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The influence of the transformation of electronic structure and microstructure on improving the thermoelectric properties of zinc antimonide thin films

Zhuang-hao Zheng [a, b], Ping Fan [a, b, *], Jing-ting Luo [a, b], Peng-juan Liu [a], Xing-min Cai [a], Guang-xing Liang [a, b], Dong-ping Zhang [a], Ye Fan [a]

[a] College of Physics Science and Technology, Institute of Thin Film Physics and Applications, Shenzhen University, 518060, China
[b] Shenzhen Key Laboratory of Sensor Technology, Shenzhen University, 518060, China

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ABSTRACT

Measurements of electronic structure, microstructure and thermoelectric properties of zinc antimonide thin films prepared by direct current magnetron co-sputtering were carried out. The as-deposited zinc antimonide thin film had a very high resistivity similar to insulating ceramics, which was due to a low binding energy of both zinc and antimony, with the electron scattering increases and impedes the current transport. With the increase in annealing temperature, the films became more crystalline and the thermoelectric properties were also improved. The resistivity of the film decreased rapidly with its crystallinity when the annealing temperature was above 350 °C. The Seebeck coefficients of the thin films were positive, indicating that the films were P-type. The Seebeck coefficient of those samples increased with increasing annealing temperature. The thin film annealed at 400 °C has an optimal power factor of 1.87×10^{-3} Wm^{-1} K^{-2} with a Seebeck coefficient of 300 μVK^{-1} and a resistivity of 4.82×10^{-5} Ωm at 573 K.

1. Introduction

Thermoelectric materials with high conversion efficiency for possible applications in energy conversion have attracted much attention in recent years [1]. The performance of thermoelectric materials is determined by the dimensionless figure of merit (ZT) which is defined as $S^2T/\rho\kappa$, where S is the Seebeck coefficient, T is the absolute temperature, ρ is the resistivity and κ is the thermal conductivity [2]. Zinc antimonide (Zn–Sb) binary system is one of the promising P-type thermoelectric materials for low cost thermoelectric application [3–5]. The ZT of Zn–Sb based bulk compound is reported to be 1.3 [6]. However, its thermoelectric properties are still inadequate for practical use compared with other thermoelectric materials [7,8]. Thin film technique is one of the methods for improving the thermoelectric properties of thermoelectric material due to the stronger quantum confinement effect with low dimensional structure materials [9–11]. For instance, a high room-temperature ZT value of 2.4 has been reported for P-type superlattices thin films [12]. Besides, thin film thermoelectric material has a huge potential application in miniaturized sensors and micropower source, etc [13–15].

Several techniques [16,17] have been used to grow Zn–Sb based thin films. Sun et al. [18] fabricated high-performance Zn–Sb based thin films by sputtering. The ZT at 573 K is estimated to be 1.15 by using bulk thermal conductivity from their data [18]. In many cases, the thermal conductivity of thin film is much lower than that of the corresponding bulk materials [19,20], indicating that the ZT of the Zn–Sb based thin films prepared by Sun is much higher than 1.15. Their results show that Zn–Sb thin film is promising for thermoelectric applications. Although several techniques have been used to grow Zn–Sb based thin films, it is still rarely reported in practice. Much work is needed in preparing high-performance zinc antimonide thin film.

Zn–Sb based thin films were deposited by direct current (DC) magnetron co-sputtering in this work. The influence of post-annealing temperature on the electronic structure, microstructure and the thermoelectric properties of the thin films were

* Corresponding author. College of Physics Science and Technology, Institute of Thin Film Physics and Applications, Shenzhen University, 518060, China. Tel./fax: +86 755 26536021.
E-mail address: fanping308@126.com (P. Fan).

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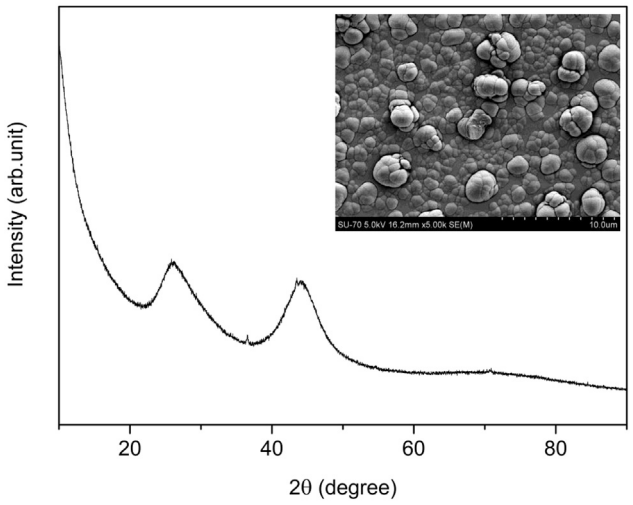

Fig. 1. XRD pattern and surface morphology of as-deposited Zn–Sb based thin film.

investigated. Besides, it is worth noting that the binding energy of Zn in the thin film was much lower than that of Zn in bulk material [21] and it may cause a great change of the electrical property. Therefore, the electronic structure of the thin films was also investigated.

