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ARTICLE

Elemental Ratio Controlled Semiconductor Type of Bismuth Telluride Alloy Thin Films

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Abstract: Bismuth telluride alloy thin films were prepared on quartz substrates by co-sputtering method and thermally annealed at 423~623 K, for 1 h. It is found that the Te/Bi ratio decreases upon thermal annealing, indicating the loss of Te as a result of evaporation. This leads to the transformation of Bi_2Te_3 thin films from n-type to p-type, and consequently the change of Seebeck coefficient from the negative value to the positive one. In addition, the grain growth occurs during thermal annealing, in particular, at higher temperature, as a result, both the electrical conductivity and the seebeck coefficient are increased.

Key words: bismuth telluride; semiconductor types; thermoelectric properties

Thermoelectric (TM) materials exhibit potential applications in both cooling and electrical power generation devices[1-3]. It has attracted much attention because of excellent features, such as, long working life, environmental protection and high reliability [4,5]. The property of TE material can be defined by a dimensionless thermoelectric figure of merit $ZT=S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity and T is the absolute temperature. The $S^2\sigma$ is commonly considered as the power factor[6]. A perfect thermoelectric material should have both high power factor and low thermal conductivity [7]. The power factor depends on the energy band structure as well as the charge carriers [1, 8]. To improve ZT, it is necessary to optimize synthesis methods and treatment processing.

Bismuth telluride (Bi_2Te_3) with a rhombohedral layered structure, has narrow band gap and exhibits the highest thermoelectric figure of merit at room temperature[9-11]. Various methods were used to prepare Bi_2Te_3 thermoelectric materials, such as molecular beam epitaxy (MBE)[12,13], metal-organic chemical vapor deposition (MOCVD)[14,15], and solvothermal[16,17]. In comparison, magnetron sputtering is one of the most attractive techniques because of its low cost[18]. However, it is difficult to effectively control the stoichiometric ratio because of evaporation of Te element [19]. In such a case, the semiconductor type may be changed and thus the thermoelectric properties will be significantly affected[20].

In the present paper, co-sputtering method was used to fabricate bismuth telluride thin films. Because the deposition process was conducted at room temperature, Bi and Te often exist in elemental states rather than a compound in the thin films. Therefore, post-thermal treatment was required to promote the chemical combination of Bi and Te. We mainly focused on the effect of thermal treatment on the elemental ratio of Bi and Te as well as on the thermoelectric properties.

1 Experiment

Co-magnetron-sputtering deposition was used to prepare Bi_2Te_3 alloy thin films. The base pressure was 1×10^{-4} Pa before deposition, Ar gas flow was 3 ml/min and the operating pressure was 0.3 Pa during the deposition. The sputtering powers of both Bi and Te targets were 15 W. The deposition rate was about 15 nm/min. The films thickness was about 200 nm. The thin films were deposited on quartz which could avoid the influence of substrate on thermoelectric properties. After deposition, the

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samples were thermally annealed at 423, 473, 523 and 623 K, respectively, for 1 h to enhance inter-diffusion and to improve the crystallinity. The annealing process was conducted under 50 Pa Ar gas for protection. X-ray diffraction (XRD) (Bruker D8 Advance) using Cu Kα radiation (λ=0.15403 nm) was used to characterize the phase structure, and field emission scanning electron microscopy (FESEM) (Quanta x50 FEG) with electron dispersive spectrometer (EDS) was used to characterize the microstructure and stoichiometric ratio. Hitachi U-4100 uv-spectrophotometer was used to measure the band gap. Both the electrical and thermal conductances were measured by Physical Property Measurement System (PPMS) (Quantum Design PPMS-9). Four Pt (Φ=100 μm) wires were connected to the film samples with In welding spots. The quartz was used as insulated substrate.

