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Preferential growth transformation of $Bi_{0.5}Sb_{1.5}Te_3$ films induced by facile post-annealing process: Enhanced thermoelectric performance with layered structure

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ABSTRACT

Preferential growth transformation from (015) plane to (00*l*) plane of the bismuth antimony tellurium ($Bi_{0.5}Sb_{1.5}Te_3$) film has been achieved through a facile post-annealing process with enhanced thermoelectric performance. The $Bi_{0.5}Sb_{1.5}Te_3$ film with preferential growth of (015) crystal plane was obtained via dc magnetron sputtering, and the Stranski–Krastanov model has been used to explain its growth mechanism. Preferential growth transformation from (015) plane to (00*l*) plane occurred after a post-annealing process. The driving force of this phenomenon is the natural tendency to reduce the total interfacial energy of the system, and the migration and coalescence of atoms along the in-plane direction form the layered structure. Moreover, the carrier concentration of $Bi_{0.5}Sb_{1.5}Te_3$ films is optimized to ~$0^{19}/cm^3$ in the film with preferential growth of (00*l*) plan. Hence, a synchronous increase of electrical conductivity and Seebeck coefficient is obtained due to the greatly enhanced carrier mobility and optimized carrier concentration. Therefore, the $Bi_{0.5}Sb_{1.5}Te_3$ film with the preferential growth of (00*l*) plane possesses power factor of 48.2 μW/cm K^2 which is three times higher than that of the film with the preferential growth of (015) plane. Our study has provided a facile strategy to induce preferential growth transformation in $Bi_{0.5}Sb_{1.5}Te_3$ films and meanwhile largely enhanced the thermoelectric performance.

1. Introduction

Thermoelectricity is based on two fundamental thermoelectric (TE) effects: the Peltier effect for refrigeration and the Seebeck effect for power generation [1–3]. TE cooling is a promising technique in the fields of microelectronics, infrared detectors and optoelectronics [4–6]. Meanwhile, heat from different sources such as solar heat, geothermal heat, and waste heat from automobiles all could be used by the TE material to generate power [7,8]. The thermoelectric figure-of-merit is given by the dimensionless value $ZT = S^2\sigma T/\kappa$, where T, S, σ, and κ are the absolute temperature, Seebeck coefficient, electrical conductivity and thermal conductivity, respectively. Recently, a lot of efforts have been done in order to enhance the ZT value by introducing the nanostructures into the TE material [9–15]. Low-dimensional nanostructures would decrease thermal conductivity by increasing the phonon scattering at boundaries and interfaces and simultaneously promote Seebeck coefficient due to the quantum confinement effect and the modification of electronic band structures [16–18]. For example, bulk Bi–Sb–Te alloy with embedded nanostructures exhibited ZT ~ 1.4 at 373 K [1], a high thermoelectric figure of merit ZT of 2.2 at 800 K was obtained in N-type semiconductors $AgPb_mSbTe_{2+m}$ [19], and a superlattice structured Bi_2Te_3/Sb_2Te_3 film with ZT ~ 2.4 was reported for a reduction of lattice thermal conductivity [9].

On the other hand, the transports of carriers are distinct along different crystal planes, so the preferential growth of a certain crystal plane would have a great effect on the thermoelectric performance [20]. It has been reported that the layered N-type Bi–Te film with the preferential growth of (00*l*) plane possesses higher electrical conductivity and Seebeck coefficient compared with the film with the preferential growth of (015) plane [21–23]. Bismuth antimony tellurium ($Bi_{0.5}Sb_{1.5}Te_3$) is the best commercially available P-type TE material at room temperature [24]. Many efforts have been done to improve the performance of Bi–Sb–Te films. For example, Takashiri et al. [15] have fabricated $Bi_{0.4}Sb_{1.6}Te_3$ thin films with a power factor 35.6 $\mu W\ cm^{-1}\ K^{-2}$ by a flash evaporation method. Nevertheless, it is still challenging to prepare a $Bi_{0.5}Sb_{1.5}Te_3$ film with specific preferential crystal growth on the substrate and the report of layered $Bi_{0.5}Sb_{1.5}Te_3$ films is particularly rare. Thus, it is expected that the preferential growth of (00*l*) plane in $Bi_{0.5}Sb_{1.5}Te_3$ films would help to improve the TE performance. Furthermore, $Bi_{0.5}Sb_{1.5}Te_3$ films still show a relatively low power factor, since the carrier concentrations in many films are $10^{20}/cm^3$–$10^{21}/cm^3$, which exceed the optimal value of carrier concentration and limit the increase of Seebeck coefficient. It was already pointed out that carrier concentration ~$10^{19}/cm^3$ is the primary requirement for higher ZT [24].

