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Electrical resistivity of thermally evaporated bismuth telluride thin films

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Abstract

Semiconducting chalcogenide thin films have been receiving considerable attention in the recent years because of their wide applications in the various fields of science and technology. The studies of the electronic properties of semiconductors have been largely stimulated by attractive micro-electronic device applications. Among the various V–VI compounds, Bismuth Telluride (Bi_2Te_3) is an established low-temperature thermo electric material and is widely employed in thermoelectric generators and coolers. The present work deals with the structural and the electrical characterization of Bi_2Te_3 thin films vacuum deposited on well-cleaned glass substrates. A constant rate of deposition was maintained through out the process. To obtain uniform and homogeneous film thickness through out on all the substrates a rotary drive was employed. Quartz crystal thickness monitor was used to measure the thickness of the samples. From the X-ray diffractogram the Bi_2Te_3 films are found to be amorphous at lower thicknesses and posses hexagonal polycrystalline structure at higher thickness, having lattice parameters $a = 4.44$ Å and $c = 29.40$ Å. The grain size of the Bi_2Te_3 thin films before annealing and after annealing are found to be 100 and 160 Å, respectively. The micro-strain and the dislocation density are found to decrease after annealing. The thermogravimetry–differential thermal analysis (TG–DTA) studies revealed that the Bi_2Te_3 films are non-decomposable. Electrical resistivity, TCR measurements have been carried out as a function of varying temperatures in the range 303–453 K are found to show the size effect. Analyzing the size dependence of electrical resistivity it is found that the electrical resistivity is a linear function of the reciprocal of thickness of the film. The energy gap of Bi_2Te_3 thin film was calculated from the graph $\ln \rho$ vs. $1/T$ and it is found that the energy gap decreases with

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increasing thickness. From the negative values of TCR, it is inferred that Bi_2Te_3 films exhibit semiconducting behavior.

Keywords: Bi_2Te_3; Thin films; Electrical resistivity; Thermal evaporation

1. Introduction

Bismuth telluride-based materials are well-known for their thermoelectric applications near room temperature. A large number of studies have been reported on the $(Bi,Sb)_2(Te,Se)_3$-based thermoelectric materials and devices because of their excellent performance in thermoelectric refrigeration and power generation at room temperature. Thermo elements have been usually fabricated from sintered blocks of the materials [1]. There are, however, certain difficulties and limitations in making highly miniaturized modules because of the fragile nature of these materials. Moreover, the number of p/n couples fitting in a limited space available makes it impossible to obtain relatively high output voltage (order of volt) for power generation. To overcome these drawbacks, thermoelectric modules based on thin film technology have been studied [2,3]. Microwatt or milliwatt power level is sufficient for electronic applications which can be easily scaled. Especially Bismuth Telluride (Bi_2Te_3) based compounds have multi-faceted applications in various electronic devices like memory alloy micro-actuator [4], thermoelectric generators [5], thermal sensors, laser diodes [6], thermopiles [7], etc., as a thermoelectric materials.

A number of techniques have been used to grow Bi_2Te_3 thin films, such as flash evaporation [8], hot wall epitaxy [9], sputtering [10], metal organic chemical vapor deposition [11], and molecular beam epitaxy [12]. The interest on this material was renewed after the report of improved thermoelectric properties by Turenne [13]. Even though many reports are available on various properties of thin films of Bi_2Te_3, to the knowledge of authors, there are not many reports available on thermo-gravimetry–differential thermal analysis (TG–DTA) studies of the vacuum deposited Bismuth Telluride thin films. Hence in this paper, we present our partial work completed in our laboratory on the structural, electrical resistivity and TG–DTA studies on vacuum deposited Bi_2Te_3 thin films of various thicknesses in our goal to miniaturize various thermo electric devices.

