STRUCTURAL, MORPHOLOGICAL AND ELECTRICAL PROPERTIES OF THERMOELECTRIC THIN FILMS OF SB_2TE_3 DEPOSITED BY CO-EVAPORATION ON SILICON SUBSTRATE

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Abstract
The optimization of vacuum evaporation process for Sb_2Te_3 thin films onto silicon substrates for thermo electric applications is reported. Thin films of different thickness of compound Sb_2Te_3 as well as bi-layers of both elements Sb and Te were developed. Thickness measured 100nm and 26nm respectively at chamber pressure of 10^{-5} mbar. Thin films were annealed at room temperature and at 340°C. Structural and morphological properties of the films were investigated using angle dispersive X-ray diffraction (ADXRD), scanning electron microscopy (SEM). Electrical studies have been carried out using four probe methods and then the activation energies of each film before and after annealing are observed. Thermoelectric behavior of each sample is also determined at room temperature. With the increment in Temperature and decrement in thickness, formation of good quality nano dimensional crystalline thin films of Sb_2Te_3 having ohmic conductive behavior reported in this work.

Keywords: Antimony telluride, ADXRD, SEM, Four Probe.

1. Introduction: The world is facing the major challenge of finding energy sources to satisfy our energy consumptions which are increasing day by day. For this purpose thermoelectric materials may play the important role to improve the efficiency of the actual energy system by harvesting wasted heat. The materials which convert heat flow into electrical current and vice-versa are known as thermoelectric materials. The thermoelectric materials have the ability to act as thermoelectric devices that directly interconvert the energy between the heat and electricity due to thermoelectric effect. Thermo electric effect is the occurrence of an electrical field along a temperature gradient established in a materials [1].

Thermoelectric devices utilizing seeback effect and peltier effect have been widely investigated for thermoelectric application. Tellurium compounds (Sb_2Te_3 and Bi_2Te_3) have been extensively studied in the past years. Sb_2Te_3 and Bi_2Te_3 are good conventional thermoelectric materials. The study of thermoelectric properties of Sb_2Te_3 has generated a lot of interest for various applications. On the other hand Sb_2Te_3 is one of the best P-type thermoelectric materials for room temperature applications [2]. Also Sb_2Te_3 shows a crystalline- amorphous phase transition at a temperature of around 140°C [3]. Sb_2Te_3 has high potential for phase- change memory devices [4]. Sb_2Te_3 is a low temperature thermoelectric material which has a high seeback coefficients, low electrical resistivity and relatively low thermal conductivity which make this material more interesting for thermoelectric applications. The efficiency of thermoelectric materials depends upon the thermoelectric figure of merit Z_T which is a function of the seeback coefficient, electrical resistivity, thermal conductivity and absolute temperature. It is desirable to increase Z_T. This figure of merit Z_T can be calculated by the following formula:

$$Z_T = \frac{s^2 \sigma}{k} T$$

Where S^2/ρ or $S^2\sigma$ is the power factor, k is thermal conductivity, *S* is Seeback coefficient, ρ is electrical resistivity (σ is conductivity) and T is temperature in Kelvin [5].

For extracting better thermoelectric performance from any material system, Seeback coefficient and electrical conductivity must be enhanced simultaneously along with the reduction in thermal conductivity [6].

Sb_2Te_3 nano structures have been prepared by various methods including solvothermal, electrochemical deposition, and many more. These methods have their merits and demerits like solvothermal process produced nano crystals with good composition with uniform size and shape but the size and shape control requires insulating capping which should be removed to achieve appropriate electrical characteristics [7]. On the other hand electrochemical deposition technique produce nano crystals with predefined shape, size but it may require the removal of aluminum oxide templates [8].

Pardyumnan et al studied about the formation of Bi_2Te_3, Sb_2Te_3 and bi-layer of Bi_2Te_3- Sb_2Te_3 over glass substrate having the thickness of 100, 150 and 200 nm respectively [9]. Lee et al studied the theoretical and experimental characteristics of thermal transport of 100nm and 500 nm thick antimony telluride thin films prepared by radio frequency magnetron sputtering [10]. This work reported lesser thermal conductivity of Sb_2Te_3 in comparison to the bulk material, confirming that the phonon- and electron- boundary scattering are enhanced in thin film of Sb_2Te_3.

