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Influence of annealing on thermoelectric properties of bismuth telluride films grown via radio frequency magnetron sputtering

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ABSTRACT

Bismuth telluride films were prepared via radio frequency magnetron sputtering. Mixed powders with different composition were used as sputtering targets. Influence of the annealing temperature on surface topography, crystal structure and thermoelectric properties of the films has been investigated. It was found that the grain size increased and the surface roughness decreased with a rising annealing temperature. X-ray diffraction analysis revealed an improved crystallization after the annealing, and that crystal planes perpendicular to c-axis became prominent. High temperature treatments resulted in a decrease of Seebeck coefficient and an increase of electrical conductivity. The highest power factor was obtained after being annealed at 300 °C.

1. Introduction

Thermoelectric (TE) materials are widely employed in power generator [1], Peltier cooler [2], and novel type sensors, including: TE hydrogen sensor [3], TE anemometer [4], TE wear sensor [5], TE humidity sensor [6], TE infrared sensor [7], and so on. Bismuth telluride and their derivatives have been regarded as the most promising materials working at room temperature. The performance of TE materials was evaluated by ZT value, where $ZT = \alpha^2 \cdot \sigma \cdot T / \kappa$, and α is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity. Due to the influences of quantum confinement effect and phonon scattering on nano-structured materials, low dimensional materials provide higher ZT values. Several technologies, such as thermal evaporation [8,9], sputtering [10,11], metal organic chemical vapor deposition [12], molecular beam epitaxy [13], and electro-chemical deposition [14], have been extensively investigated for the preparation of bismuth telluride films. All of these technologies or require complicated starting materials or are too expensive to use. Magnetron sputtering, as an improved sputtering technology, using direct current or radio frequency (RF) as power, has been widely applied to large-scale fabrication of high quality films.

In this paper, bismuth telluride films were prepared via RF magnetron sputtering. Powders of the two constituent elements were mixed and directly adopted as targets for sputtering. This method is quite different from the traditional sputtering of bulk alloy targets or co-sputtering of pure Bi and Te targets. The latter displayed many problems on obtaining stoichiometric Bi_2Te_3 films, due to the difference in the Bi and Te sputtering rates. Moreover, several sputtering parameters, including the physical properties of the target, the sputtering power, the working pressure, the temperature of the substrate, influence the quality of the produced films. In this paper, the chemical composition of powder targets and annealing temperature were varied while keeping the other parameters constant. The relationship between the chemical composition of the targets and films showed the advantage of the proposed method in achieving stoichiometric films.

2. Experimental details

2.1. Preparation of films

High-purity (5N) bismuth and telluride powders were mixed together and placed into a non-magnetic disk as the sputtering target. Sputtering was started after the chamber was pumped to a vacuum of less than 1×10^{-3} Pa. Amorphous structure quartz glass with a dimension of 20×10 mm^2 was used as substrate, after being adequately cleaned by formaldehyde, distilled water and absolute alcohol successively in an ultrasonic agitator. Considering the possible re-evaporation of Bi and Te at high temperature, the substrate was not heated but was cooled by recycling water during the entire sputtering process. Low sputtering power with an intensity of about 1 W/cm^2 was used in order to prevent scattering of powder. High repeatability of film composition was obtained by re-mixing the target powder before every sputtering. Homogeneous composition of films was ensured by revolving the substrate holder at a speed of 30 rpm. As-deposited films were annealed at different temperatures for 60 min under N_2 atmosphere. All heat treatments were done below 300 °C,

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because the films would be destroyed at higher temperatures, resulting in parts of the films being lost.

2.2. Measurements and characterization

A temperature difference (about 5 °C) was built up for Seebeck coefficient measurement, by putting a tungsten filament connected with a constant current controller (6613C, Agilent, USA) under one side of a specimen. The temperature was monitored by R-type thermocouples with a diameter of 0.07 mm. The Seebeck voltage was captured by a nano-voltmeter (2182, Keithley, USA), and saved in a computer by a data acquisition/switch unit (34970A, Agilent, USA) and Labview program (NI Corp., USA). The electrical conductivity of films was measured using the four-probe technique. In order to prevent the errors caused by the incidental Peltier effect, the average value of two data with conversed direction current was taken as the result.

The thickness of films was measured by a Surface Profiler (Talystep, Taylor-Hobson, UK). The chemical compositions of films was inspected by an energy dispersive spectrometer (EDS) (Falcon, EDAX, USA), with operating voltage of 20 keV, and dwell time of 50 ms per pixel. The crystal structure of films was measured by a X-ray diffraction (XRD) (D/MAX 2550, Rigaku, Japan) with Cu/K-alpha1 radiation ($\lambda = 0.154056$ nm) using 40 kV and 100 mA. The surface morphology was investigated by a atomic force microscope (AFM) (NanoScope IIIa MultiMode, Veeco, USA) at ambient condition in tapping mode using etched Si tips. The Hall coefficient of films was measured at a room temperature using the Van der Pauw technique with a Hall effects measurement system (7704A, Lake shore, USA). A current of 3 mA and a variable magnetic field in the range of ± 3980 kA/m were used to evaluate the average Hall coefficient.