2. Experimental procedure

Bi_2Te_3 alloy (99.999% Aldrich Co. USA) was evaporated in a vacuum of about 10^{-5} Torr in a vacuum coating unit (12″ Hind High Vac., India) to obtain Bismuth Telluride films. The Bi_2Te_3 films of various thicknesses were deposited on to well-cleaned glass substrates. The substrates were placed at 30 cm from the source of

evaporation and it was maintained throughout the process. The glass substrates were cleaned with NaOH, distilled water, ultrasonic agitator and isopropyl alcohol, in that order, before using them for thin film deposition. The films were deposited at a constant rate of evaporation as 1 Å/s. The thicknesses of the films were monitored using a Quartz Crystal Monitor. The structure of the samples was analyzed by X-ray diffractometer (Rigaku RINT 2100 attached with AFC-7 *R*-Axis rapid type X-ray generator, using CuKα radiation with $\lambda = 0.15418$ nm).

The physical property of Bi_2Te_3 thin films were analyzed using TG–DTA technique. In this technique the mass of the substance under consideration is measured as a function of temperature while the substance is subjected to controlled temperature. Simultaneous TG–DTA experiments were carried out on 10 mg of the sample using STA 1500 system. The heating rate employed was $10^{\circ}C\,min^{-1}$ in Nitrogen atmosphere.

Electrical resistivity measurements in the range 303–453 K as a function of temperature were performed on Bi_2Te_3 films of different thickness using Four Probe Method. In this technique four sharp probes are placed on a flat surface of the material to be measured, current is passed through the two outer electrodes and the floating potential is measured across the inner pair. A nominal value of probe spacing, which has been found satisfactory, is an equal distance of 2 mm between adjacent probes.

3. Results and discussions

The XRD analysis revealed that the films are amorphous in nature at lower thicknesses and as thickness increases polycrystalline films are obtained. Fig. 1 shows the X-ray diffraction pattern of Bismuth Telluride thin film of thickness 2485 Å which confirms its polycrystalline nature. The peaks at 12.4° and 27.4° correspond

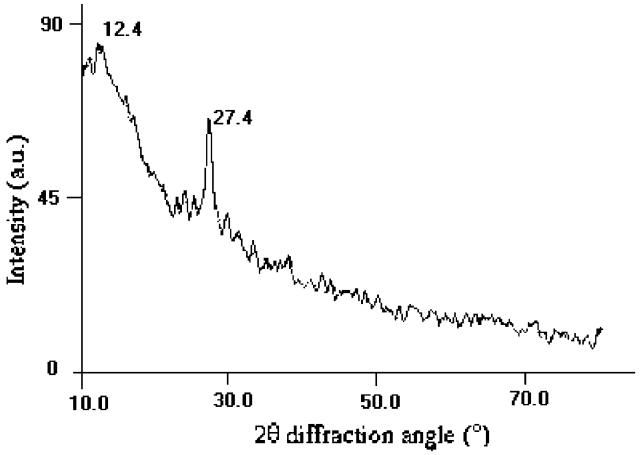

Fig. 1. X-ray diffraction pattern of as grown Bi_2Te_3 film.

to diffraction of (0 1 5) plane and these peaks agree with the standard American Standard for Testing and Materials (ASTM) values of Bi_2Te_3. This confirms the formation of Bi_2Te_3 in the thin-film state. In addition to the above mentioned peaks, the XRD (Fig. 2) of the Bi_2Te_3 thin film annealed at 373 K for 1 hr shows an additional peak at 37.7° due to diffraction of (1 0 1 0) plane, indicating the polycrystalline nature.

The lattice parameters deduced from the XRD analysis are found to be $a = 4.44$ Å and $c = 29.40$ Å which are close agreement with the values reported for Bi_2Te_3 films by Francombe [14]. This indicates that the structure of Bi_2Te_3 thin film is hexagonal polycrystalline [15,16]. The grain size (D) was calculated using Scherer's relation [17] and the micro-strain (ε) and the dislocation density (ρ) were evaluated using the equations [18,19]

$$D = k\lambda/\beta\cos\theta, \tag{1}$$

$$\varepsilon = (\beta\cos\theta)/4, \tag{2}$$

$$\rho = 15\varepsilon/aD, \tag{3}$$

where λ is the wavelength of radiation, k the constant (0.94), β the full-width half-maximum and θ the diffraction angle.

