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EFFECT OF ALTERNATE LAYERS OF Bi_2Te_3 - Sb_2Te_3 THIN FILMS ON STRUCTURAL, OPTICAL AND THERMOELECTRIC PROPERTIES

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There is an increasing demand for the development of new thermoelectric materials with high figure of merit. This is due to the fact that convectional energy generating methods causes many environmental problems. Thermoelectric materials have capacity to harvest waste energy as they convert directly any type of waste heat into electricity. Telluride based materials are known as best thermoelectric materials as they have high figure of merit. Present work is based on multilayered structure of bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) thin films. In this work thin film of single layered Bi_2Te_3, Sb_2Te_3, their bilayers (Bi_2Te_3-Sb_2Te_3), 5 layers and 10 layers have been deposited on clean glass substrate by e-beam evaporation method. X- Ray diffraction (XRD) has been done for the characterization of these thin films. In this paper, studies of electrical properties are also reported which have been carried out by Hall and I-V measurements while optical properties have been studied by employing by UV – Vis spectrometer. Thermoelectric characteristics have been measured by laboratory thermoelectric measurement setup.

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1. Introduction

Our energy resources have been exhausted day-by-day and it has become an essential need for the energy storage. Thermoelectric effect is the simplest and low cost technology for the conversion of temperature difference into electricity [1]. Thermoelectricity has many applications like in generators, cooling devices, solar cells, photo detectors, optoelectronics, electrophotography, LED's etc. Narrow band gap with multilayered structured thermoelectric material have large efficiency for practical applications [2]. The efficiency of presently available TE devices are very poor to be used extensively but their efficiency can be enhanced by selecting appropriate material and a dimensionless parameter known as figure of merit (ZT). The value of 'ZT' around (2 to 3) is good for practical applications. Highest value of 'ZT' has been achieved to 2.4 [3]. Figure of merit which is expressed as $ZT = S^2\sigma T/(k_L+k_e)$, where S is Seebeck coefficient, σ is electrical conductivity, T is absolute temperature and k_L, k_e are the thermal conductivity due to lattice and electronic contributions respectively. To maximize 'ZT', the value of 'S' and 'σ' should be large with reducing the part of thermal conductivity. But by reducing thermal conductivity the part of electrical conductivity also decreases. Thermal conductivity decreases independently by introducing the concept of low dimensional superlattice structure due to quantum confinement [4]. Among all the materials Bi_2Te_3 shows best thermoelectric properties with high figure of merit at room temperature and its value can be enhanced by doing some modifications in its structure. [5].

Bi_2Te_3 and Sb_2Te_3 are the topological insulators but their conductivity lies in the range of semiconductors. Topological insulators have wide range of applications and it has become a hot topic in today's research. Studies have shown that Bi_2Te_3 and Sb_2Te_3 exhibit semiconducting properties with better Seebeck coefficient, good electrical conductivity and relatively low thermal conductivity than other materials [6]. So, these materials have potential to convert directly heat

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into electricity with high efficiency. Researches show that superlattice structures can increase the value of ‘ZT’ due to reduction in thermal conductivity part without any effect in electrical conductivity by introducing the low dimensional effect as they have better scattering structures [7].

Present paper is focused on enhancing the efficiency of thermoelectric devices by maximize the value of ‘ZT’. For this multilayer superlattice structures of telluride based compounds were formed in form of thin film. The samples are single layers of Bi_2Te_3 and Sb_2Te_3, their bilayers and their alternate layers upto 5 and 10 layers. All these samples have been prepared on clean glass substrate by using electron beam evaporation method. To analyze the effect of thickness on structural properties X- Ray diffraction (XRD) has been employed for the structural characterization. Studies of electrical properties have also been reported which were carried out by Hall and I-V measurements. To analyze the UV and VIS spectrum range for the optimum absorption of radiation, the optical properties have been studied by employing UV-VIS spectroscopy. Thermoelectric characteristics have been measured by laboratory thermoelectric measurement setup.