3. Results and discussion

3.1. Elaboration of stoichiometric films

Targets with different chemical compositions were sputtered with the same sputtering parameters, and the molar ratio of Bi:Te was chosen as 5:3, 4:3, 3:3, 2:3, 2:4 and 2:8. A higher Te concentration was obtained in the films due to the higher Te sputtering rate. Te is more easily sputtered from the target than Bi at the same sputtering energy, because the thermal evaporation of Te and Bi are 52.5 and 104.8 kJ/mol, respectively. The Te concentration relationship between the targets and the as-deposited films is described in Fig. 1. The stoichiometric Bi_2Te_3 films, with Te concentration of 60 at.%, were clearly found to be prepared with the target containing 45 at.% Te in Fig. 1.

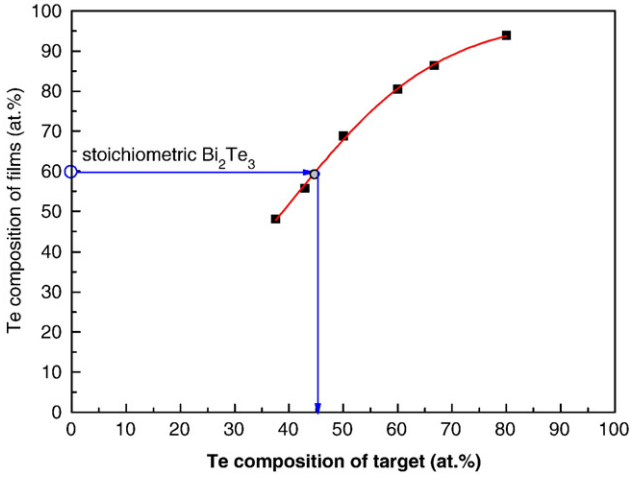

Fig. 1. Relationship between the Te composition of the targets and corresponding as-deposited films.

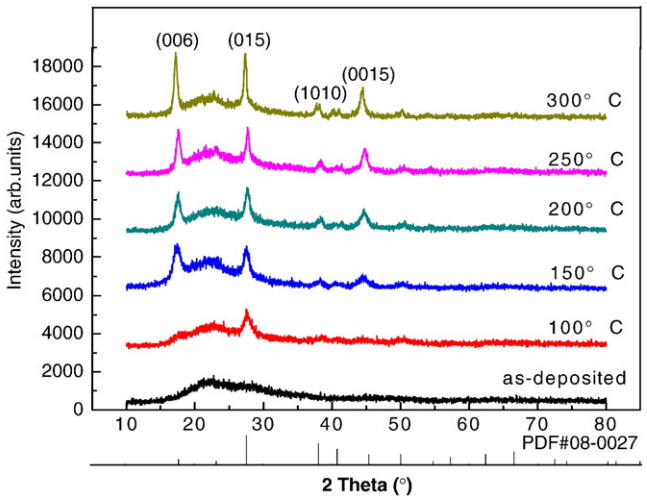

Fig. 2. X-ray diffraction spectra of as-deposited film and films annealed at 100 °C, 150 °C, 200 °C, 250 °C, 300 °C for 60 min under N_2 atmosphere.

Actually, the films with Te concentration of 59 at.% were obtained, which is close to the wanted stoichiometry of 60 at.% within a relative error inside of 2%. It is well known that the composition of films is difficult to control precisely. Comparatively, films with Te concentration of 59 at.% were prepared by Kim et al. [10] via co-sputtering as stoichiometric Bi_2Te_3 film, and films with Te concentration of 47 wt.% were attained by Zou et al. [9] via co-evaporation. Considering the existing error of EDS measurement, the as-deposited films could be regarded as the stoichiometric Bi_2Te_3 films and researched further in this paper.

3.2. Characterization of annealed films

X-ray diffraction patterns of as-deposited and annealed bismuth telluride films are shown in Fig. 2. An amorphous structure was obtained for the as-deposited films. Because the films were deposited on the un-heated, amorphous quartz substrate, thus, the generation of crystal was not triggered, and epitaxial film growth was impossible. With the increase of the annealing temperature, diffusion and agglomeration of atoms were accelerated, and then film crystallization was obviously improved. The crystallization was respectively computed as 0%, 10.7%, 13.2%, 15.5%, 19.3% and 22.4% using Jade 5 software (Materials Data Inc). Meanwhile, the Bi_2Te_3 crystal was evaluated using the standard powder XRD pattern [15]. The (0 1 5) crystal plane of bismuth telluride appeared when the films were annealed at the 100 °C. The (0 0 6) plane and the (0 0 15) plane, which were perpendicular to the *c*-axis of crystal, showed up after being annealed at 150 °C. With the rising annealing temperature, the intensity of *c*-axis perpendicular planes became stronger, which means the classical layered structure of bismuth telluride was formed. Some other small diffraction peaks in Fig. 3 indicated the existence of different crystal orientations, which confirmed the polycrystalline structure of annealed films.

Besides the crystallization, annealing also imposed effects on the grain size and the roughness of the films. It was verified by AFM observation in Fig. 3. Uniform grains were observed on the as-deposited films, and the grain size was about 60 nm. The grains grew and some even reached to 120 nm after annealing at 300 °C and within a N_2 atmosphere. The roughness degrees (Ra) of films for as-deposited and annealed at 100, 200, 300 °C were respectively measured as 4.0, 2.8, 2.8 and 1.8 nm, respectively. All the films had a shiny grayish-