Applied Surface Science xxx (2013) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Temperature and size effects on electrical properties and thermoelectric power of Bismuth Telluride thin films deposited by co-sputtering

Zhigang Zeng[a,b,*], Penghui Yang[a], Zhiyu Hu[a,b,*]

[a] Department of Physics, Shanghai University, Shanghai 200444, China
[b] Institute of NanoMicroEnergy, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:
Received 14 August 2012
Received in revised form
21 November 2012
Accepted 27 December 2012
Available online xxx

Keywords:
Bismuth telluride
Thermoelectric
Size effect
Electrical property

ABSTRACT

N-type Bismuth telluride thin films of different thicknesses were deposited on cleaned glass substrate at room temperature by co-sputtering technique. The films were annealed at 300 °C for 12 h in nitrogen atmosphere to improve their properties. The thermoelectric power and electrical properties measurements were carried out on the films with thickness from 70 nm to 480 nm in the temperature range 300–430 K. The thickness dependence of electrical resistivity and Seebeck coefficient of annealed films was analyzed using the effective mean free path model. Some physical parameters such as effective mean free path of charge carriers in hypothetical bulk, the exponent of the energy term of mean free path, activation energy, and the Fermi energy were calculated. Both the electrical conductivity and the Seebeck coefficient of the bismuth telluride films increased with increasing of film thickness and grain size. Films with fewer grain boundaries and defects have longer effective mean free path of carriers and the mean free path decreases with the increase of temperature. The electron–phonon interaction was considered as the main scattering mechanism in the annealed bismuth telluride thin films.

1. Introduction

Bismuth telluride (Bi_2Te_3) is known as one of the best thermoelectric materials with potential for a diverse range of applications, such as power generators [1], refrigerators [2], gas sensors [3]. It is a narrow band gap (0.15 eV [4]) semiconductor and exhibits a rhombohedral crystal structure. It is also known that bulk Bi_2Te_3-based materials have the highest thermoelectric figure of merit, $ZT \sim 1.14$ at room temperature [5]. The thermoelectric figure of merit is defined as $ZT = S^2\sigma T/\kappa$, where S [$V K^{-1}$] is the Seebeck coefficient, σ [$S m^{-1}$] is the electrical conductivity, T [K] is the absolute temperature, and κ [$W m^{-1} k^{-1}$] is the thermal conductivity, which has contributions from carriers and phonons [6]. Thus, it is important to improve thermoelectric figure of merit by increasing the thermopower $S^2\sigma$ and decreasing the thermal conductivity κ.

Current researches are focused on materials with nano-scale dimensions, such as thin films, quantum-dots superlattices, and nanowires, where manipulation of quantum confinement effects can further enhance thermoelectricity [7]. Low-dimensional structures may improve ZT drastically by confining electrons or holes in one or two dimensions [8]. Hicks and Dresselhaus predicted that ZT may be enhanced in a Bi_2Te_3 quantum well by a factor of ~13 over the bulk value [9]. In addition to its attractive thermoelectric properties, the band structure of Bi_2Te_3 makes it a promising candidate material for realization of a topological insulator [10,11], which is characterized by conductive states at the surface and insulating states in the bulk.

Several deposition techniques have been reported in the literatures for the fabrication of Bi_2Te_3 thin films: flash thermal evaporation [12], sputtering [13], electrochemical deposition [14], metal-organic chemical vapor deposition [15] and mechanically exfoliated method [16], are some examples. In this paper, the structural and electric characterization of bismuth telluride thin films deposited by co-sputtering was investigated. Thickness and temperature dependence of electrical resistivity and thermoelectric power of Bi_2Te_3 films were studied using the effective mean free path model of size-effect theory. From this analysis, important physical parameters have been deduced and they are reported in this paper.

2. Experiment

Bismuth telluride thin films were grown on cleaned glass substrate at room temperature from high-purity (4 N) Bi and Te target in a magnetron sputtering system (PVD75, Lesker). The background pressure was 3×10^{-6} mbar and the working pressure was 4×10^{-3} mbar. The RF sputtering power of Te and Bi was kept

* Corresponding authors. Tel.: +86 2166135201; fax: +86 2166135201.
E-mail addresses: zgzeng@shu.edu.cn, zeng.zigang@gmail.com (Z. Zeng), zhiyuhu@shu.edu.cn (Z. Hu).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.12.134

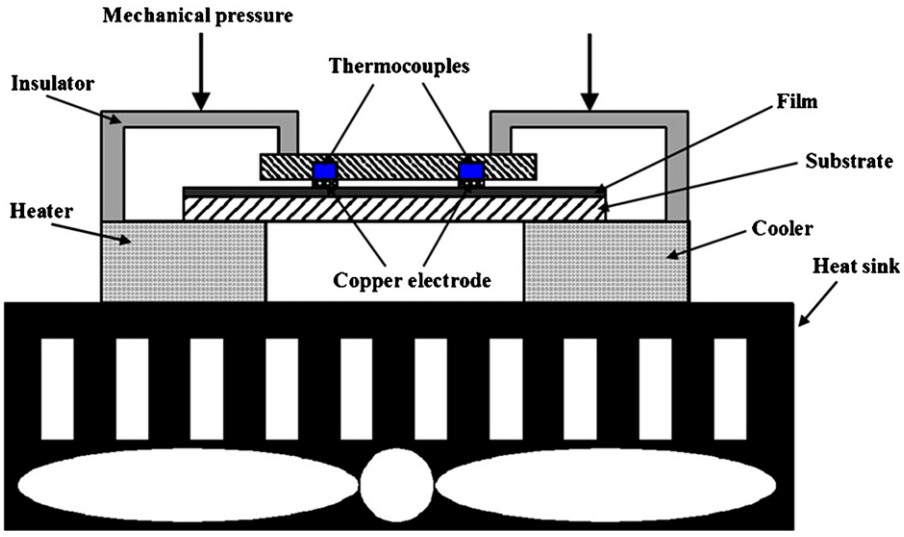

Fig. 1. Schematic of experimental set-up for Seebeck coefficient measurement.