2. Experimental work

The samples single layers of Bi_2Te_3 and Sb_2Te_3 (50 nm) each, their bilayers Bi_2Te_3 - Sb_2Te_3 (total 103 nm), 5 layers of thickness (total 510 nm) and 10 layers of thickness (total 1024 nm) have been fabricated on clean glass substrate by electron beam evaporation method. The Bi_2Te_3 and Sb_2Te_3 are purchased in the powder form from sigma company with 99.99% purity. Substrate were cleaned with acetone and dried at room temperature. All the films have been deposited in a vacuum chamber under the pressure of ~10^{-6} Pa at variable rates of evaporation. For Bi_2Te_3 it is ~2Å/Sec. and for Sb_2Te_3 it is ~10 Å/Sec. Structural properties are analyzed by XRD in the department of physics, Banasthali Vidyapeeth, Banasthali. The electrical properties Hall measurement, Carrier concentration, mobility, conductivity, sheet resistance and I – V measurements were carried out through four probe method in MRC, MNIT, Jaipur. The optical properties like absorbance, transmittance and reflectance were measured by LAMBDA 750 (Perkin Elmer) UV-Vis NIR Spectrophotometer in MNIT, Jaipur to determine the band gap of the samples.

3. Results and discussion

3.1. Structural analysis

The XRD patterns of multilayered structure of alternate layers of Bi_2Te_3 and Sb_2Te_3 has been shown in Fig.1 for different thicknesses ranging from 30 nm to 1000 nm at room temperature. The XRD pattern of multilayers Bi_2Te_3 and Sb_2Te_3 has characteristic features corresponding to (101), (015), (110), (205) for single layer of Bi_2Te_3 and (009) and (015) planes for Sb_2Te_3 are in good agreement with hexagonal structure JCPDS data with ICSD: 44983 (a = b= 4.3900, and c = 30.4600) and earlier report [8]. The intensity of peaks (101), (015) and (110) are strong as compared to other peaks. The intensity of planes are decreases from single layer Bi_2Te_3 to bilayer but then increases for 5 and 10 layers which confirms that 10 layered sample is more crystalline than single layer. The XRD pattern of the samples shows hexagonal structure and it is in good agreement with JCPDS data. But as number of layers increases more peaks are generate.

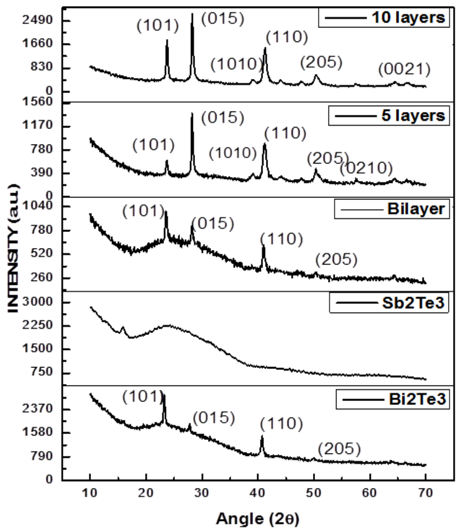


Fig. 1. XRD of multilayers of Bi_2Te_3 - Sb_2Te_3 of thicknesses from (50 – 1000) nm.

The intensity of the peak (015) increases very strongly with thickness as compared to other peaks. The behavior of Sb_2Te_3 curve shows amorphous crystalline nature and a small peak is observed at 15.68^0 which disappeared as thickness increases [9].There is no peak observed for Sb_2Te_3 in x-ray diffraction pattern in multilayer structure of Bi_2Te_3- Sb_2Te_3 due to non- crystalline behavior of Sb_2Te_3.

Table 1. Shows diffraction angles, (hKl) value and d spacing for multilayers of Bi_2Te_3 - Sb_2Te_3 of thicknesses (50 – 1000) nm.

