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Studying Thermoelectric Power Behaviors of Bi_2Te_3 Nanoparticles Prepared by Thermal Evaporation

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Abstract

Thin films of Bismuth Telluride (Bi_2Te_3) are prepared by thermal evaporation from nanopowders on the glass substrates. The XRD patterns of films show that all the films are polycrystalline and the crystalline increased by annealing temperature. Measuring of the thermoelectric power of thin films in the temperature range 300 to 380 K shows that Seebeck Coefficients have both negative and positive values, indicating that the films have both n-type and p-type conductivity. The re-crystallization of films is done by annealing from 130˚C to 175˚C and Seebeck Coefficient varied from −150 to 100 μV/K.

Keywords

Bismuth Telluride, Thermoelectric Power, Thermal Evaporation, Thermal Annealing

1. Introduction

Thermoelectric materials are of interest for applications as heat pumps and power generators. The performance of thermoelectric devices is quantified by a figure of merit, ZT, where Z is a measure of a material's thermoelectric properties and T is the absolute temperature. A material with a figure of merit of around unity is first reported over four decades ago, but since then-despite investigation of various approaches-there has been only modest progress in finding materials with enhanced ZT values at room temperature [1]. This device makes possible cooling without the use of CFCs and electricity generation under naturally-occurring temperature-diff-

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erences. That is to say the thermoelectric module is a very simple device to convert electric energy into heat and *vice versa* directly. So far, the use of the thermoelectric modules has been limited because of the low efficiency of energy conversion. Theoretical predictions [2] and subsequent experimental evidence [3] for a significant increase in the thermoelectric efficiency have attracted attention to a detailed study of the thickness dependence of the thermoelectric properties in thin film structures. Because of relatively high thermoelectric efficiency near room temperature, Bismuth Telluride, and its solid solutions have been extensively studied [4]. Bismuth telluride is one of the most promising thermoelectric materials for applications in thermoelectric power generation and cooling near room temperature [4]. The performance of thermoelectric devices is characterized by the dimensionless figure of merit of thermoelectric materials, ZT = α^2 σ T/k, where T is the temperature, α Seebeck Coefficient, σ the electrical conductivity, and K the thermal conductivity. The ZT values of Bismuth Telluride based alloys are close to unity [4]. Recently it is reported that the figure of merit of thermoelectric materials can be significantly increased if the materials are nanostructured, such as quantum dot, super lattices and nanowires [5].

Bismuth Telluride thin films have been elaborated by a variety of deposition techniques such as evaporation [6], sputtering [7], electrochemical deposition [8], metal organic chemical vapor deposition (MOCVD) [9], and mechanically exfoliated method [10]. Here we employ the thermal evaporation method to fabricate Bismuth-Telluride-based alloy thin films. This deposition method has the potential for low production cost comparing any other deposition methods. It is well known that thermoelectric properties of thin films are strongly dependent on the stoichiometry [11]. The annealing temperature is varied from 130˚C to 175˚C in order to investigate the influence of annealing temperature on thermoelectric power properties of Bi_2Te_3 films. Also the influence of variation thickness of Bi_2Te_3 films is investigated. Bi_2Te_3 is a semiconductor with 0.150 ev energy gap and a rhombohedra unit cell belonging to space group R-3m ($D^5{}_{3d}$) [12].

2. Experimental

Powders of $Bicl_3$ (analytical pure) and pure tellurium (99% purity, Merck Co.) with a molar ratio 2:3 were put into a beaker, using distilled water as the solvent, $NaBH_4$ as the decrescent and NaOH to control the PH-value of the solution. The solution was sonicated at 501 K for 4 hours under the ultrasonic frequency of 28 kHz. The resulting dark gray powders were filtered, washed several times with distilled water, ethanol and acetone and dried at room temperature [5]. Structures of the powders were investigated from the diffract grams obtained from an X-ray diffractometer (Mechanism Phillips) using the CuK α radiation.