2. Experimental details

Zn–Sb thin films were deposited at room temperature by co-sputtering. High purity (4N) Zn and Sb targets were used in a DC magnetron sputtering facility with a sputtering angle of 45° and a target–substrate distance of 10 cm. BK7 glass substrates were ultrasonically cleaned in acetone and alcohol for 10 min successively. The chamber was pumped down to a pressure less than 6.0×10^{-4} Pa prior to deposition. The working pressure was 0.4 Pa with Ar of 40 sccm as the sputtering gas. A 3-min pre-cleaning process was performed to remove contaminants on the surface of the targets before thin film deposition. The sputtering power for Zn and Sb was 40 W and 24 W respectively. The as-deposited thin films were annealed for 1 h at 300 °C, 350 °C, 400 °C and 450 °C, respectively, under Ar atmosphere with an annealing pressure of 440 Pa. The as-deposited thin films were named as T1, and those annealed at 300 °C, 350 °C, 400 °C and 450 °C were named as T2, T3, T4 and T5, respectively.

The surface morphology and composition of the thin films were obtained by scanning electron microscopy (SEM, S-4700) with an energy dispersive X-ray microanalysis system and atomic force microscope (AFM, CSPM5500). X-ray photoelectron spectroscopy (XPS) with Al K_α (Axis Ultra) was used to investigate the electronic structure of the thin films. The structure of the thin films was characterized by X-Ray diffraction (XRD) technique (Bruker-D8-Advance) in the conventional θ-2θ mode with the Cu K_α radiation of 0.15406 nm. The thermoelectric properties of the thin films at various testing temperature were measured using the four-probe technique and Seebeck coefficient measurement system (SDFP-I) with the temperature gradient method at temperatures from 300 K to 573 K. The temperature difference between the cold and hot side was 20 K. The thickness of the samples was obtained by characterizing the cross sectional area of the thin film with SEM.

3. Results and discussions

Fig. 1 shows the XRD pattern of the as-deposited thin film (named as T1) with the inset showing its surface morphology. It is difficult to obtain the real crystal structure of T1 due to the wide main diffraction peaks. It can be found that T1 has an amorphous phase from the XRD pattern. Since the thin film was deposited at room-temperature and Zn is easy to form clusters [22], the big humps on the surface of T1 are very likely metallic Zn clusters. From the XRD and surface morphology analyses, T1 might be made of Zn and Sb mixed metal phase. The thermoelectric properties and composition of T1 is listed in Table 1. It can be found that T1 has a very high resistivity and its Seebeck coefficient was not obtained due to the huge resistivity.

The thermoelectric properties and compositions of the annealed samples are also shown in Table 1. It can be found that the compositions of T1 ~ T5 are similar. Though T2 has better electrical property than T1, it still has a huge resistivity and the Seebeck coefficient was not obtained neither. The resistivity of the thin films decreases with the increasing annealing temperature and the resistivity of T3 ~ T5 are much lower than that of T1 ~ T2. The Seebeck coefficient of T3~T5 was measured to be 181 μVK^{-1}, 172 μVK^{-1} and 130 μVK^{-1} at room-temperature. The results indicate that the thin films annealed at 350, 400, 450 °C have much better thermoelectric properties than that of as-deposited sample.

Fig. 2 shows the XRD patterns of the annealed thin films. From Fig. 2, it can be found that T2 has poor crystallinity. The highest peak located at 27.2° in T2 is from the diffraction of ZnSb (231) plane [23,24]. Compared with T2, T3 has better crystallinity and it can be confirmed that T3 is made of compounds. The three major diffraction peaks located at ~28.7°, ~29.3° and 33.0° of T3 are due to the diffraction from ZnSb (112), (121) and (211) plane [23,24]. Other strong peaks observed from T3 are also related to the ZnSb phase. Besides, few extra diffraction peak is observed from T3, indicating T3 has a single phase of ZnSb. The XRD patterns of T4 and T5 are very similar to that of T3, which implies that the phase of ZnSb is also dominant in T4 and T5. Though a few weak peaks related to the Sb plane and Zn_4Sb_3 plane can be observed from T5, the intensity is much smaller than the major ZnSb diffraction peaks and the ZnSb is still the dominant phase in T5. From the XRD results shown in Figs. 1 and 2, it can be concluded that the as-deposited thin film is almost amorphous. The crystallinity of the thin films improves and the thin films are transformed to be ZnSb phase which is almost the dominant phase when the annealing temperature was above 350 °C.

Table 1
The thermoelectric properties, thickness and composition of as-deposited and annealed thin films.

Sample	Annealing temperature (°C)	Thickness (nm)	Resistivity ($\times 10^{-5}$ Ωm)	Room-temperature Seebeck coefficient (μVK^{-1})	Composition	
					Zn (%)	Sb (%)
T1	As-deposited	714	>50,000	Immeasurability	61.1	38.9
T2	300	700	>10,000	Immeasurability	57.2	42.8
T3	350	659	14.3	181	59.3	40.7
T4	400	654	12.9	172	59.7	40.3
T5	450	632	9.5	130	60.9	39.1