Present work carries Synthesis of thin films of Sb_2Te_3 and bi layer of Sb and Te of thickness 100nm and 26 nm respectively on the silicon substrate employing vacuum evaporation technique and their characterization using ADXRD, SEM and Four probe methods.

2. Experiment

Thin films of Sb and Te bi-layer and Sb_2Te_3 thin films were fabricated on Si base using co evaporation technique in a high vacuum chamber. Thickness of these films is kept 26 nm and 100 nm at chamber pressure of 10^{-5} mbar. These are grown on Si substrates. Power applied to each boat is controlled to maintain the deposition rate at a fixed value during the deposition. The deposition rate controlled by a thickness monitor (in built) and designed to compute real time values of power necessary to apply to corresponding boats to achieve user defined constant evaporation rate. The thickness monitor, basically a quartz crystal oscillator placed inside the chamber.

The substrates were heated to the temperature range up to 340°C. The film composition and structure were observed by SEM and ADXRD and Electrical characteristics were observed by four probe method.

2.1. Synthesis of Sb_2Te_3 thin films

Te powder (Aldrich, 99.8%, 200 mesh) and Sb powder (sigma- Aldrich, 99.5%, 100 mesh) were used as received. Si wafer were carefully washed by acetone. The experiment of deposition of thin films (bi-layer and compound of Sb_2Te_3) on silicon substrate was carried out in a vacuum chamber using vapor deposition technique. In a vacuum chamber Sb was placed in a boat located downstream to Te boat and deposition done at the chamber pressure of 10^{-5} mbar. Thickness of Sb and Te Bi-layer was measured 26 nm by thickness monitor. Thickness of Compound layer was kept 100nm. Thin films were also annealed at 340°C

2.2. Characterizations

The as- deposited and annealed Sb_2Te_3 thin films and bi-layers thin films on Si substrates were directly used for ADXRD and SEM measurements. The Angle dispersive X-ray diffraction was obtained at beam line 12 at INDUS-2, RRCAT, Indore, India. Which is a bending magnet based, high resolution XRD beam line having 2.5GeV, 300mA with a photon energy range of 5-25 KeV. The size and morphology of the particles in the thin films were characterized using Field emission gun-scanning electron microscopes (FEG- SEM) (JEOL JSM-7600F) at INUP, IIT bombay, India.

2.3. Electric Properties characterization

The measurement of resistivity was carried out by one of the standard and most widely used four probe apparatus. The experimental set up consists of probe arrangement, sample, oven 0-200°C, constant current generator, oven power supply and digital panel meter (measuring voltage and current). Voltage and current readings were measured for both compound and bi-layer thin films of as deposited and annealed thin films.

2.4. Thermoelectric Characterization

The samples were tested in a chamber, where the difference in temperature at two ends of the sample was measured by placing two thermocouples at the ends of the sample. In order to create a temperature gradient along with the sample, only one end of the sample was heated leading to the creation of a hot junction and cold junction. One of the thermocouple measures the temperature at the hot junction of the sample whereas the other thermocouple measures the temperature at the cold junction. A graph of the measured thermoelectric against temperature difference is plotted. The slope of the curve thus obtained gives the Seeback coefficient of the film. The Seeback coefficient of the deposited thin film was found to be positive confirming to the P type behavior of the thin films.

3. Results

3.1 ADXRD analysis

The ADXRD diffraction analysis (fig 3) shows the diffraction patterns of compound Sb_2Te_3 and bi-layer films of antimony and tellurium grown at Room temperature and annealed at 340°C. Graph A shows the XRD pattern of Sb_2Te layer at room temperature whereas graph B shows the XRD pattern of same thin film annealed at 340°C, Graph C shows the XRD pattern of bi layer of Sb and Te annealed at 340°C. From the figure 3 it reveals the crystalline structure of annealed Sb_2Te_3 thin film comparatively as deposited Sb_2Te_3 at room temperature. Similar behavior reported by bi-layer thin films of Sb and Te annealed at 340°C as shown in Graph C.

