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Thickness Dependence Electric and Thermoelectric Properties of Thermally Evaporated Nanostructured Bismuth Selenide Thin Films

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Abstract: *This paper investigates the thermoelectric and electrical characteristics of bismuth selenide (Bi_2Se_3) thin films, a promising topological insulator, at various thicknesses. We reveal how precise control over growth parameters can significantly influence carrier mobility, which is critical for optimizing the material's thermoelectric figure of merit. The Bi_2Se_3 films of various thicknesses have been prepared by thermal evaporation technique at room temperature and then annealed in vacuum ($\approx 10^{-5}$ torr). All the film samples of annealed Sb_2Te_3 thin films have positive temperature coefficients of resistivity, which suggested their conducting nature. The resistivity decreases with increasing film thickness for all the samples, it varies from 0.627 to 2.114 mΩ cm. Thermo emf as well as thermoelectric power of Sb_2Te_3 thin films found to be positive for all thicknesses indicating that Sb_2Te_3 is p-type material. The Seebeck coefficient shows oscillatory behavior with the film thickness.*

Keywords: Thermal evaporation**,** thermo emf, thermoelectric power, resistivity, Seebeck coefficient

I. INTRODUCTION

The utilization of bismuth selenide (Bi_2Se_3) as a thermoelectric material has garnered considerable interest due to its unique electronic band structure and robust topological surface states [1]. To construct high-performance thermoelectric devices, superior thermoelectric materials must be developed, which necessitates optimizing key parameters such as the Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ) [2]. The overall efficiency of a thermoelectric material is quantified by its dimensionless figure of merit, ZT [3]. For fabrication of the Bi_2Se_3 thin films a variety of preparation techniques have been employed such as chemical bath deposition [4], SILAR method, [5], electro deposition [6], Molecular beam epitaxy [7], reactive evaporation [8] and thermal evaporation [9]. All these techniques have their own merits and demerits in producing high quality Bi_2Se_3 thin films.

However, challenges remain in scaling up the production of these advanced materials while maintaining their exceptional thermoelectric performance and ensuring their long-term stability [10]. Thus, the development of robust, flexible and high-performance thermoelectric materials, particularly thin films, is critical for addressing the growing demand for efficient waste heat recovery and advanced thermal management in diverse applications, ranging from wearable electronics to industrial processes. This paper, therefore, aims to thoroughly investigate the thermoelectric and electrical properties of Bi_2Se_3 thin films, analyzing the impact of film thickness on their performance. Specifically the effect on resistivity and Seebeck coefficient of Bi_2Se_3 films, which are crucial for optimizing their power factor.

II. EXPERIMENTAL

The Bi_2Se_3 films of various thicknesses were deposited onto unheated well cleaned glass substrates by thermal evaporation in vacuum ($\approx 10^{-5}$ torr) using Bi_2Se_3 powder (Sigma-Aldrich 99.99+ % purity) and molybdenum boat as a source. All samples of different thicknesses were deposited under almost the same environment and deposition conditions. The rate of deposition and thickness of the films were roughly estimated by using quartz crystal thickness

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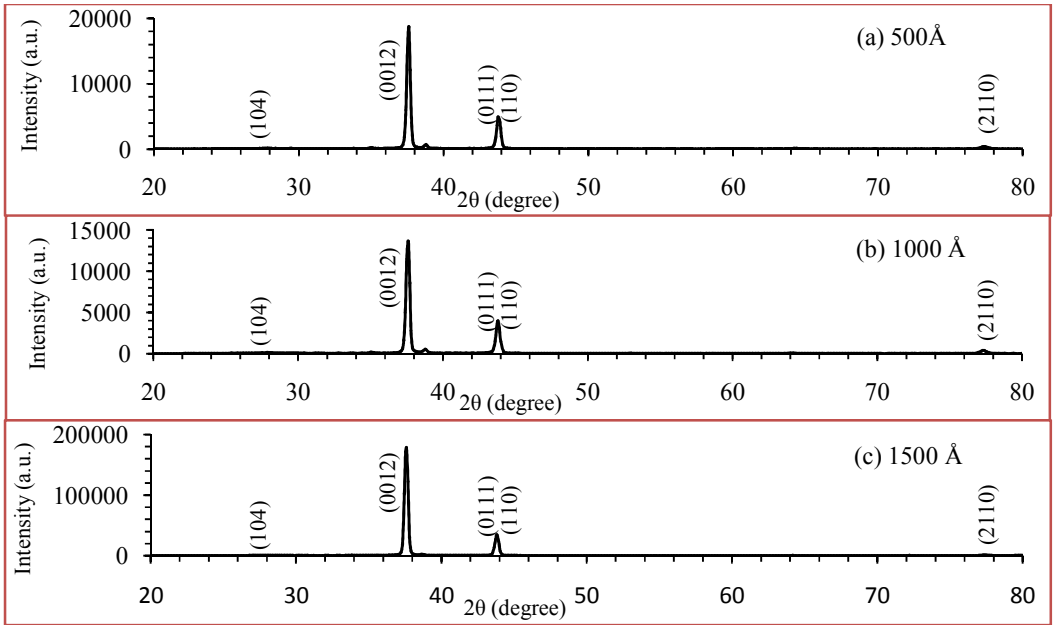
monitor model no. DTM-101 provided by HINDHIVAC. The deposition rate was maintained 3–5 Å/sec constant throughout the samples preparations. The film thicknesses were confirmed by using weight - difference method with the help of digital balance (DENOVER-Germany, Model: TB-214) having accuracy of 0.1 mg. The source to substrate distance was kept 14 cm and the alumel-chromel thermocouple placed in contact with the substrates revealed that the substrate temperature remains practically constant (≈ 305 K) during the deposition. Deposited samples were kept under vacuum overnight. The set of selected samples with six different thicknesses were annealed at 423 K for 60 min. in vacuum (≈10^{-5} torr).