Bi_2Te_3					Bilayer					5 layers					10 layers				
2(θ)	d(A^0)	h	k	l	2(θ)	d(A^0)	h	k	l	2(θ)	d(A^0)	h	k	l	2(θ)	d(A^0)	h	k	l
23.25	3.830	1	0	1	23.44	3.793	1	0	1	23.70	3.756	1	0	1	23.40	3.802	1	0	1
27.81	3.205	0	1	5	28.12	3.170	0	1	5	28.20	3.160	0	1	5	28.22	3.158	0	1	5
41.09	2.193	1	1	0	41.03	2.200	1	1	0	41.08	2.194	1	1	0	41.09	2.193	1	1	0
50.22	1.816	2	0	5	50.20	1.815	2	0	5	44.29	2.045	0	0	15	44.32	2.187	0	0	15
-	-	-	-	-	64.41	1.446	0	0	21	47.71	1.905	0	2	1	47.94	1.896	0	2	1
-	-	-	-	-	-	-	-	-	-	50.46	1.807	2	0	5	50.44	1.808	2	0	5
-	-	-	-	-	-	-	-	-	-	57.55	1.600	0	2	10	57.78	1.594	0	2	10
-	-	-	-	-	-	-	-	-	-	64.64	1.452	0	0	21	64.64	1.452	0	0	21

Grain Size: The grain size of the samples of different thicknesses can be calculated using Scherer's formula;

$$D = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

where D is the grain size, k is the shape factor (0.94), λ is the wave length of X-ray source ($1.5406A^0$), θ is the Bragg's angle and β is full width at half maxima.

Microstrain: The microstrain (ε) is developed in thin films is the root mean square of variations in lattice parameters. It can be calculated from the relation;

$$\varepsilon = \frac{\beta cos\theta}{4} \quad (2)$$

Dislocation density: Dislocation in Xrd is an imperfection in crystal which occurs due to misregistry of lattice in one part with another part of the lattice [10]. The dislocation density (δ) is the length of dislocation lines per unit volume of crystal and it can be determined by the relation;

$$\delta = \frac{1}{D^2} \quad (3)$$

Table 2. The calculated structural parameters, Full width at half maxima (FWHM), Grain size (D), microstrain (ε), and dislocation density (δ) for alternate layers of Bi_2Te_3 - Sb_2Te_3 of thickness from (50 – 1000 nm) for (0 1 5).

Samples	2θ (^{0})	FWHM (β^0)	Grain Size D (nm)	Strain ε x10^{-4} (lines^{-2}m^{-4})	Dislocation density δ x 10^{13} (lines/m^2)
Bi_2Te_3	27.81	0.205	41.59	8.70	57.81
Sb_2Te_3	15.68	0.492	16.29	21.26	376.84
Bilayer	28.12	0.235	36.40	9.94	75.47
5 layers	28.20	0.256	33.42	10.82	89.53
10 layers	28.22	0.283	30.22	11.99	109.49

3.2. I-V measurements

Fig. 2 represents the graph of I-V curves from which it can be determined whether the prepared sample show linear or non-linear behavior. Linear behavior shows metallic nature whereas non- linear behavior show semiconducting nature. The current is flowing through the samples in milliampere range. It was observed from I-V curves that the slope of Sb_2Te_3 is minimum. The slope of the curves slightly increase from single to 5 layers and show nonlinear behavior but a large increment in slope is shown for 10 layer sample and shown linear behavior. It means that 10 layered sample exhibit metallic conduction with high conductivity.

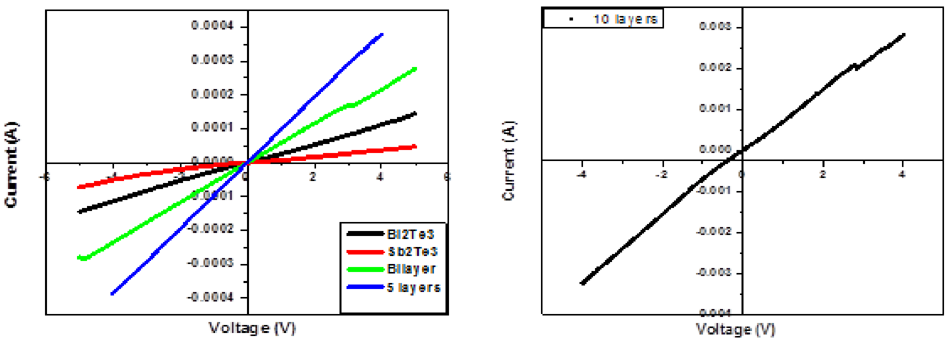


Fig. 2. I-V curves of alternate layers of Bi_2Te_3 - Sb_2Te_3 of thickness from (50 – 1000) nm.