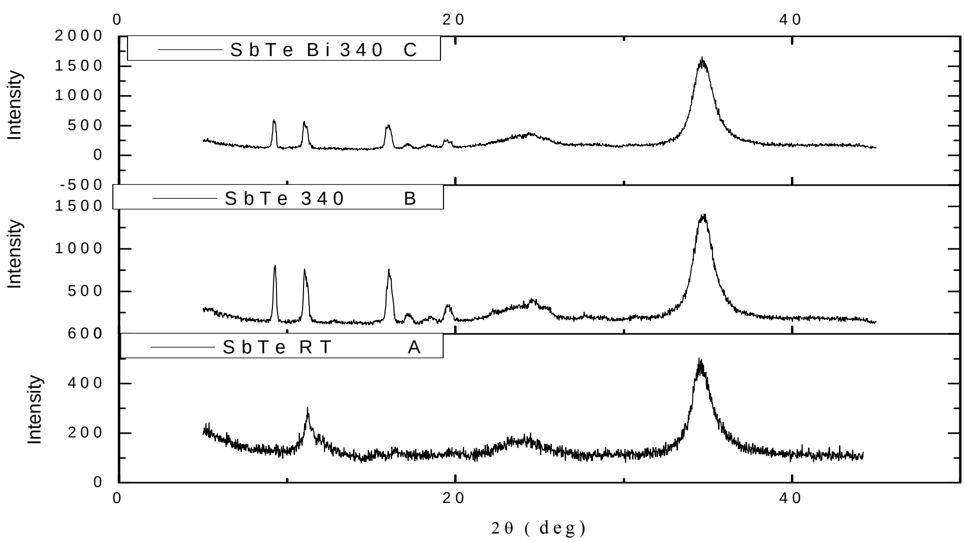
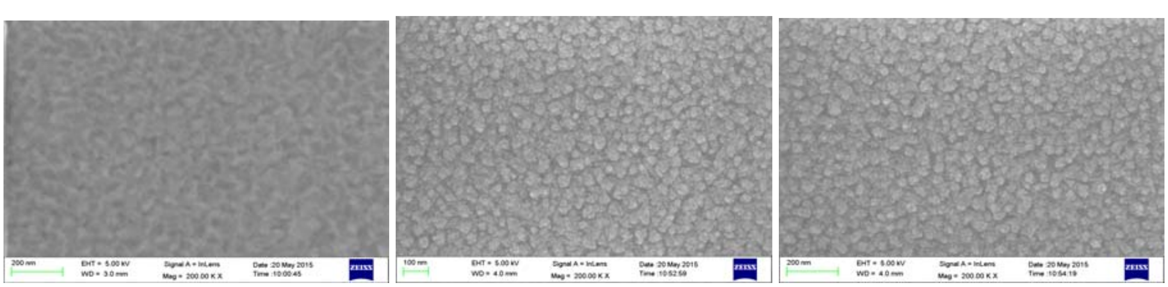


Fig. 1 : ADXRD patterns of Sb_2Te_3 and bi layer as deposited and Annealed at 340°C

3.2 Surface Morphology

The surface morphology of antimony telluride compound thin films and bi-layer thin films of Sb and Te by the SEM measurements as shown in fig 2. From the SEM measurements it can be seen that films are continuous, homogeneous with high compactness whereas figure 2.2 and figure 2.3 shows the grain size larger and crystalline than that of as deposited thin film (figure 2.1) Which satisfy the agreement with the ADXRD results.



(2.1) (2.2) (2.3)

Fig. 2: SEM patterns of different thin films

(2.1) As deposited Sb_2Te_3 (2.2) Sb_2Te_3 annealed at 340, (2.3) Sb Te bi- layer annealed at 340°C

3.3 I-V characteristics

I-V characteristics were taken for samples of Sb_2Te_3 thin films as deposited at room temperature and annealed at 340°C along with bi-layer thin film of Sb and Te annealed at 340°C. The plot 'a' is for compound Sb_2Te_3 grown at room temperature and 'b' is for this same thin film annealed at 340°C while 'c' is for bi-layer thin film of Sb and Te annealed at 340°C.