Thin films were prepared by thermal evaporation of powder at initial pressure of about 5×10^{-5} torr using a coating system (VAS-Multimode 500). The thickness of the films were in the range 70 to 100 nm. We expect that the deposited thin films have approximately the same compositions as Bi_2Te_3 nanopowder. Because it is known that in thermal evaporation method one has a good control of the composition [13]. We expect that the deposited films have approximately the same compositionastheBi$_2$Te$_3$ powder. In order to measure the Seebeck Coefficients two gold electrodes (1 × 0.3 cm) were deposited by thermal evaporation on the surface of thin films. The distance between two electrodes is about 2 centimeters.

At each desired temperature the Seebeck Coefficient was determined by measuring the output voltage (ΔV) of thin films while imposing a temperature difference of (ΔT) between two electrodes (hot and cold junctions) of each sample which is known as differential method [13].

The schematic configuration of the homemade apparatus for measuring the thermoelectric power is shown in **Figure 1**. This apparatus consists of two heaters, one is the fundamental heater and the other is called the secondary heater. By applying a DC current to the fundamental heater, it reaches the desired ambient temperature. Two thermocouples are used to measure the temperature of the both electrodes, which in this stage usually are the same. The secondary heater is used to provide a temperature difference of ΔT between the cold and hot electrodes (by controlling the current passing through the secondary heater it is possible to maintain a temperature difference of about 1 to 8 K between the hot and cold electrodes). The developed thermal emf across the film (ΔV) is measured by a Keithely millimeters (Keithely 610c electrometer).The temperature of each electrode is monitoring by a millimeters (TTi) using copper constantan thermocouple. The thermocouples are attached near the center of the hot and cold junctions and very close to the edge of Bi_2Te_3 thin film. It is important to notice that, the thermocouples are not attached directly to the Bi_2Te_3 thin film, because this may peel off the Bismuth Telluride from the substrate.

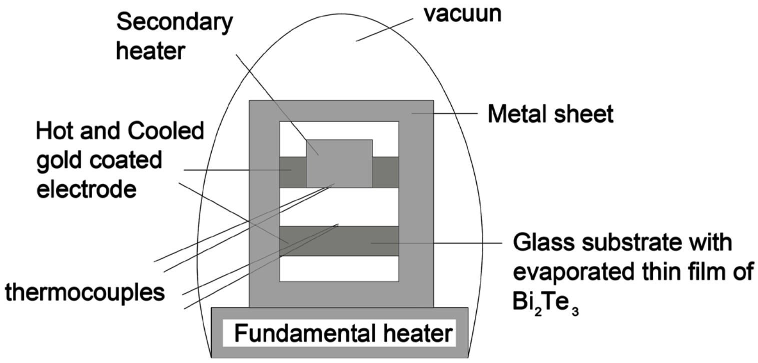


Figure 1. Schematic diagram of the measurement for the output voltage of the bismuth-telluride-based alloy thin film thermoelectric samples.

For annealing of Bi_2Te_3 films, samples are heated up at atmospheric pressure in an electric furnace. The temperature is increased steadily at 5 k/min until the temperature reaches the set temperature. The samples are annealed for 1 hour at the desired temperature and then they are cooled down naturally to room temperature by switching off the furnace.

3. Result and Discussion

The X-ray diffraction pattern of Bismuth Telluride nanopowder is shown in **Figure 2(a)**, which is confirming its polycrystalline nature. The weak and broad peaks indicate different orientations. The plane indices from these peaks were in agreement with the values which are given for Bismuth Telluride by JCPDScard 15 - 863, it is seen that the patterns of the films can be attributed to the rhombohedra Bi_2Te_3 structure. **Figure 2(b)** shows the XRD patterns of as-deposited Bismuth Telluridethin film which annealed at 175˚C temperature. We can see that in **Figure 2(b)**, the as-deposited thin film has an amorphous structure nature. After annealing five major diffraction peaks are noticed in XRD pattern, which located at 38.021˚, 41.08˚, 45˚, 64.1˚, 78˚ and 80.8˚. These peaks are related to the diffraction from planes (1010), (0111), (110), (116), (0021), (2113) and (2020), which shows a rhombohedra structure belonging to the R-3m space group of Bi_2Te_3 film [14] [15]. The grain size of the thin film are obtained by using Scherer's Formula [14] and the results are shown that the grain size gets larger as the annealing temperature increase. From the XRD results, it can be concluded that Bi_2Te_3 thin films of high crystallin equality are obtained after annealing. By improving the crystalline quality, interface and impurity scattering may reduce which are contributed to the improvement of thermoelectric properties of Bi_2Te_3 thin films.