3.3. Electrical properties

The study of electrical properties is most important to determine the nature of sample. To attain high value of 'ZT' conductivity of the sample should lie in the range of semiconductor. Conductivities of each sample were carried out through standard Vander paws technique at room temperature. Results have been shown in table 3. Electrical conductivity varies with sample thickness and the order of 10^{2}(Ω-m)$^{-1}$. Its value going to decrease upto 5 layers [11,12]. This may be due carrier concentration decrease with thickness, but its value increases slightly for 10 layered sample. The conductivity of all the samples lies in the range of semiconductor. The dependence of electrical conductivity with thickness follows Fuchs-Sondheimer size theory. The value of sheet resistance decreases from single layer to 10 layers. This is due to lattice defects and scattering of electron decreases with thickness [12]. Free charge carrier concentration in the samples are the order of (10^{21}) which signifies high order of carriers and as the thickness of the alternate layers increases, carrier concentration going to decrease while mobility of the samples increases with thickness. As mobility and charge carriers are inversely proportional to each other. Higher will be the carrier conc. lower will be the mobility of carriers. The increment in mobility is due to structural defects like impurity centers, voids and grain boundaries. For larger thickness the concentration of these defects are reduced due to filling of voids and other imperfections [13]. It can also be realized that negative value of Hall coefficient for Bi_2Te_3 show n-type of charge carriers and positive value of Hall coefficient for all other samples show p-type carriers. The variation in Hall coefficient with thickness follows galvanometric size theory and its value decreases with thickness [12]. Magnetoresistance (MR) also measured for various Bi_2Te_3 -Sb_2Te_3 thin films of various thicknesses between (50 to 1000 nm). It is the ability of change of resistance on application of magnetic field. It is observed that -Sb_2Te_3 has maximum MR value and its value decreases with thickness.

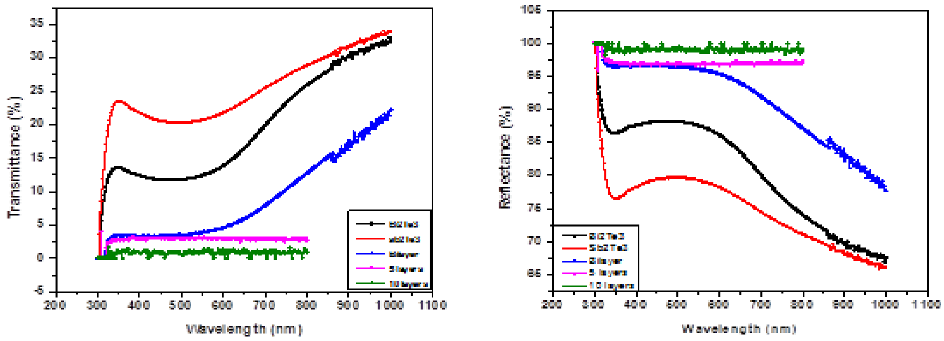
Table 3. Represents the electrical properties of multilayers of Bi_2Te_3 - Sb_2Te_3 of thickness from (50 – 1000) nm.

SAMPLES	**BULK CONC. 10^{21}/cm^3**	**SHEET RESISTANCE 10^3 (Ω)**	**CONDUCTIVITY 10^2 (Ω-cm)$^{-1}$**	**HALL COEFFICIENT, R_H 10^{-3} (cm^3/C)**	**MOBILITY,µ (cm^2/V-sec.)**	**MAGNETO RESISTANCE 10^{-1} (m^2·V^{-1}·s^{-1})**
Bi_2Te_3	1.00	1.02	1.95	-8.75	1.31	4.07
Sb_2Te_3	2.64	1.00	1.87	2.35	4.58	16100
Bilayer	0.65	0.79	1.21	8.22	1.52	2.32
5 layers	0.36	0.16	1.15	6.84	2.39	1.47
10 layers	0.10	0.07	1.24	5.99	3.57	1.07