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Zhao et al. [25] adjusted the carrier concentration of Bi_2Te_3 from $10^{20}/cm^3$ to $10^{19}/cm^3$ by introducing antisite acceptor defects during chemical synthesis to improve the thermoelectric performance. Therefore, for further improvement in the thermoelectric performance of the $Bi_{0.5}Sb_{1.5}Te_3$ film, it is significant to develop a simple technique to control the preferential growth of optimal crystal plane, and simultaneously optimize the carrier concentration.

For the deposition, magnetron sputtering is simpler, cheaper and applicable for large-scale industrial applications compared with molecular beam epitaxy and pulsed laser deposition. However, thermoelectric properties of $Bi_{0.5}Sb_{1.5}Te_3$ thin films fabricated by magnetron sputtering methods are still very low (power factor about 10 μW cm^{-1} K^{-2}) [11], and few reports have explored the technique to control the preferential growth of certain crystal planes in the $Bi_{0.5}Sb_{1.5}Te_3$ film. In the perspective view of improving the performance for the TE material, Duan et al. [26] found that the annealing plays a key role in the micro-structural and transport properties of $Bi_2Te_{2.7}Se_{0.3}$ thin films under a flash evaporation process, so the annealing would be a very efficient method for tuning the crystallinity of the nanostructure [27]. Bottner et al. [28] prepared the superlattice Bi/Te/Bi/(Se,Te) with an individual layer thickness down to 4–5 nm, and XRD results show that the annealing process up to 300–350 °C would result in highly c-oriented due to the well-defined (00*l*) peaks. But as we know, it is very difficult to prepare the superlattice using common techniques. Hence, in this work, we use the simple magnetron sputtering method to make a $Bi_{0.5}Sb_{1.5}Te_3$ thin film with the preferential growth of (015) plane and annealing was used to adjust the preferential crystal growth. The $Bi_{0.5}Sb_{1.5}Te_3$ thin film was obtained at an annealed temperature of 300 °C with proper carrier concentration and preferential growth of (00*l*) plane. The correlation between crystal planes and thermoelectric performance has been explored. Based on these results, formation mechanism of different morphologies has been demonstrated.

2. Experimental section

2.1. Film deposition and annealing

The $Bi_{0.5}Sb_{1.5}Te_3$ films were deposited by a dc magnetron sputtering device (JGP-450a, SKY Technology Development Co., Ltd. Chinese Academy of Sciences). Commercial 60 mm diameter hot-pressed $Bi_{0.5}Sb_{1.5}Te_3$ target (99.99%) (Purchased from General Research Institute for Nonferrous Metals, China) was used in the sputtering process and the polished aluminum nitride (AlN) was used as a substrate with 10 × 10 mm^2 and 5 × 15 mm^2 dimensions, respectively. The substrates were cleaned thoroughly by acetone, alcohol and de-ionized water in sequence for 15 min in an ultrasonic bath. The distance between the $Bi_{0.5}Sb_{1.5}Te_3$ target and the AlN substrates was maintained at 90 mm. The base pressure of the deposition chamber was below 5.0×10^{-4} Pa and the working pressures of sputtering gas Ar were set at 2.0 Pa with a flow rate of 25 sccm. The $Bi_{0.5}Sb_{1.5}Te_3$ target was connected to a direct current power supplier with a power of 20 W. The sputtering rate is about 600 nm per hour. A 10 min pre-sputtering was used to eliminate surface contamination of the target before deposition. The $Bi_{0.5}Sb_{1.5}Te_3$ film with the preferential growth of (015) plane was deposited at 450 °C for 2 h, while the $Bi_{0.5}Sb_{1.5}Te_3$ film with the preferential growth of (00*l*) plane was obtained by post-annealing with the annealed temperature of 300 °C in N_2 atmosphere for 20 min by tube furnace (OTF-1200X-4-RTP, Hefei KJ Material Technology Co., Ltd). As deposited $Bi_{0.5}Sb_{1.5}Te_3$ films were also annealed at 200 °C, 250 °C, 350 °C for 20 min and 300 °C with different annealing time to demonstrate the growth mechanism.