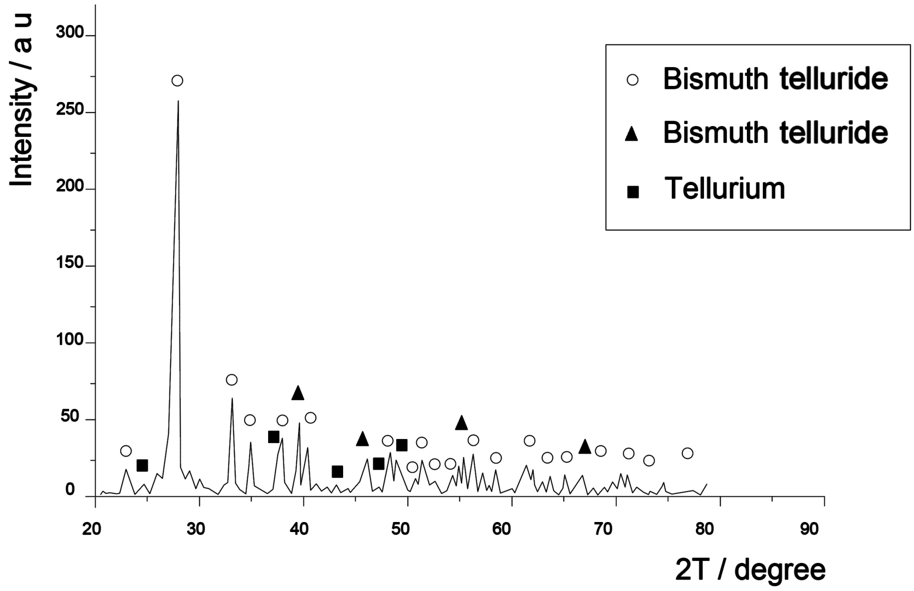
In **Figure 3**, the thermal emf (ΔV) developed across the film at various ambient temperatures are shown as a function of temperature difference (ΔT). With increasing temperature the slope of lines were changed from positive to negative, that indicate the change of the type of conduction.

The Seebeck Coefficient of the Bi_2Te_3 thin films as a function of test temperatures for various films with different thicknesses are shown in Fig4. As it is shown in **Figure 4**, the sign of the Seebeck Coefficient and their value for films annealed at 130˚C depend on the testing temperature while for films annealed at higher temperature the sign is without alteration but the value of the Seebeck Coefficient is changed very gradually.

