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Preparation and thermoelectric properties of p-type $Bi_{0.52}Sb_{1.48}Te_3$ + 3% Te thin films

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Thin films of p-type $Bi_{0.52}Sb_{1.48}Te_3$ + 3% Te were deposited on glass substrates by flash evaporation. X-ray diffraction and field-emission scanning electron microscopy were performed to characterize the thin films, and the effects of preparation and annealing parameters on the thermoelectric properties were investigated. It was shown that the power factors of the films increased with increasing deposition temperature. Annealing the as-deposited films improved the power factors when the annealing time was less than 90 min and the annealing temperature was lower than 250°C. A maximum power factor of 10.66 μW cm^{-1} K^{-2} was obtained when the film was deposited at 200°C and annealed at 250°C for 60 min.

flash evaporation, thin film, thermoelectric properties, bismuth telluride

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Because of their potential applications in microelectronics and other high-technology fields, Bi_2Te_3-based thermoelectric materials have attracted much attention in recent years [1–3]. The performances of thermoelectric materials depend on the thermoelectric figure-of-merit, ZT, which is defined as $ZT = S^2T\sigma/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. The product σS^2 is defined as the thermoelectric power factor. The power factor should be maximized and the thermal conductivity should be reduced in order to achieve high-efficiency thermoelectric materials. It is apparent that improvements in the thermoelectric figure of merit are possible by increasing S and σ, and by decreasing the thermal conductivity. However, thermoelectric figures of merit are still low for large-scale applications. Low-dimensional Bi_2Te_3-based materials, which show special quantum confinement effects and electrical transport properties [4], have proved to be an effective route for improving thermoelectric properties [5]. Many deposition methods have been used to prepare Bi_2Te_3-based thin films; these include co-evaporation [6,7], metal organic chemical vapor deposition [8], pulsed laser deposition [9,10], electrochemical deposition [11,12], electrochemical atomic layer epitaxy [13,14], molecular beam epitaxy [15], co-sputtering [16], closed space vapor transport techniques [17], hot-wall-epitaxy techniques, and electron-beam evaporation [18]. In this work, because of the simple configuration of the deposition system, we use a flash evaporation method [19–22] for the fabrication of Bi_2Te_3-based alloy thin films.

Annealing can strongly influence the electrical transport behavior of semiconductor films. It has been reported that annealing has a positive effect on the thermoelectric properties of Bi_2Te_3-based materials [23,24]. However, the thermoelectric properties of Bi_2Te_3-based materials depend not only on the carrier concentration but also on the grain size and grain orientation, and these will also be altered during the annealing process. Little systematic research has been done on the effects of preparation and annealing conditions on the thermoelectric properties of Bi_2Te_3-based thin films. In this study, we prepare p-type $Bi_{0.52}Sb_{1.48}Te_3$ + 3% Te thin

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films by flash evaporation. To improve the thermoelectric properties of the thin films, preparation conditions and annealing effects on the electrical transport properties were investigated.

1 Experimental

1.1 Film deposition

Pulverized p-type $Bi_{0.52}Sb_{1.48}Te_3$ + 3% Te ingot powders with particle sizes between 0.2 and 0.3 mm were used as the starting materials for flash evaporation. Thin films were deposited on glass substrates under a vacuum of 5 Pa. To study the effects of deposition temperature, four films were fabricated at 140, 160, 180 and 200°C. The deposition rates of the thin films were controlled by adjusting the rotation speed of the stepper motor of the feeding component. Four rotation speeds, 0.0625, 0.125, 0.1875, and 0.25 r/s, were used.

1.2 Film annealing

After deposition, the films were annealed in an argon flow atmosphere at different temperatures. To study the effects of annealing temperature, films deposited at 160°C with a rotation speed of 0.125 r/s were annealed at between 225 and 300°C for 60 min; the effects of annealing duration were studied using films deposited under the same conditions at a constant annealing temperature of 250°C, with annealing times ranging from 30 to 120 min.

1.3 Film characterization

Details of Seebeck coefficient and electrical resistivity measurements can be found elsewhere [25]. X-ray diffraction (XRD) patterns were obtained using a Philips X'Pert PRO diffractometer (CuKα radiation, λ = 1.5406 Å), and field-emission scanning electron microscopy (FE-SEM; Sirion 200) was used for microstructural observations. To study the effects of deposition temperature on the thermoelectric properties, the thin films were deposited at different temperature with a rotation speed of 0.125 r/s and annealed at 250°C for 1 h.