The I-V curves (Figure 3) indicate ohmic conduction throughout the voltage (from lower voltages to higher voltage region) i.e. the current changes linearly with voltage, for all thin films of Sb_2Te_3 as deposited as well as annealed at 340°C and bi-layer of Sb and Te annealed at 340°C. Also the slope of Sb_2Te_3 annealed at 340°C is increased; this confirms the presence of injected space charge due to high temperature. Whereas resistance of bi-layer thin film report close to as deposited compound thin films.

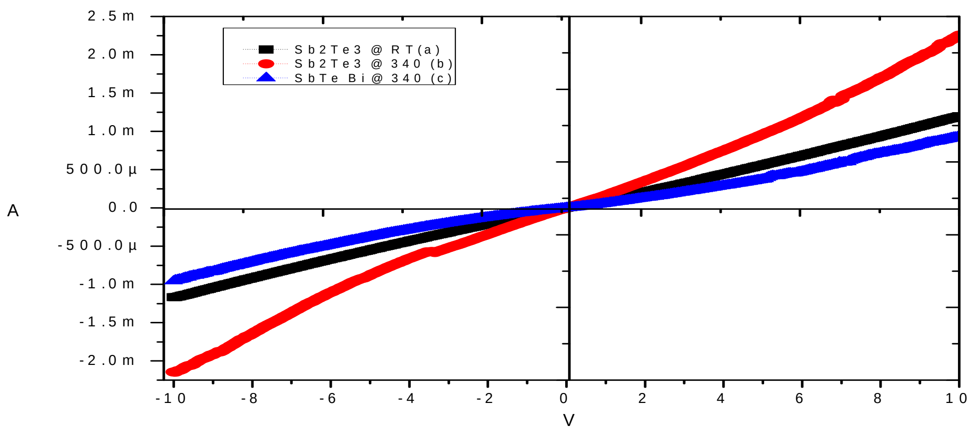


Fig. 3: IV Characteristics

3.3.1 Resistivity: Fig.4 shows the result of resistivity measurement by four-probe apparatus within the range of 320K to 380K. It reveals that all three types of thin films have low electrical resistivity in the range of $4X10^{-5}$ Ω-m. for thermoelectric semiconductors low electrical resistivity is essential to achieve high ZT value. For all three types of thin films the electrical resistivity decrease with the temperature. As shown in figure 4, annealing of thin films decreases the electrical resistivity. It means it leads to enhance the contact between the particles in the annealed samples which is evident from the SEM observations.

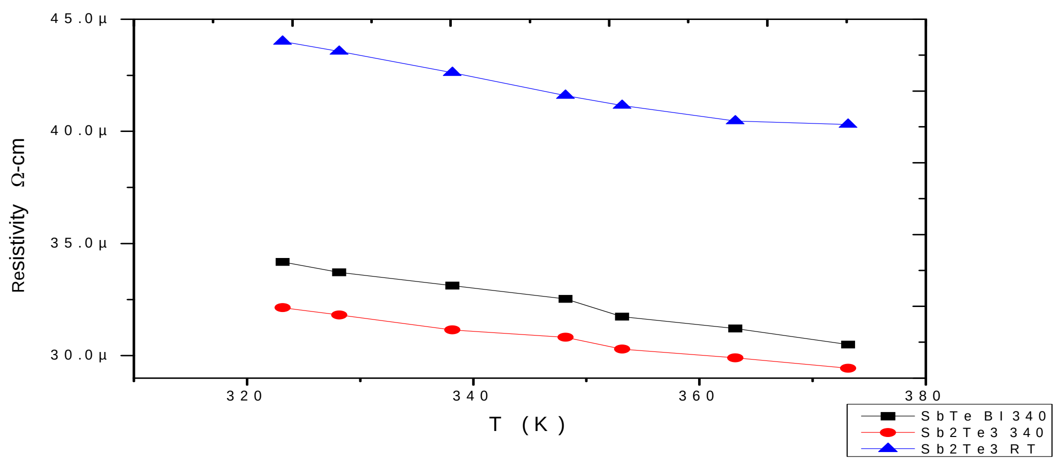


Fig.:4 Electrical Resistivity of Bi-layer and compound Sb_2Te_3 thin films as deposited and annealed at 340°C

3.4 Thermoelectric characteristics

The Seeback coefficients, S dependence on the temperature are shown in fig. 5 In the extrinsic conductive region, the increase in thermoelectric power with temperature is due to the increasing number of thermally excited carriers. The Seeback coefficients of the films increases with the increment in temperature.