Structural Characterization: The X-ray diffraction (XRD) patterns of selected Bi_2Se_3 samples were recorded by an X-ray diffractometer (Bruker, model D-8 Advance) with CuKα radiation (1.5406 Å). The surface morphology and the chemical composition of these films were investigated by field emission scanning electron microscope (FESEM) attached with EDAX using the model Hitachi S-4800-II (Japan).

Thermoelectric Characterization: Using the four probe set-up model: DFP-03 provided by "SES Instruments Pvt. Ltd., Roorkee" the electrical resistivity of annealed samples having different thicknesses was determined in the temperature range from 303 K to 473 K. The thermoelectric studies of annealed Bi_2Se_3 samples have been carried out by means of the experimental set up provided by "Pushpa Scientific Co., Hyderabad" in the temperature range from 308 K to 473 K.

III. RESULT AND DISSCUSSION

Microstructural Analysis: The X-ray diffraction pattern of the Bi_2Se_3 film of thicknesses 500 Å, 1000 Å, 1500 Å, 2000 Å, 2500 Å and 3000 Å annealed at 423 K for 60 min. in vacuum (≈10^{-5} torr) is shown in Fig. 1 (a) to (f). All XRD patterns exhibits polycrystalline nature. For the films of all the thicknesses 500 Å to 3000 Å major diffraction peaks are observed at 2θ ≈ 37.6° and 2θ ≈ 43.77° which corresponds to the (0012) and (110) plane respectively of rhombohedral phase, confirmed by JCPDS X-ray powder file data (33-0214).



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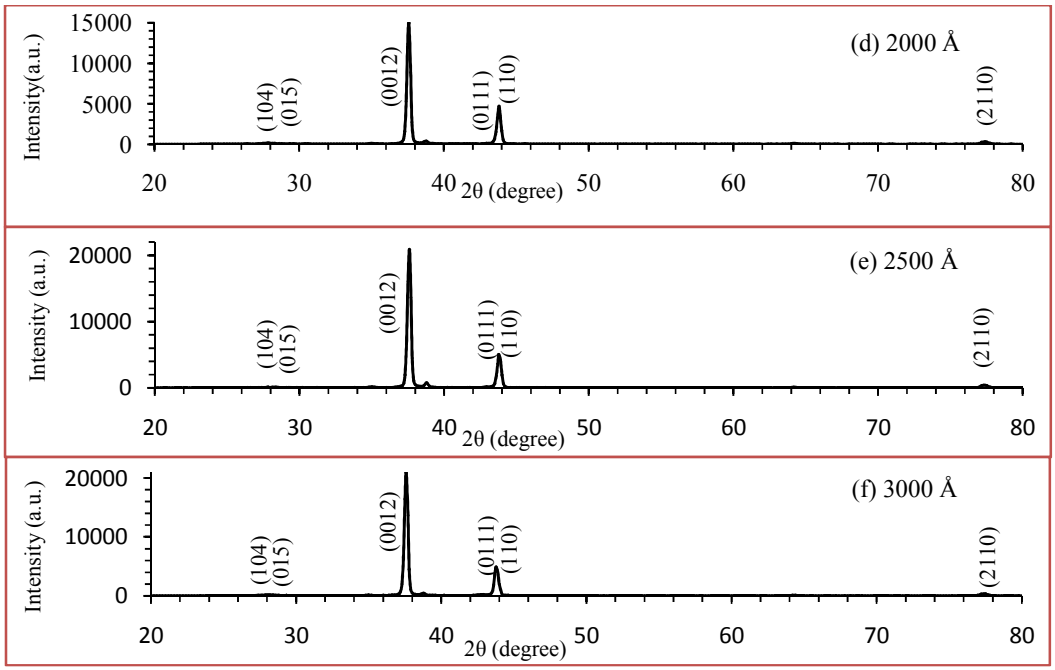