constant at 22 W and 15 W, respectively, to ensure the films have stoichiometric Bi:Te ratio of ~2:3. After the deposition was complete, the films with thickness varying from 70 nm to 480 nm were then annealed at 300 °C for 12 h in N_2 atmosphere. The thickness of the films was determined using a surface profiler (XP-200, Ambios).

The microstructure of the films was studied by X-ray diffraction (XRD). XRD measurements were carried out in a DLMAX-2200 diffractometer using CuK_α radiation ($\lambda = 0.154$ nm). The morphology and composition were characterized using a scanning electron microscope (SEM, JSM-6700F) attached with Energy dispersive X-ray spectroscopy (EDS). The electrical properties of the films were determined using four probes technology. The Seebeck coefficients were obtained from the fit of linear of the measured Seebeck voltage versus the thermal gradient along the films. The Seebeck coefficient measurement system was homemade according to the method detailed in ref. [17]. The schematic of the experimental set-up are shown in Fig. 1. A temperature difference (<5 K) was built up for Seebeck coefficient measurement by putting a heater with a constant current controller under one side of a specimen. The distance between the thermocouple was 1 cm. A suitable mechanical pressure was applied to ensure good thermal and electrical contact. Each contact region between thermocouple with test film was 1 mm in diameter. An aluminum film (~100 nm) was evaporated on test films with mask to ensure ohmic contact. The thermoelectric power factor $S^2\sigma$ was calculated from the measured results of the electrical conductivity and the Seebeck coefficient.

3. Results and discussion

3.1. Structural analysis

XRD patterns of films with thickness of 360 nm using CuK_α radiation are shown in Fig. 2. The bismuth telluride films obviously has (0 1 5) preferred phase. After the films annealed at 300 °C for 12 h in N_2 atmosphere, the intensity of (0 1 5) and (1 0 1 0) peaks increased and the (0 0 6) phase showed up. It exhibits that prepared films have polycrystalline structure and that the annealing treatment helps the films eliminate defects and increase the degree of crystallinity. The grain size of the films with different thickness was obtained from the X-ray diffractogram peaks using the Scherrer formula $D = 0.9\lambda/\beta\cos\theta$, where D is the grain size, λ is the wavelength of the radiation used, β is the full width at half maximum and θ is the diffraction angle [18]. The values of grain size of films were calculated from preferred peak (0 1 5) and were listed in Table 1.

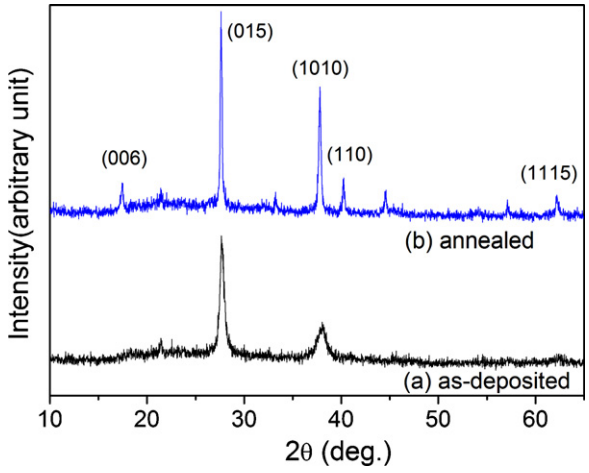

Fig. 2. X-ray diffraction spectra of (a) as-deposited and (b) annealed Bi_2Te_3 thin films with thickness of 360 nm.

It was found that the grain sizes of as-deposited films prepared by co-sputtering method had no obvious relationship with the thickness. However, the grain size of annealed films was larger than as-deposited films, and the value increased with increasing thickness of the film. This indicates that the micro-crystalline grains grow during annealing of the films and the grain size of annealed films is affected by the thickness of films.

The surface structure of the bismuth telluride thin films with thickness of 360 nm was investigated by SEM shown in Fig. 3. Both from surface and cross-section images, it clearly demonstrates that the annealed films have larger grains and more obvious grain boundaries. The composition of films was determined by ESD. The

Table 1
Variation of grain size and activation energy with thickness for Bi_2Te_3 thin films.

Thickness (nm)	Grain size (nm)/(0 1 5)		Activation energy (meV)
	As-deposited film	Annealed film	
70	14.6	21.1	42.6
130	17.3	34.1	38.6
260	18.4	40.4	33.3
360	17.9	45.9	27.7
470	18.9	53.4	–

Please cite this article in press as: Z. Zeng, et al., Temperature and size effects on electrical properties and thermoelectric power of Bismuth Telluride thin films deposited by co-sputtering, Appl. Surf. Sci. (2013), http://dx.doi.org/10.1016/j.apsusc.2012.12.134