2 Results and discussion

2.1 Structural analysis

Figure 1 shows the XRD patterns of the as-deposited and the as-annealed p-type $Bi_{0.52}Sb_{1.48}Te_3$ + 3% Te thin films. After annealing, the diffraction peaks become sharper and more intense. Figure 2(a) shows the SEM morphology of the as-deposited thin film. It can be seen that the film contains some lamellar grains. After annealing at 250°C for 1 h, as shown in Figure 2(b), the film is recrystallized into isometric grains.

2.2 Effects of deposition rate on thermoelectric properties

The deposition rate of the thin films was controlled by ad-

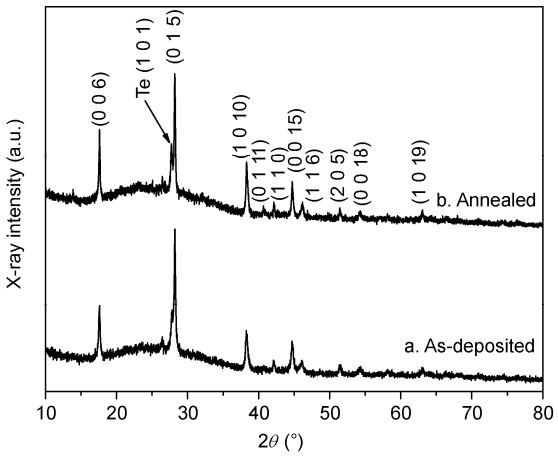

Figure 1 XRD patterns of $Bi_{0.52}Sb_{1.48}Te_3$+3% Te thin films. (a) As-deposited; (b) annealed thin film.

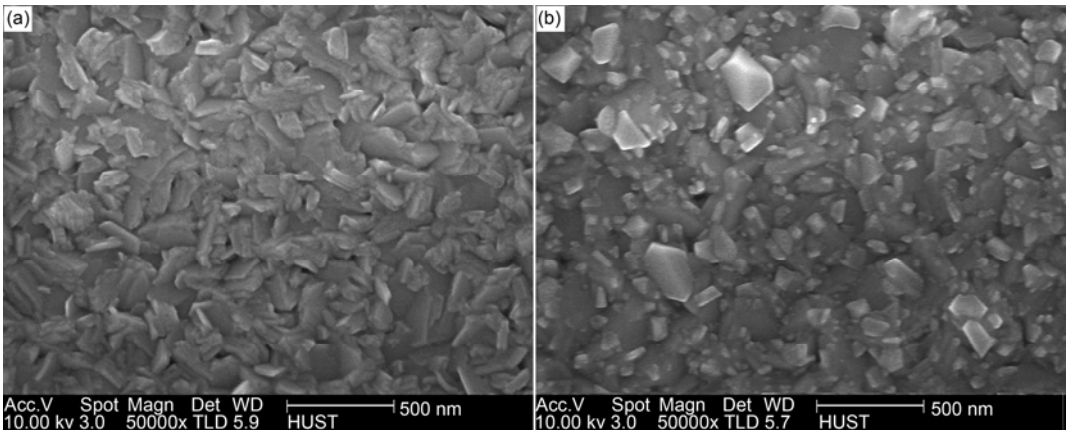

Figure 2 FE-SEM micrographs of the as-deposited film (a) and the film annealed (b) at 250°C for 1 h.

justing the rotation speed of the stepper motor of the feeding component. Figure 3(a) shows the variations in Seebeckcoefficients and electrical conductivities with rotation speed. When the rotation speed is lower than 0.1875 r/s, both the Seebeck coefficient and electrical resistivity are unaffected by the rotation speed. However, when the rotation speed is 0.25 r/s, the electrical resistivity increases rapidly. High rotation speeds mean larger amounts of powder are evaporated at the same time, and this may lead to small grain sizes and more crystal imperfections, resulting in high electrical resistivities and lower power factors (Figure 4(b)) of the thin films. To obtain the best deposition efficiency, the deposition rotation rate was fixed at 0.125 r/s.

2.3 Effects of deposition temperature on thermoelectric properties of thin films

Figure 4(a) shows the variations in Seebeck coefficients and electrical resistivities with deposition temperature. It can be seen that the Seebeck coefficient increases with increasing deposition temperature. Correspondingly, the electrical resistivities of the thin films decrease with increasing deposition temperature. The power factors of the films obviously increase with deposition temperature, as shown in Figure 4(b). A maximum thermoelectric power factor of 10.66 μW cm^{-1} K^{-2} was obtained when the film was deposited at 200°C.