2 Results and Discussion

2.1 Composition and microstructure of the as-received thin film

Fig.1 displays the XRD patterns of the as-deposited and the annealed samples. There is no clear diffraction peak except two quartz peaks in the as-deposited thin film, indicating the amorphous features of Bi_2Te_3 compounds as well as Bi and Te elemental components. After thermal annealing at 423 K for 1 h, XRD peak of Bi_2Te_3 appears with (015) as the preferred orientation, indicating that the thin film becomes crystallized, Bi_2Te_3 (110) and (00 15) orientations are also observed in the XRD patterns. As the annealing temperature is raised, no additional XRD peaks emerge but the intensity of each peak is increased considerably, indicating enhanced crystallization. When the temperature is increased up to 523 K, Bi (104) peak is observed but the intensity is lower than others' and the full width at half maximum (FWHM) is larger, indicating the coexisting of both compound and elemental grains. This will affect the semiconductor type of thin films to some degree.

Fig.2 shows the SEM images of the surface morphologies of the thin films annealed at different temperatures. The surface of the as-deposited film is smooth without large particles.

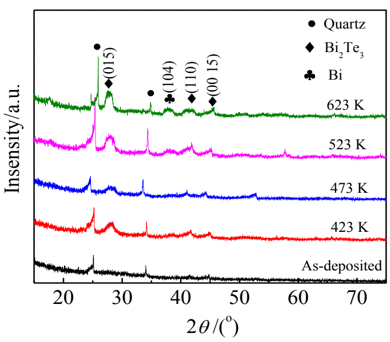

Fig.1 XRD patterns of co-sputtered Bi_2T_3 thin films as deposited and those after annealing at different temperatures

It is indeed composed of nano-grains in amorphous matrix, as revealed in XRD pattern. When the annealing temperature is raised up to 473 K, some particles appear on the surface. The film surface becomes rougher and rougher with many large particles after annealing at 623 K. At the same time, the grain grows larger and larger with elevated temperature[20]. EDS characterization in Table 1 demonstrates that the atom percentage of Te is 73.55% in the as-deposited thin film, higher than that of Te in Bi_2Te_3 compound. However, the atom percentage of Te decreases upon thermal annealing, particularly, at higher annealing temperature, for instance, 43.58% at 473 K and 32.24% at 623 K. The evaporation energy of Te(1) (52.55 kJ/mol) is much lower than that of Bi (104.80 kJ/mol) in rhombohedral-Te(1)-Bi-Te(2)-Bi-Te(1) -layered crystal structure, it is easier for Te to be evaporated [21]. This leads to the reduced elemental ratio of Te in the film, and may affect the electrical properties.

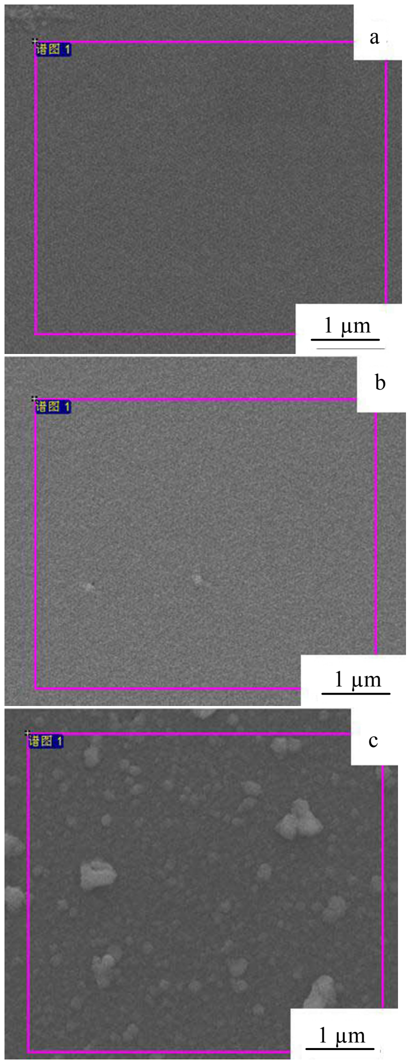

Fig.2 SEM images of surface morphologies of the thin films as-deposited (a) and thermally annealed at 473 K (b) and 623 K (c)