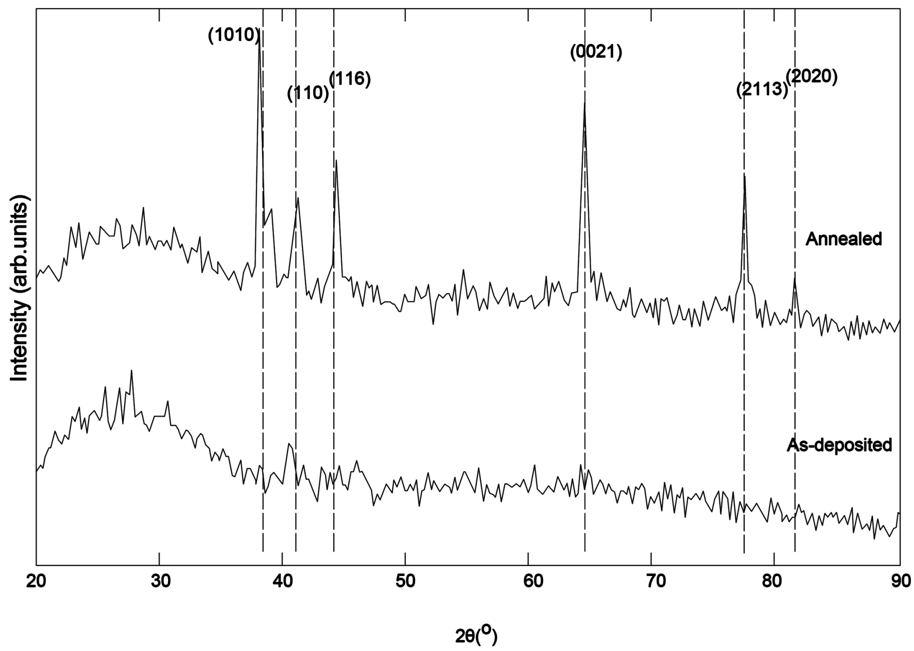
We can explain the changes of Seebeck Coefficient against different thickness with effective mean free path model [16] when the thickness of the film is lower or near to the mean free path length because of the small grain size the scattering of charge carrier is low and therefore the mobility and Seebeck Coefficients are high.

In **Figure 5**, the Seebeck Coefficient as a function of annealing temperatures for 70 nm thickness sample is shown. The variation of Seebeck Coefficient value with temperature in a specified temperatures range (280 - 400 K) is more noticeable for films annealed at higher temperature. The film annealed at 130˚C showed the most variation.

We can explain these results following Mott transition theory [15] that relates the density of localized states and thermal energy in thin films. According to the Mott transition model with increasing the annealing temperature the density of localized states, is decreased and therefore the conductivity is increased so that the Seebeck Coefficient and Power factor are improved. When the annealing temperature is increased, grain size and mobility of films are increased so Seebeck Coefficient is improved. This shows that the Seebeck Coefficient of thin



(a)



(b)

Figure 2. X-ray diffraction pattern of Bismuth Telluride nanopowders.

film depends strongly on the annealing temperatures [16].

For annealing temperature of 403 - 448 K the value of Seebeck Coefficient gradually increase as the annealing temperature increases. At an annealing temperature of 448 K the Seebeck Coefficient of the films reaches 245 µv/k at the temperature difference of 5 K.

We also try to treat the annealing over 448 K but the junctions between the bismuth telluride thin film and electrodes break and mound defects were observed on surface due to the evaporation of Te elements.

4. Conclusion

Thermoelectric Power of Bi_2Te_3 has been carried out on thin films in the temperature range 300 - 380 K. The

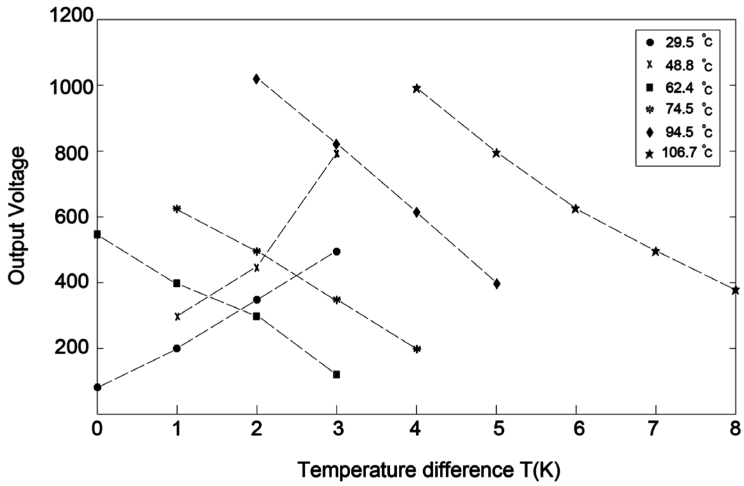


Figure 3. The generated output voltage of Bismuth Telluride based alloy thin film measured as a function of temperature difference.