2.4 Effects of annealing time on thermoelectric properties of films

In order to investigate the effects of annealing time, the films deposited at 160°C were annealed at 250°C for different times. As the annealing time increases, grain growth occurs in the films and the amounts of crystal defects decrease, therefore the electrical resistivities of the films decrease, as shown in Figure 5(a); however, the Seebeck coefficients of the films are unaffected by the annealing time. Variations in the power factors of the films with annealing time are shown in Figure 5(b). It can be seen that the power factors of the films level off when the annealing time is over 90 min, therefore longer annealing time will not further improve the thermoelectric performances of the thin films.

2.5 Effects of annealing temperature on thermoelectric performances of the thin films

Figure 6 shows the annealing temperature dependence of the thermoelectric properties of the thin films; the annealing time is 60 min. It can be seen that the thin film annealed at

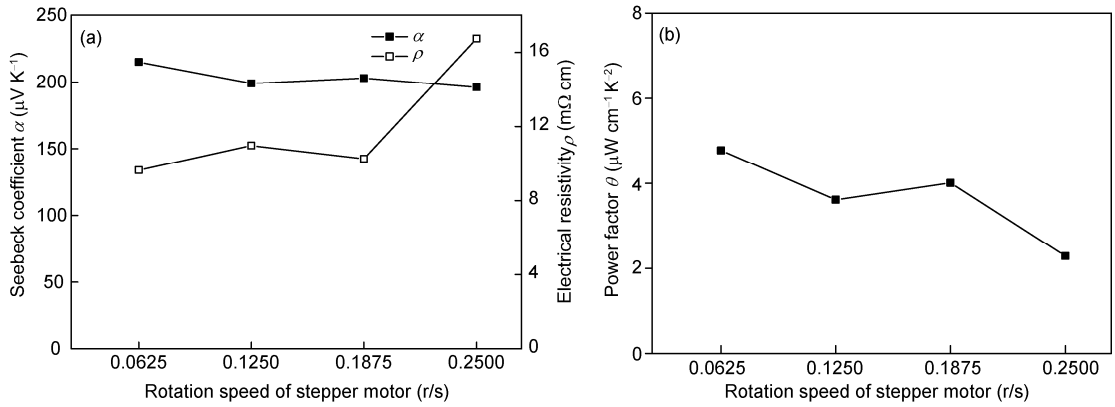

Figure 3 Deposition rate dependence of the thermoelectric properties of the thin films (deposition temperature: 160°C).

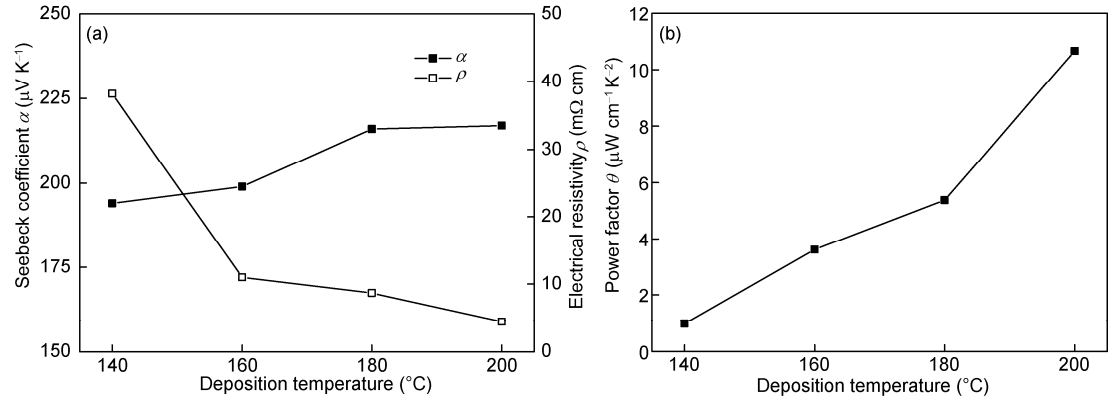

Figure 4 Deposition temperature dependence of the thermoelectric properties of the thin films.