Fig. 1 XRD spectrum of Bi_2Se_3 films annealed at 423 K for 60 min in vacuum (≈ 10^{-5} torr)

Weak peaks corresponding to the reflection planes (104), (1010), (0111) and (2110) appears proving the microcrystalline nature of the film. A minor peak is observed at 2θ equal to 29.35°corresponding to the (015) plane at higher film thickness of 2000 Å, 2500 Å and 3000 Å. The diffraction peaks were observed corresponding to the rhombohedral crystal structure of Bi_2Se_3 which consists of hexagonal atomic layers of Bi and Se stacked along the c-axis.

All the films possess enhanced crystallanity. It is observed that the diffraction intensity for (0012) orientation increases with increase in film thickness due to the growth of the materials incorporated in the diffraction process [11]. This improvement in orientation is a result of the sufficient amount of energy acquired by the atoms on annealing which enable them to arrange themselves to the optimum orientation along the plane [12].

FESEM Micrograph and EDAX analysis: Fig. 2 (a) to (c) shows the FESEM images of thermally evaporated Bi_2Se_3 thin films annealed at 423 K for 60 min. in vacuum (≈ 10^{-5} torr) of thicknesses 1000 Å, 2000 Å and 3000 Å respectively. The FESEM micrographs are analyzed at a resolution of 0.2 µm with 60000 X magnification. It was observed that the surface has smooth and dense morphologies without any cracks. The micrographs show total coverage of the substrate surface with clear grains. FESEM images also shows whitish randomly spread nano size particles; the number of these whitish nano particles gets reduced with the increase in film thickness. The grains are found to be closely packed, this result in better crystallanity of the films. The crystallites with dimensions of the order of 30 to 50 nm are seen on the film surface which clearly supports the crystallite size calculated from the XRD pattern. The grains are very clear and hexagonal shaped with orientation along the C axis with less defect density and good crystalline quality.

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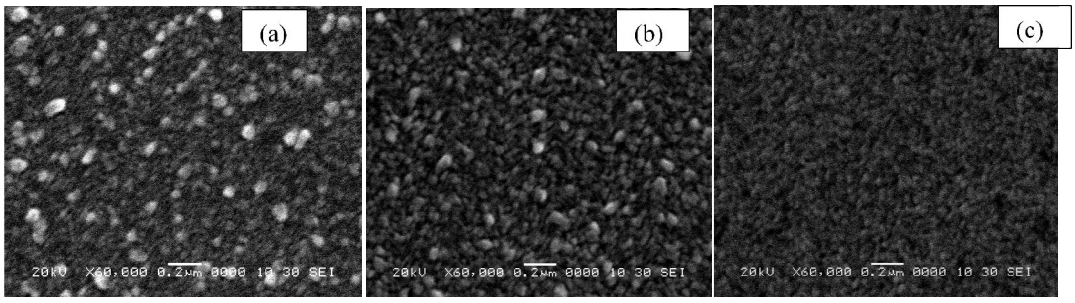

Fig. 2 FESEM images of Bi_2Se_3 thin films of thicknesses (a) 1000 Å, (b) 2000 Å and (c) 3000 Å annealed at 423 K for 60 min. in vacuum (≈10^{-5} torr)

The elemental analysis by EDAX of the annealed Bi_2Se_3 thin films shows that all the films are non-stoichiometric. With increase in thickness; the contents of the films go close to stoichiometry. For all thicknesses the films are Bi rich, this large selenium loss could be due to small thickness of the film and high partial pressure of selenium at higher temperature [5].

Resistivity analysis: The variation of log of resistivity (1+ Logρ) as a function of inverse of temperature (1/T) for the annealed Bi_2Se_3 thin films is given away in Fig. 3. From the graph it is apparent that the resistivity decreases with increase in temperature, representing that all the films have negative temperature coefficients of resistivity, which suggested their semiconducting nature as earlier reports [13,14,15].The graphs shows linear variation of (1+ Logρ) in the temperature range 303-473K.