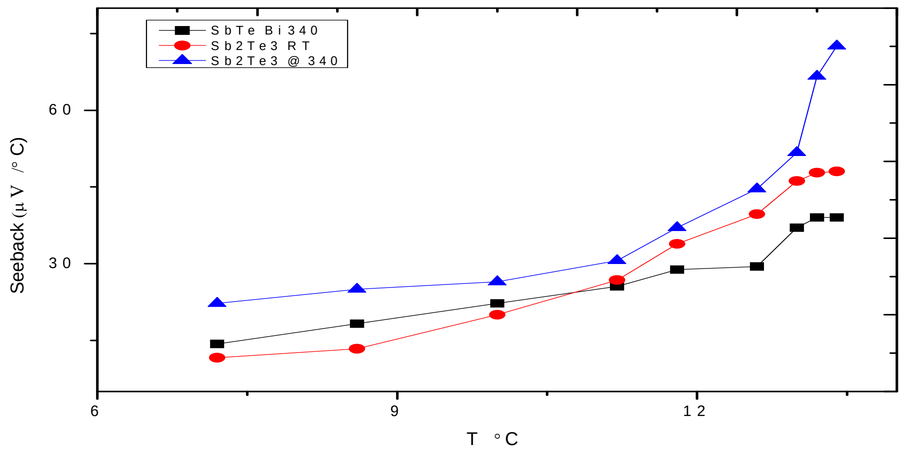


Fig.:5 Variation of Seeback coefficient with temperature for different samples

Table 1: Properties of Selected Sb2Te3 and Bi-layer of Sb-Te thin films

Samples	Seeback coefficient (S) (μV/°C)	Resistivity (ρ) Ω-m	P.F. $x10^{-3}$ $W.K^{-2}.m^{-1}$
Sb_2Te_3 RT	46.15	4.15939E-05	.05
Sb_2Te_3 340	72.58	3.18079E-05	.16
SbTe Bi 340	37.03	3.41787E-05	.04

It can be realized from the table 1 that the Seebeck coefficient value is with positive sign suggesting P-type charge conduction. When the bi-layer structure was formed, the positive value of overall Seebeck coefficient suggests that p-type charge carrier dominates in this arrangement also. When the compound thin film composition is done at 340°C we observe the high value of Seebeck coefficient compare to as deposited compound thin films and bi-layer of Sb- Te thin film. The Seebeck coefficient of the Bi-layer arrangement was close to as deposited Sb_2Te_3 thin films. Also the electrical resistivity increased at increased substrate temperature. In the given table 1 we observe max electrical resistivity of annealed thin films of Sb_2Te_3 also power factor reported maximum for same thin film. Here from the table 1, it is observed that annealed Bi-layer thin film has close behavior to as deposited Sb_2Te_3 thin films.

4. Conclusion

Sb_2Te_3 compound and bi-layer Sb and Te thin films were fabricated by co-evaporation deposition methods. Thin films were deposited on silicon substrate. ADXRD, SEM results show the crystalline and homogenous structure of Sb_2Te_3 as-deposited, annealed at 340°C and bi-layer thin film of Sb and Te annealed at 340°C. Increment in the substrate temperature of bi-layer thin films reports the close behavior to that of compound thin films. The thermoelectric properties of the thin films have been evaluated at room temperature via Seebeck coefficient, and electrical resistivity measurement. The power factor value has increased reasonably well in case of annealed compound Sb_2Te_3 thin film whereas the power value of bi-layer reached approximately close to that of Compound Sb_2Te_3 as deposited thin film. These results indicate that good quality antimony telluride, bi-layer combination of thin films were grown by evaporation technique and enhancement of seebeck coefficient and power factor by increasing Temperature will be a good engineering aspect which designing and fabrication of micro-peltier modules.

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