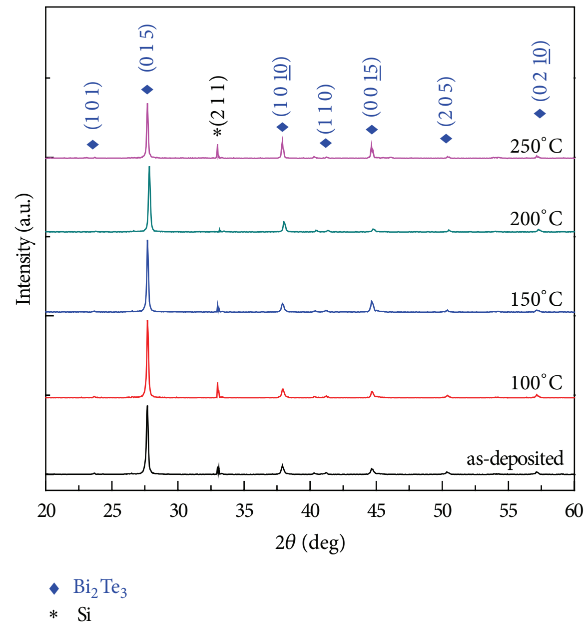


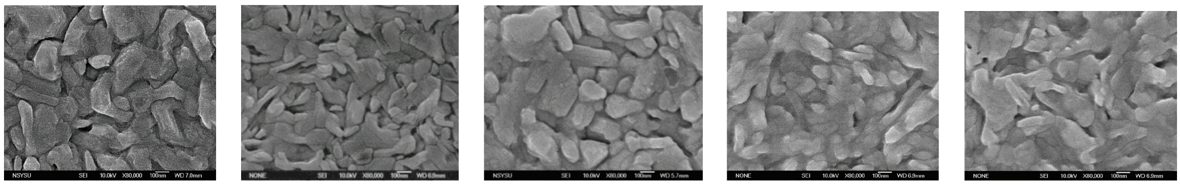
FIGURE 3: XRD patterns of Bi_2Te_3 thin films deposited at the substrate temperature of 150°C and annealed at various temperatures for 60 min in N_2 atmosphere.

properties obtained previously, the effect of thermal annealing on the microstructures and thermoelectric properties is evaluated in this paper. Because thermal annealing can affect the defect [17] and carrier concentration [18] of materials, it will influence the thermoelectric properties of the Bi_2Te_3 thin films.

2. Experimental

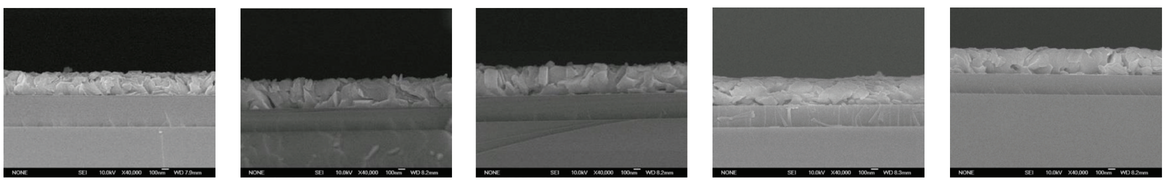
The p-type (100) silicon wafers were used as substrates. After the standard RCA cleaning process, a 400 nm silicon oxide layer was thermally grown on the silicon substrate in an atmospheric pressure chemical vapor deposition (APCVD) furnace. Then, the thermoelectric films were deposited on SiO_2/Si substrates by the thermal evaporation method. The high-purity (99.99%) Bi_2Te_3-based powder was used as evaporant source. The deposition rate of Bi_2Te_3 film was estimated to be 13 Å/s. The details of the experimental method were described in the previous report [16]. The Bi_2Te_3 thin films were evaporated on a preheated (150°C) Si substrate in a vacuum chamber with working pressure below 3.75×10^{-5} torr. The thickness of deposited thin films was approximately 0.4 μm. Then, the thermoelectric thin films were annealed at temperature range from 100°C to 250°C for 30 and 60 min under N_2 atmosphere. The heat treatment temperature was kept lower than 300°C to avoid the evaporation of the composition of films. The influence of thermal annealing on the microstructures and thermoelectric properties of Bi_2Te_3 thin films was investigated.

The crystalline structures of the thermoelectric thin films were determined by X-ray diffraction (XRD) analysis (Cu-Kα, Bruker D8) with diffraction angles between 20° and



(a) (b) (c) (d) (e)

Figure 4: FE-SEM top-viewed photographs: (a) as-deposited Bi_2Te_3 thin film at the substrate temperature of 150°C; (b), (c), (d), and (e) thin films annealed at 100°C, 150°C, 200°C, and 250°C for 30 min, respectively.