3.4. Optical properties

In optical properties, transmittance and reflectance spectra of all the samples with different thickness were recorded using UV-VIS-NIR double beam spectrometer in the range of 200 -1100 nm. Fig.3 (a) and 3(b) shows the transmittance and reflectance spectra for the alternate layers of Bi_2Te_3 and Sb_2Te_3 thin films of different thicknesses at room temperature. In fig.3 (a) it is clearly shown that transmittance increases with wavelength and decreases with film thickness [8]. High transmittance was observed near ultraviolet and visible regions in all the samples [14]. For 5 and 10 layered samples peaks are not clearly observed because at large thickness samples became partially opaque and light will not properly transmit to the samples.

Fig.3 (b) illustrate the reflectance spectra for different thicknesses. Graph shows that reflectance decreases with increasing wavelength and increases with thickness which is just opposite as transmittance spectra. For all the films minimum peaks in reflectance spectra and maximum peaks in transmittance spectra are found to be at same position which confirms the uniformity of the films.



(a) *(b)*

Fig. 3. (a) Transmittance spectra of Bi_2Te_3-Sb_2Te_3 thin films;
(b) Reflectance spectra of Bi_2Te_3-Sb_2Te_3 thin films.

The absorption coefficient (α) is determined from transmittance measurements using relation[14].

$$\alpha = \frac{2.303}{d}\log_{10}\left(\frac{1}{T}\right) \tag{4}$$

where ‘T’ is transmittance and ‘d’ is the thickness of the film.

The electronic transition between valence band and conduction band can also be calculated from absorption coefficient using,

$$\alpha = A(h\nu - E_g)^p \tag{5}$$

where A is a constant ‘E_g’ is band gap, ‘hν’ is incident photon energy and ‘P’ has discrete values like 1/2 3/2, 4/2…. etc. depending upon the transition. For direct and allowed transition P = ½, in direct but forbidden case P = 3/2, and for indirect and allowed transition P = 2 and for forbidden case it will be 2 or more. The band gap is determined by extrapolation on x-axis in curve between $(\alpha h\nu)^2$ and hν. The optical band gap has been determined for different thickness. Fig.4 shows that band gap increases with thickness and showing direct and allowed bands. These band gaps are in the range of semiconductor. These thin films having wide range of band gap (1.67 – 3.2) eV.