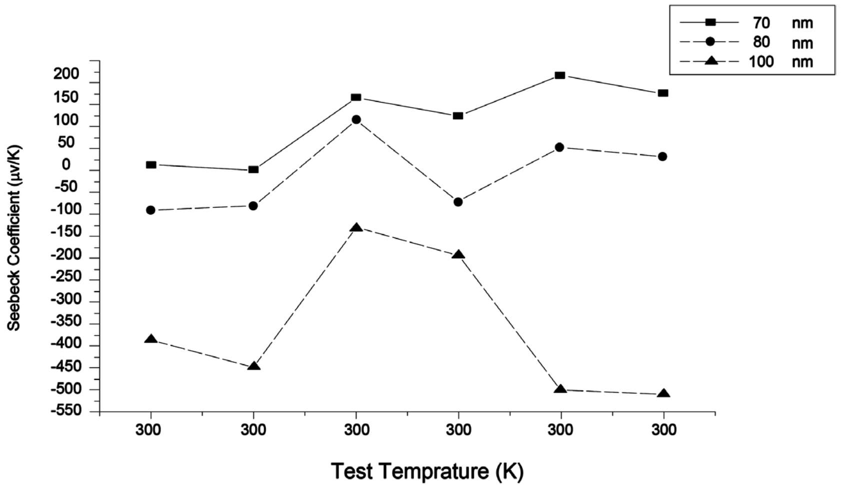


Figure 4. Seebeck Coefficient measured as functions of ambient temperatures for 70, 80 and 100 nm thicknesses.

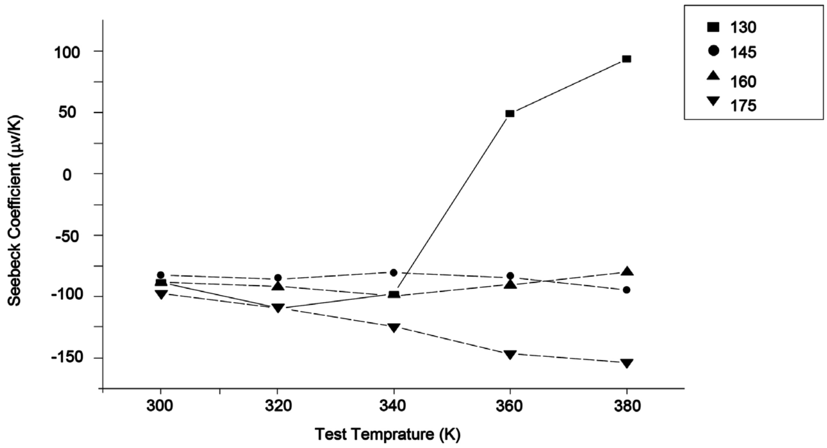


Figure 5. Thin film of Bi_2Te_3 with thickness 70 nm annealed at 130˚C, 145˚C, 160˚C, 175˚C.

effective mean free path model has been used to analyze the size effect of thermoelectric power of the films. Influence of thermal annealing on thermoelectric properties of Bi_2Te_3 films is investigated. The variation of Seebeck Coefficient value with annealing temperature is changed from 100 to −150 µV/k in 70 nm thickness. The maximum Seebeck Coefficient value which is measured for grown thin films with 100 nm thickness is about −500 µv/K. It is noticeable that it is higher than bulk value (−150 µv/K) of Bi_2Te_3. Seebeck Coefficient in nanostructured especially thin Bi_2Te_3 films is higher than bulk because there are many interfaces between crystal, which scatter phonons, more effectively than electrons, so the thermal conductivity is reduced [17]. In fact the achieved heat-flow density in thin films (500 Wcm-2) has higher value than typical large scale devices (10 W cm^{-2}) [18].

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