(a) (b) (c) (d) (e)

Figure 5: FE-SEM cross sectional photographs: (a) as-deposited Bi_2Te_3 thin film at the substrate temperature of 150°C; (b), (c), (d), and (e) thin films annealed at 100°C, 150°C, 200°C, and 250°C for 30 min, respectively.

Table 1: Thermoelectric properties of Bi_2Te_3 thin films deposited at different substrate temperatures.

Substrate temperatures (°C)	Conductivity ($S{\cdot}cm^{-1}$)	Seebeck coefficient ($\mu V/K$)	Power factor ($\mu W/cm{\cdot}K^2$)
R.T.	1139.12	−22.26	0.56
50	569.12	−27.27	0.42
100	719.73	−57.79	2.4
150	619.33	−88.83	4.89
200	1269.19	12.32	0.19

60° at the scanning speed of 0.05° per second. The surface morphologies of thermoelectric thin films were investigated by scanning electron microscopy (FE-SEM, JEOL JSM6700), with an accelerating voltage of 10 kV. Annealing effects on the thermoelectric properties of thin films were investigated, while the Seebeck coefficients (S) and electrical conductivity (σ) were measured at room temperature. The Seebeck coefficient is measured by applying a temperature gradient across the sample, and then the resulted Seebeck voltage was measured by a Keithley 2700 system. The electrical conductivity of the specimens was measured by a four-point probe method at room temperature. From S and σ, the power factor ($S^2\sigma$) can be calculated.

3. Results and Discussion

In our previous study [16], the thermoelectric properties of Bi_2Te_3 thin films deposited at different substrate temperatures are presented in Table 1. The power factor can be calculated according to the Seebeck coefficient and electrical conductivity. The maximum Seebeck coefficient and power factor of n-type Bi_2Te_3 thin films at substrate temperature of 150°C were found to be about −88.83 μV/K and 4.89 $\mu W/cm{\cdot}K^2$, respectively.

Figure 1 shows the X-ray diffraction patterns of the Bi_2Te_3 JCPDS card and as-deposited thin film at the substrate temperature of 150°C. The XRD diffraction peaks were adopted from JCPD data of binary Bi_2Te_3. For the as-deposited thin film at the substrate temperature of 150°C, it shows that diffraction angles of 27.64°, 37.8°, and 41.13° corresponding to (0 1 5), (1 0 $\underline{10}$), and (1 1 0) diffraction planes appeared.

The samples obtained above are the proceeded to postannealing treatment to improve the thermoelectric properties. Figure 2 shows the XRD patterns of the Bi_2Te_3 thin films annealed at different temperatures for 30 min. The XRD patterns show that the thin films are polycrystalline structure. The (0 1 5), (1 0 $\underline{10}$), (1 1 0), (0 0 $\underline{15}$), and (1 1 0) and diffraction peaks were observed. The peak intensity of (0 1 5) orientation was slightly decreased with the increased annealing temperature. The variation of the intensity of the peak (1 0 $\underline{10}$) is not obvious. As the thin films are annealed at 200°C, the intensity of the diffraction peak (1 1 0) became stronger. With the increase of annealing temperature, the peak intensity of (0 0 $\underline{15}$) became stronger. Figure 3 shows the XRD patterns of the Bi_2Te_3 thin films annealed at different temperatures for 60 min. The peak intensities of (0 1 5) and (1 0 $\underline{10}$) slightly increased with annealing temperature, whereas the intensity of the peak (1 1 0) was not obvious.

Figure 4 shows the surface photographs of the films under various annealing temperatures for 30 min. At the substrate temperature of 150°C, the grain of as-deposited thin film shows irregular shape. After annealing treatment, the grain shapes did not change obviously in surface morphology; however, with the increasing of annealing temperature, the grains grew up. Figure 5 shows the SEM cross sectional microstructures of films under various annealing

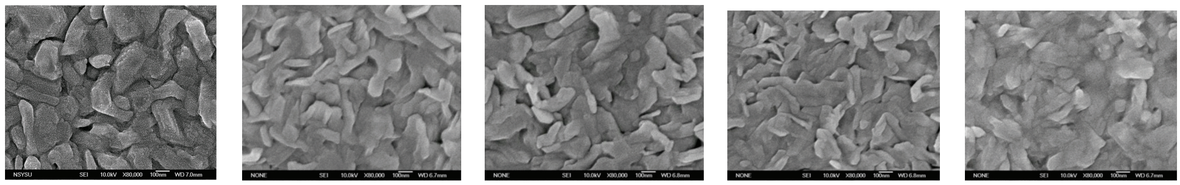


Figure 6: FE-SEM top-viewed photographs: (a) as-deposited Bi_2Te_3 thin film at the substrate temperature of 150°C; (b), (c), (d), and (e) thin films annealed at 100°C, 150°C, 200°C, and 250°C for 60 min, respectively.