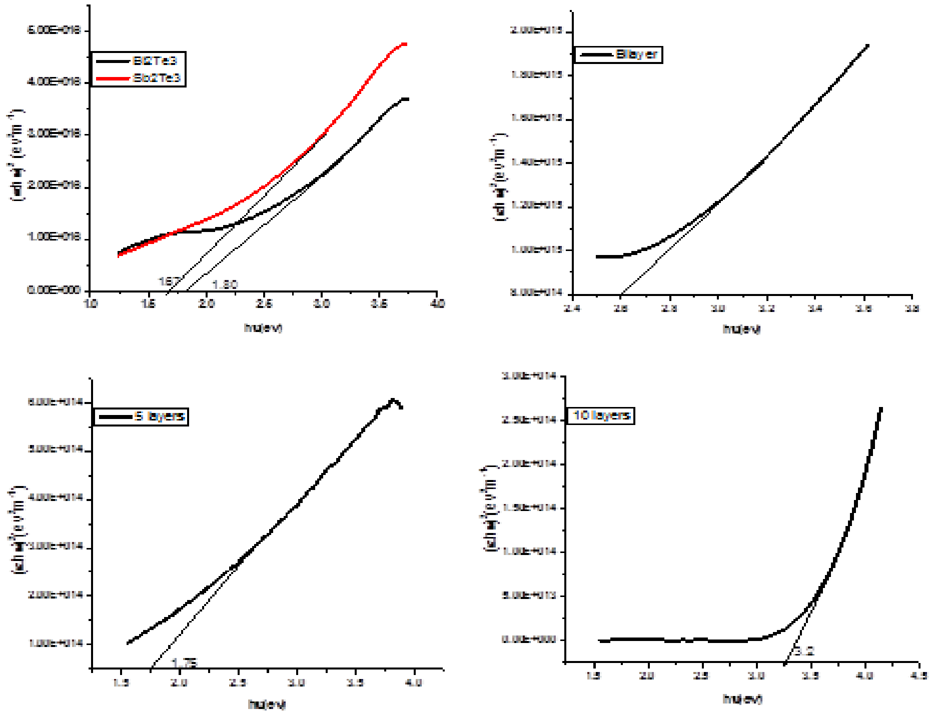


Fig. 4. Tauc Plots for Bi_2Te_3-Sb_2Te_3 thin films.

3.5. Thermal properties

In thermoelectric measurement Seebeck coefficients are measured at room temperature for all the prepared samples of various thicknesses. This is the most important measurement for selecting an efficient thermoelectric material. Results have been shown in table 4 that Single layer Bi_2Te_3 has negative Seebeck coefficient showing n-type charge conduction and others have positive seebeck coefficient showing p-type semiconductor. It can also be realized that maximum Seebeck coefficient and power factor is achieved for Sb_2Te_3 but when multilayer structure was formed their values decreases with thickness. The variation in Seebeck coefficient is may be due to diffusion of charge carriers between the layers. Graph in fig.5 has shown variation in Seebeck coefficient and power factor.

Table 4. Represent the Thermoelectrical properties of multilayers of Bi_2Te_3 - Sb_2Te_3.

Sample details	**Seebeck coefficient S (μV/K)**	**Resistivity ρ (μΩ-m)**	**Power factor (10^{-3} * W/m.K^2)**
Bi2Te3	-100	51.1	0.195
Sb2Te3	210	53.4	0.825
Bilayer	205	82.6	0.508
5 layers	150	86.9	0.258
10 layers	110	80.6	0.150

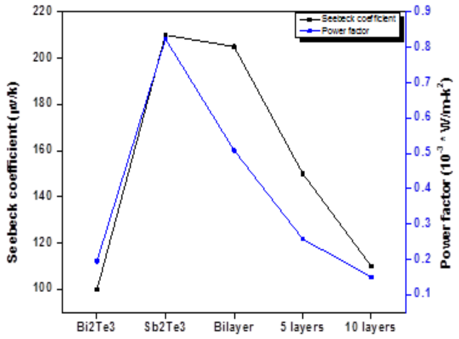


Fig. 5. Seebeck coefficient and power factor of Bi_2Te_3-Sb_2Te_3 thin films.

4. Conclusion

Multilayered thin films of alternate layers of Bi_2Te_3 and Sb_2Te_3 of thicknesses (50 to 1000 nm) were deposited using electron beam evaporation method. Some structural properties like XRD, electrical properties like I-V measurements, Hall Effect and optical properties of Bi_2Te_3 - Sb_2Te_3 thin films have been studied. XRD studies indicate that prepared samples having hexagonal structure with preferred orientation along (0 1 5). It is observed that crystallinity increases with thickness. Results have been shown that microstrain and dislocation density increases with thickness whereas grain size decreases. In Electrical properties, I-V measurement result shows that current flowing through the samples is in milliampere range which show semiconducting and non-ohmic behavior. Hall measurements show that conductivity decreases upto 5 layers and slightly increases for 10 layered sample. In optical properties, transmittance, reflectance and absorption coefficient are determined from absorption spectra. The possible optical transition is direct and allowed.

Optical band gap of the thin films are lies from (1.67 – 3.2)eV. Thermoelectric behavior of all the samples have been shown that maximum Seebeck coefficient (210μV/K) and power factor (0.825 $*10^{-3}$ W/m.K^2) is achieved for Sb_2Te_3 and their values decreases with sample thicknesses. From all the measurements it has been concluded from above discussion that prepared samples show semiconducting nature but as thickness increases they behave as topological insulators due to wide range of band gap. The thermoelectric measurements shows that single layer Sb_2Te_3 shows better thermoelectric properties than multilayer arrangement and as number of alternate layers increases its value going to decreases.

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