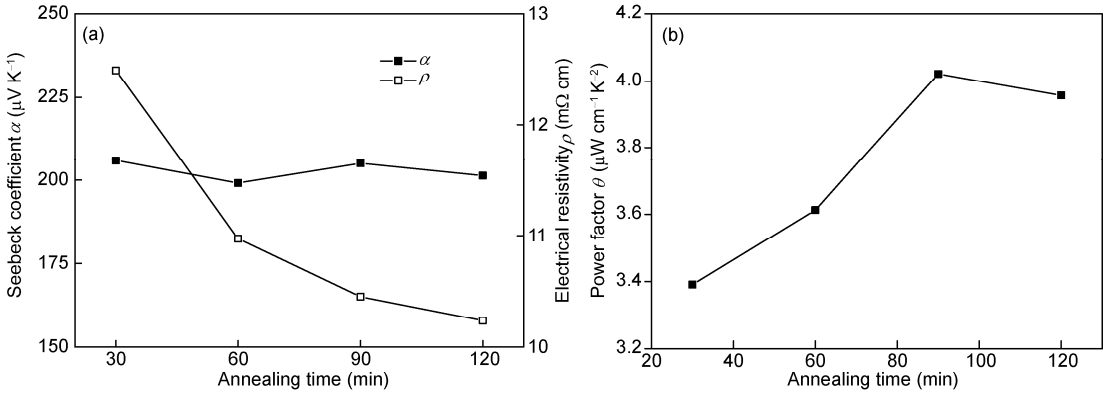

Figure 5 Variations in thermoelectric properties of the thin films with annealing time; the annealing temperature is 250°C.

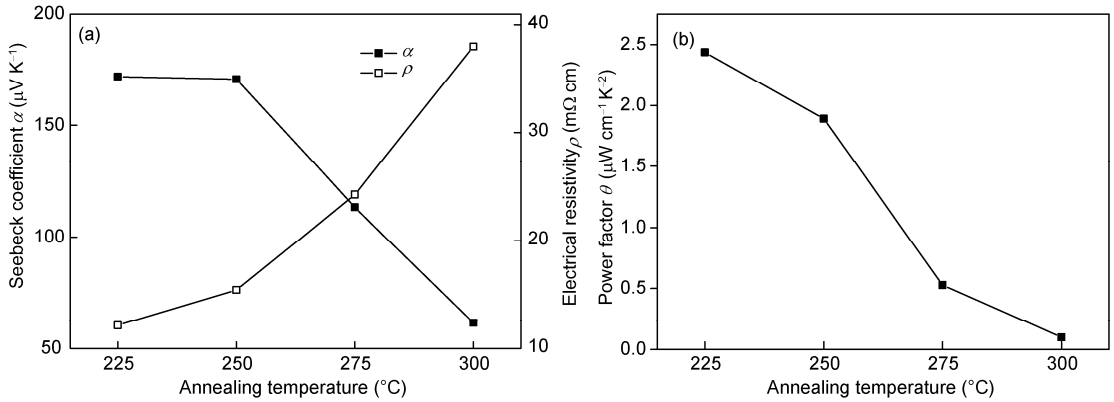

Figure 6 Variations in thermoelectric properties of the films with annealing temperature; annealing time is 60 min.

225°C has the highest Seebeck coefficient and smallest resistivity. When the annealing temperature exceeds 250°C, both the Seebeck coefficient and the electrical conductivity decrease rapidly, therefore the power factor deteriorates rapidly. During the annealing process, the grain sizes of the films increase and the film crystallinity improves. On the other hand, Te is a volatile element, and volatilization increases with increase of annealing temperature. When the annealing temperature is over 250°C, the negative effect of Te volatilization prevails over the positive effect of crystallinity improvement on the thermoelectric properties. A very low power factor of 0.1 μW cm^{-1} K^{-2} was therefore obtained when the film was annealed at 300°C for 1 h, as shown in Figure 6(b).

3 Conclusion

Thin films of p-type $Bi_{0.52}Sb_{1.48}Te_3$ + 3% Te were fabricated on glass substrates by flash evaporation. The effects of deposition and annealing parameters on the thermoelectric performances of the films were studied in detail. Increasing the substrate temperature decreased the electrical resistivities and improved the power factors of the films. Annealing the as-deposited films improved the power factors when the annealing time was less than 90 min and the annealing temperature was lower than 250°C. When the annealing temperature was over 250°C, the thermoelectric performances of the films deteriorated rapidly. A maximum power factor of 10.66 μW cm^{-1} K^{-2} was obtained at a deposition temperature of 200°C, deposition rate of 0.125 r/s, annealing temperature of 250°C, and annealing time of 60 min.

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