2.2. Film characterization

The crystalline structure of the films was investigated by X-ray diffraction (XRD) (Rigaku D/MAX 2200 PC, Cu Kα radiation with $\lambda = 0.154056$ nm) with operation voltage and current maintained at 40 kV and 40 mA, respectively. The surface morphology and cross-sectional morphology of the films were analyzed by field emission scanning electron microscopy (FE-SEM) (FEI Sirion 200) equipped with energy dispersive X-ray spectroscopy (EDS). For the quantitative analysis of the different elements, at least five different regions of each sample were analyzed. Carrier concentration and mobility were measured at room temperature on films deposited on 10 × 10 mm^2 AlN substrates by the Hall effect measurement system (ECOPIA HMS-3000). The temperature dependent in-plane electrical conductivity and Seebeck coefficient were simultaneously measured on films deposited on 5 × 15 mm^2 AlN substrates by ZEM-3 (Ulvac Riko, Inc.).

3. Results and discussion

3.1. Film crystallinity and morphology

The $Bi_{0.5}Sb_{1.5}Te_3$ film with the preferential growth of (015) plane was prepared on the AlN substrate at 450 °C with a working pressure 2.0 Pa and a sputtering power of 20 W. The phase structure was investigated by XRD, as shown in Fig. 1b. Compared with the standard pattern of $Bi_{0.5}Sb_{1.5}Te_3$ (JCPDS 49-1713), the strong peaks (1010) and (110) are much lower than the (015) peak, and the peaks of (003), (006), (009), (0018) and (0021) disappear in the XRD pattern. This indicates that a significant preferential growth along the (015) plane of the $Bi_{0.5}Sb_{1.5}Te_3$ crystal has been developed. The surface morphology of as deposited $Bi_{0.5}Sb_{1.5}Te_3$ film is shown in Fig. 2a. The uniform nanoscale grains in hexagonal-flake shape are observed. These grains are well crystallized with a size of 400 nm and a thickness of 100 nm. They are closely adhesive to or embedded in the surface on which it grows, but there is a large angle between the hexagonal flakes and substrate plane, so the film appears rough and incompact. Fig. 2b illuminates the detailed cross-sectional morphology of the film with a thickness of about 1300 nm. It has a compact layer on the substrate with hexagonal flakes stacked on. The flakes are not perpendicular to the substrate, which is consistent with the surface morphology.

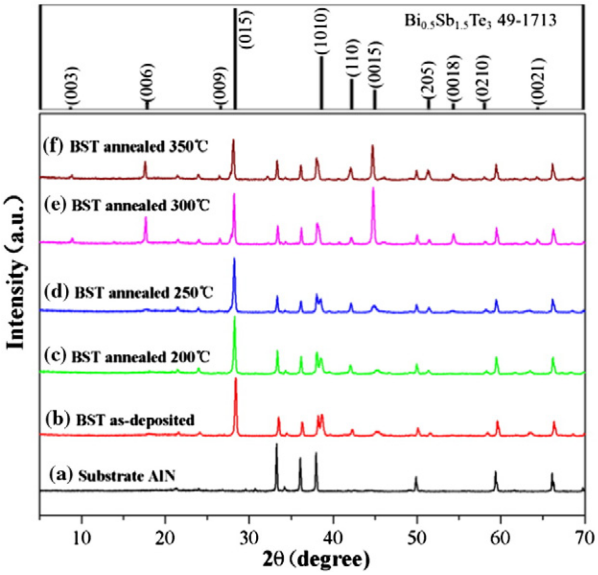

Fig. 1. XRD patterns of as-deposited $Bi_{0.5}Sb_{1.5}Te_3$ films and $Bi_{0.5}Sb_{1.5}Te_3$ films annealed at 200 °C, 250 °C, 300 °C and 350 °C, respectively.