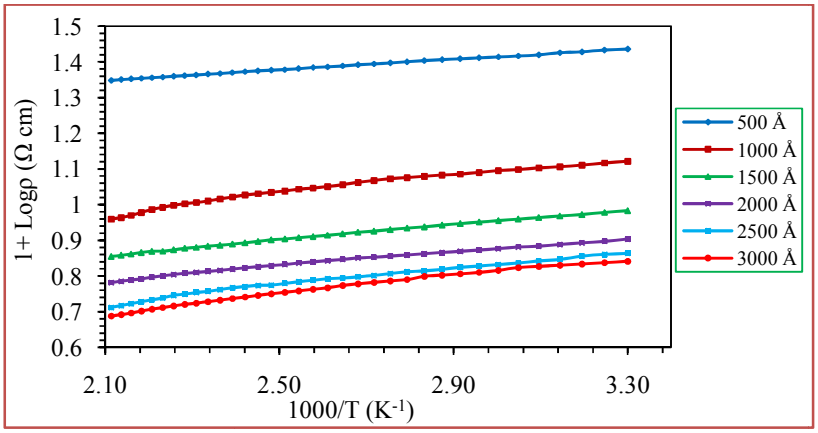

Fig. 3 Variation of 1+ Logρ Vs reciprocal of temperature for annealed Bi_2Se_3 thin films

Resistivity - thickness dependence: Fig. 4 illustrates the variation of the electrical resistivity ρ with film thickness at temperature 473 K for annealed Bi_2Se_3 films. It is seen that for annealed samples the resistivity decreases stridently with increasing film thickness from 500 Å to 1000 Å, then it sluggish for higher thicknesses and becomes almost constant. Thus the conductivity increases for higher film thicknesses [11]. This suggests that the lattice defect becomes slighter for higher thickness films. C. D. Lokhande [13] reported the dark electrical resistivity of chemically deposited Bi_2Se_3 films about 10^4 Ω cm, conversely the minimum value 18.2 μΩ m was reported by A. Al Bayaz [16] for reactive evaporated Bi_2Se_3 films. The present work shows the optimum value of electrical resistivity about 2 Ω cm, it needs more study. The low resistivity films are very important for applications in the Peltier micro-module.

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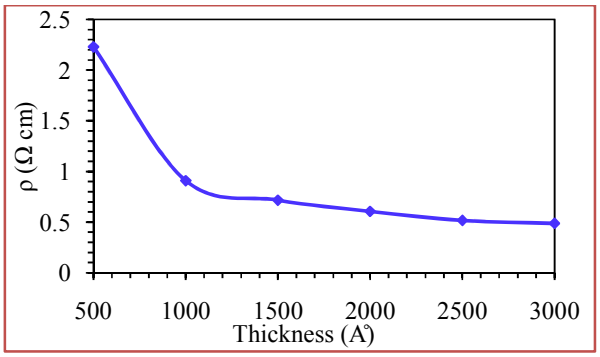

Fig. 4 Effect of film thickness on the electrical resistivity ρ of annealed Bi_2Se_3 thin films

TEP analysis: The temperature gradient in a semiconductor gives away thermoelectric effect, in which phonons travels preferentially from the hot end to cold end because of electron – phonon interactions. Throughout TEP measurements, thermal gradient established changes of the density of charged defect state by capturing electrons and holes. The motion of the electrons and holes can take place through the process of diffusion.

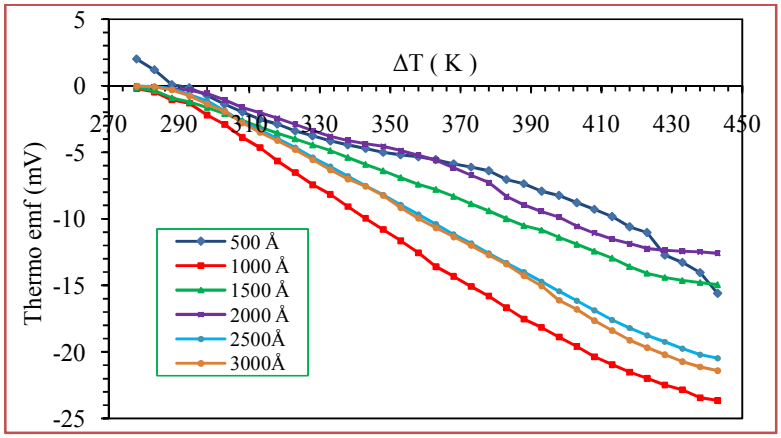

Fig. 5 Thermo emf as a function of temperature difference for the annealed Bi_2Se_3 thin films

Fig. 5 shows the variation of thermo emf with temperature difference for the annealed Bi_2Se_3 films of various thicknesses. It was seen that thermo emf is negative for all the films throughout the temperature range, signifying that the samples are n-type semiconductor, except for the film of thickness 500 Å up to temperature difference of 15 ^oC. The thermo emf increases with increasing temperature difference, which can be attributed to increase in concentration and mobility of charge carriers with rise in temperature [14].