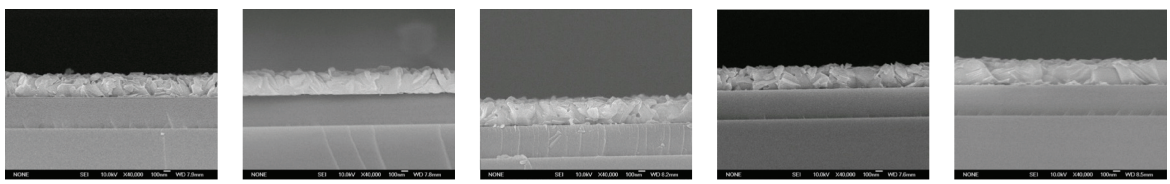


Figure 7: FE-SEM cross sectional photographs: (a) as-deposited Bi_2Te_3 thin film at the substrate temperature of 150°C; (b), (c), (d), and (e) thin films annealed at 100°C, 150°C, 200°C, and 250°C for 60 min, respectively.

temperatures for 30 min. The thickness of thin films was around 400 nm. Figure 6 shows the surface photographs of the films under various annealing temperatures for 60 min. The crystalline shapes of thin films showed no obvious difference in surface morphology of the Bi_2Te_3 thin films before and after annealing. Similarly, with the increase of annealing temperature, the grains will grow up. Figure 7 shows the SEM cross sectional microstructures of films under various annealing temperatures for 60 min. The thickness of thin films was around 350–400 nm.

The influence of on the annealing temperature and time and the Seebeck coefficient are illustrated in Figure 8. The results show that all samples are n-type, having a negative Seebeck coefficient. As the annealing temperature increased, the Seebeck coefficient increased in the temperature range 100–250°C. (for 30 min: −88.83 μV/K to −132.02 μV/K; for 60 min: −88.83 μV/K to −122.18 μV/K). This is due to the reduction of the defects on the annealing temperature increases, which results in a carrier concentration reduction and increased Seebeck coefficient. According to the results, the sample annealed at 250°C for 30 min shows a maximum Seebeck coefficient of −132.02 μV/K.

Figure 9 shows the influence of thermal annealing on the electrical conductivity of thin films. It is clear that the electrical conductivity decreases in the temperature range 100–200°C. For the case of 30 min, when the annealing temperature is below 200°C, the electrical conductivity tended to be reduced by the increased annealing temperature. This is due that the electrical conductivity was related to the carrier concentration and mobility. As the annealing temperature increased up to 250°C, the electrical conductivity slightly increased to be around 347.3 S·cm^{-1}. For the case of 60 min, the trend was similar to that of the case of 30 min. The sample annealed at 200°C for 60 min shows an electrical

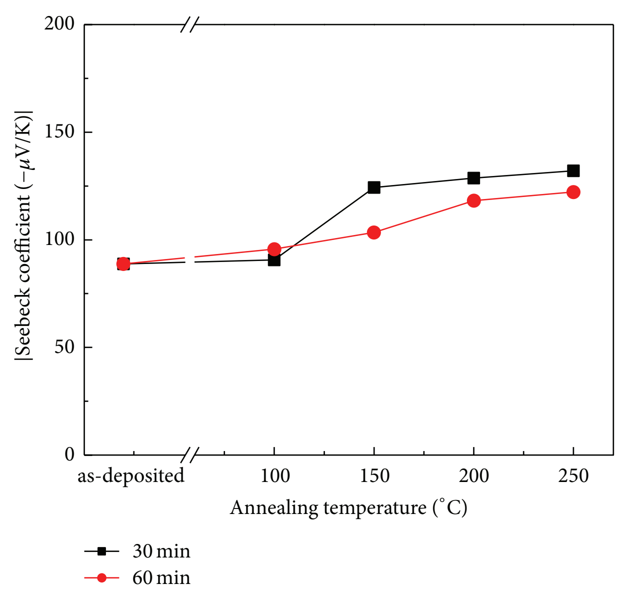


Figure 8: Variations of Seebeck coefficient of Bi_2Te_3 thin films on the annealing temperature and time.

conductivity of 165.8 μV/K. When the annealing temperature was increased, the electrical conductivity was slightly increased.

The power factor is an important thermoelectric parameter, which determines the property of thermoelectric converter. It can be calculated according to the Seebeck coefficient and electrical conductivity. Figure 10 shows the power factors for the Bi_2Te_3 films annealed at different temperatures

Table 2: Thermoelectric properties of the Bi_2Te_3 thin films annealed at different temperature and time.