The grain size of the thin film before and after annealing is found to be 100 and 160 Å, respectively. The increase in the grain size may be attributed to the reorientation of the grain boundaries due to annealing. The micro-strain (ε) and the dislocation density (ρ) of the as grown films were found to be 3.53×10^{-3} and $11.62 \times 10^5\,cm^{-2}$, respectively. The values of ε and ρ for the annealed Bi_2Te_3 films was found to be 2.26×10^{-3} and $4.77 \times 10^5\,cm^{-2}$. It is observed that, the micro-strain and dislocation density of the annealed film decreased when compared to unannealed film. This may be due to the movement of interstitial Bi atoms from

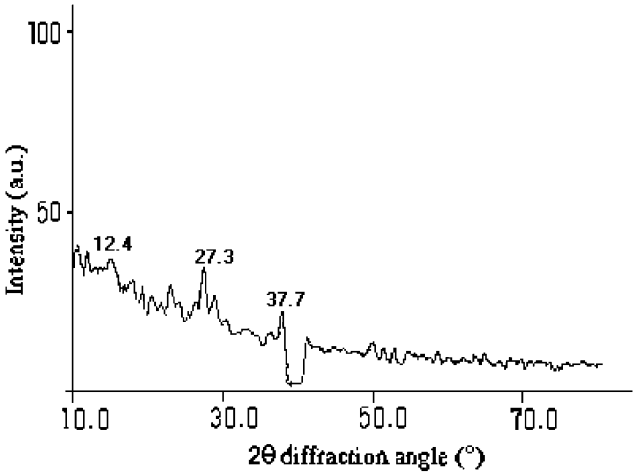

Fig. 2. X-ray diffraction pattern of annealed Bi_2Te_3 film.

its grain boundary to the crystallites, which may be leading to reduction in the concentration of lattice imperfections.

Simultaneous TG–DTA studies were carried out at the heating rate $10^{\circ}C\,min^{-1}$ in the nitrogen atmosphere. Fig. 3 shows the TG–DTA pattern of Bi_2Te_3 thin films of thickness 2485 Å. The compound is stable up to 400°C and after that it increases with its mass about 4% till 560°C. The simultaneous DTA shows the exothermic reaction at 410°C which may be due to the formation of an intermediate product with nitrogen. The intermediate formation undergoes immediate exothermic decomposition, which is supported by mass loss in TG by 11%.

To examine the temperature dependence of the resistivity in more detail, electrical resistance measurements were made in the temperature range 303–453 K for various thicknesses under constant current source (1 mA). The resistance has been plotted as a function of temperature for different thickness is shown in Fig. 4. The resistance is found to be a linear dependence on inverse thickness for all the temperatures, which may be probably due to the discontinuous structure of the film. It was observed that the carriers were strongly nondegenerate, and hence the resistivity decrease with increase in temperature [20]. Also, the Bi_2Te_3 thin films studied in the present work exhibit the normal semiconducting behavior of exponential decrease of resistivity with temperature.

The activation energies can be evaluated from the graph plotted between $\ln \rho$ vs. $1/T$. The graph to calculate the activation energy for the Bi_2Te_3 thin film of thickness 760 Å is shown in Fig. 5 and the activation energies for other films of various thicknesses were calculated in the similar way and the values are given in Table 1. It is seen that the activation energy decreases as the thickness increases [21], which can be explained on the basis of island structure of the film formation and thereby, tunneling of charged carriers between islands separated by a few angstrom of distance. The temperature coefficient of resistance of the films studied is found to be negative indicating the semiconducting behavior of the films [22].

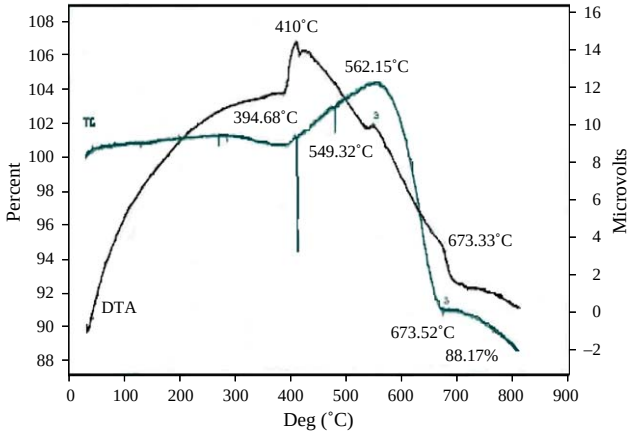

Fig. 3. TG–DTA pattern of Bi_2Te_3 film.