The Fig. 6 shows variation of thermoelectric power or Seebeck coefficient as a function of hot junction temperature for annealed Bi_2Se_3 films of different thicknesses. Thermo emf and thermoelectric power of Bi_2Se_3 films was found to be negative for all samples, is an indication of n-type semiconductor material. The thermo electric power increases with increase in temperature about linearly. Similar results were reported by S. H. Pawar [17] and R. H. Bari [18]. It was observed that Seebeck coefficient has its maximum value around the hot junction temperature of 468 K.

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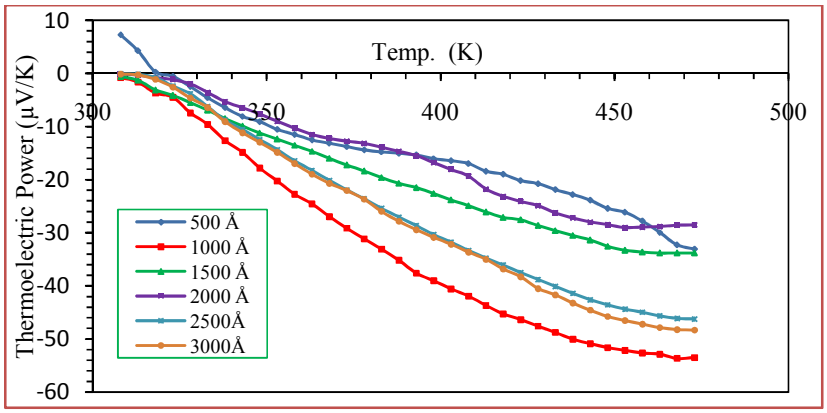

Fig. 6 Variation of thermoelectric power with temperature for the annealed Bi_2Se_3 thin films

The dependence of Seebeck coefficient at 473 K on the thickness of annealed Bi_2Se_3 thin films is exposed in Fig. 7, it show the oscillatory behavior.

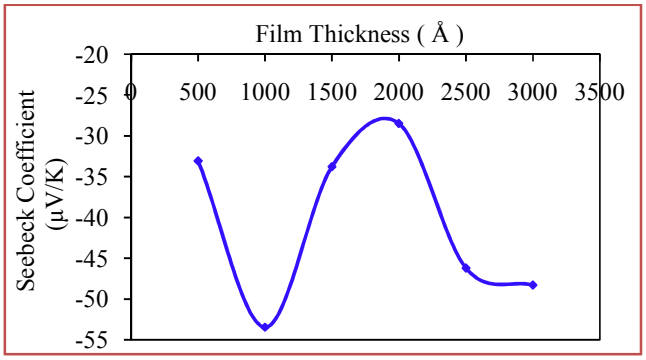

Fig. 7 Seebeck coefficient- thickness dependence at 473 K of annealed Bi_2Se_3 thin films

The maximum negative value of Seebeck coefficient is obtained for the film of thickness 1000 Å. The thermoelectric properties shows oscillatory behavior as a result of quantum size effects, i. e. the size quantization taking place in a film when its thickness becomes comparable to the de-Broglie wavelength [19].

IV. CONCLUSION

The XRD of the thermally evaporated Bi_2Se_3 films annealed at 423 K for 60 min. in vacuum shows that all patterns exhibits polycrystalline nature which corresponds to the (0012) plane of rhombohedral structure. The increase in the film thickness gives rise to increase the diffraction intensity for (0012) orientation, the grain size and the degree of preferred orientation. The EDAX analysis shows that all the films are non-stoichiometric. With increase in thickness; the contents of the films go near to stoichiometry. The grains are found to be closely packed having better crystallanity and crystallites with dimensions of the order of 30 to 50 nm. The resistivity of all the films decreases with increase in temperature; it represents negative temperature coefficients of resistivity and implies their semiconducting nature. Thermo emf and thermoelectric power was found to be negative for all the samples, indicates n-type semiconductor material. Thermoelectric power increases almost linearly with increase in temperature and has maximum value for the film of thickness 1000 Å. Variations in thermoelectric power with respect to film thickness found to be oscillatory.

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