Annealing time (min)	Annealing temperatures (°C)	Conductivity ($S \cdot cm^{-1}$)	Seebeck coefficient ($\mu V/K$)	Power factor ($\mu W/cm \cdot K^2$)
without annealing	without annealing	619.33	−88.83	4.89
30	100	362.53	−90.62	2.98
30	150	327.71	−124.26	2.69
30	200	302.5	−128.62	5.01
30	250	347.27	−132.02	6.05
60	100	601.05	−95.65	5.49
60	150	328.16	−103.42	3.51
60	200	165.81	−118.24	2.32
60	250	321.68	−122.18	4.8

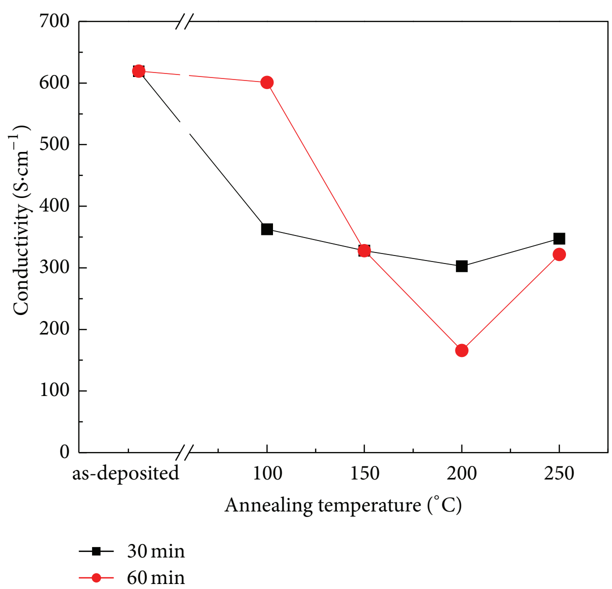


Figure 9: Variations of electrical conductivity of Bi_2Te_3 thin films on the annealing temperature and time.

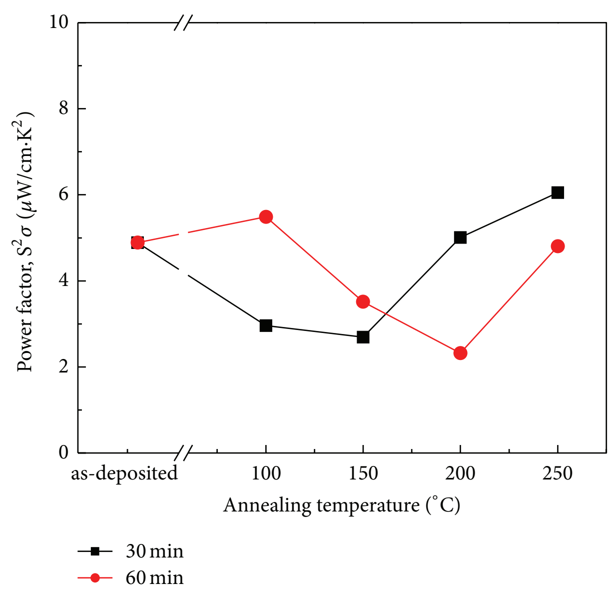


Figure 10: Variations of power factor of Bi_2Te_3 thin films on the annealing temperature and time.

and time. The maximum power factor of 6.05 $\mu W/cm \cdot K^2$ was obtained in this experiment, which is achieved by the 250°C and 30 min annealing, owing to its low electrical conductivity of 347.27 $S \cdot cm^{-1}$ and relatively large Seebeck coefficient of −132.02 $\mu V/K$. The thermoelectric properties of the Bi_2Te_3 thin films annealed at different temperature and time are presented in Table 2. From the results, the optimized Seebeck coefficient and power factor of n-type thin films were found to be about −88.83 $\mu V/K$ and 4.89 $\mu W/cm \cdot K^2$ for the 250°C and 30 min annealed film. The value of power factor increases from 4.89 to 6.05 $\mu W/cm \cdot K^2$; it means that thermal annealing can improve the thermoelectric properties of the Bi_2Te_3 thin films.

4. Conclusion

A thermal evaporation method was adopted for the preparation of low-cost thermoelectric thin films. In this study, the Bi_2Te_3 thermoelectric material was deposited on the SiO_2/Si substrate to form thin films. The effects of annealing time and temperature on the microstructures and thermoelectric properties was investigated. The crystalline structures and surface morphologies of thin films were characterized by X-ray diffraction and SEM. The Seebeck coefficient and electrical conductivity were measured at room temperature. The power factor of 4.89 $\mu W/cm \cdot K^2$ for the as-deposited thin film can be improved to be 6.05 $\mu W/cm \cdot K^2$ as the sample was thermally annealed at 250°C for 30 min.

Acknowledgments

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