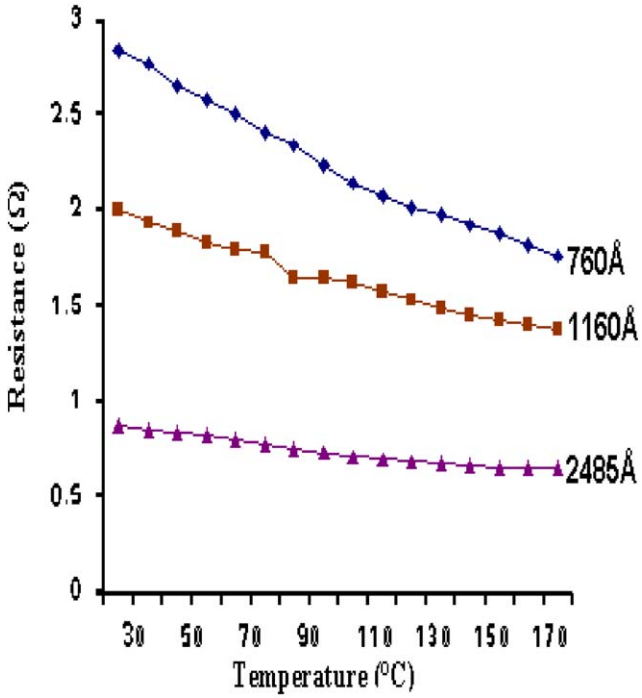

Fig. 4. Resistance vs. Temperature graph of Bi_2Te_3 thin film.

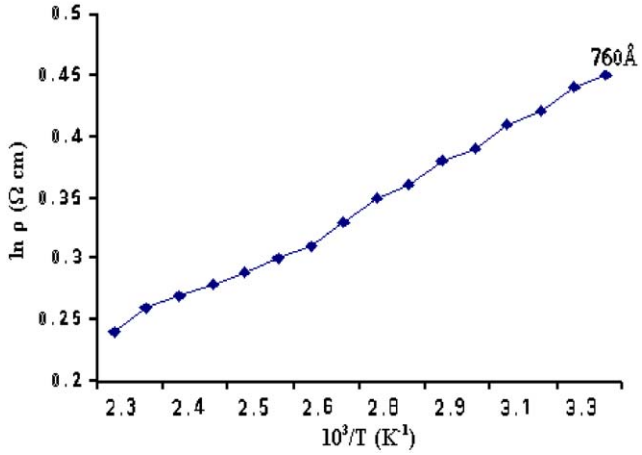

Fig. 5. $\ln \rho$ vs. $1/T$ plot of the Bi_2Te_3 thin film.

4. Conclusion

The Bi_2Te_3 thin films were grown by thermal evaporation onto glass substrates. The structural analysis using XRD reveals that the films are amorphous at lower

Table 1
Variation of activation energy with the thickness for various Bi_2Te_3 films

Thickness Å	Activation energy (eV)
760	1.225
1160	1.200
2485	1.175

thicknesses and polycrystalline at higher thickness possessing hexagonal structure and having lattice parameters $a = 4.44$ Å and $c = 29.40$ Å. There is an increase in grain size and decrease in the micro-strain and dislocation density with annealing. The simultaneous TG–DTA of the material shows the exothermic heat transfer during the process, the increase in the mass indicate the possibility of an intermediate product. The resistivity decrease with increase of film thickness. The activation energy increases with decreasing film thickness. The TCR is found to be negative for all the Bi_2Te_3 films. It is found that films deposited by vacuum evaporation have the same properties as that used in the thermoelectric generators. Hence it is concluded with out sacrificing the basic properties, with minimum material Bismuth telluride films can be prepared by vacuum evaporation for various device applications realizing the miniaturization of devices.

Acknowledgements

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