SYNTHESIS AND CHARACTERIZATION STUDIES ON DIFFERENT THICKNESSES OF VACUUM EVAPORATED Bi_2Se_3 THIN FILMS

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***Abstract* - Polycrystalline bismuth selenide films of different thickness were deposited by thermal evaporation technique under vacuum of about 10^{-5} torr onto precleaned amorphous glass substrate. The structural, morphological, Thermal, electrical, optical and magnetic properties of the different thickness samples were studied by X-ray diffraction, scanning electron microscope (SEM) and atomic force microscope (AFM), TEP setup, Four probe technique, UV- Vis spectrophotometer and Hall effect setup respectively. It is observed that the activation energy, Fermi energy etc. decreases whereas the value of band gap energy goes on increasing with increasing in thickness of Bi_2Se_3 Thin Films.**

***Keywords*— Thermal evaporation, Activation energy, Fermi energy, Energy band gap, TEP.**

1. INTRODUCTION

In recent years, many research work has been done on the material properties such as change in grain size, thickness etc. and it opened a new chapter in the field of electronic applications [1]. The Bi_2Se_3 semi-conducting thin film materials, have recently attracted much interest as materials for optoelectronics technology. The Bi_2Se_3 is a member of the family of V – VI semi-conducting materials, which is most powerfull material in the field of thermoelectric power, photosensitivity, photoconductivity etc. applications [2-4]. The Bi_2Se_3 is a narrow gap semiconductor with 0.24 eV energy band gap [5] and motivated from its suitable optical and electrical properties for construction of optical and photosensitive devices, modern thermoelectric, Hall effect, magnetometer, high frequency power sensor, wide band radiation detector and humidity sensor using the Seeback and Peltier effects [6-9]. The Bi_2Se_3 have been prepared using various techniques [10-14]. This variety in preparation leads to inconsistencies in properties of Bi_2Se_3 thin films in the literature. Therefore, in the present investigation, Bi_2Se_3 thin films have been deposited by vacuum thermal evaporation technique. The preparative parameters are adjusted to get nanocrystalline thin films. These films are characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscopy (AFM), Four probe, Hall effect etc. for structural, morphological, electrical and magnetic studies.

2. EXPERIMENTAL

2.1 PREPARATION OF COMPOUND INGOT

The bulk samples of Bi_2Se_3 have been prepared by melt quench method. The direct mixture of extremely pure Bi and Se (purity 99.999%), in accordance with their atomic ratio was kept back in evacuated quartz ampoule at pressure 10^{-5} torr. The ampoule was heated at temperature about 970ºC for 12 hours duration. Then the ampoule is quenched in ice cooled water.

2.2 SYNTHESIS OF THIN FILMS

Polycrystalline bismuth selenide films have been deposited by thermal evaporation technique under vacuum of about 10^{-5} torr onto precleaned amorphous glass substrate. The substrate to source distance was kept 13 cm. The samples of different thicknesses were deposited under similar conditions. The thickness of the films was controlled by quartz crystal thickness monitor model No. DTM-101 provided by Hind-Hi Vac. Further confirmation of thickness was estimated by Tolansky's method using multiple beam Fizeau fringes. The deposition rate was maintained 5-10 Å/sec throughout sample preparation. Before evaporation, the glass substrates were cleaned thoroughly using concentrated chromic acid, detergent, isopropyl alcohol and distilled water.

Various characterization technique such as X – Ray diffractograms (Bruker, Germany), optical microscopy, Scanning Electron Microscope (Zeiss EVO 50) and Atomic Force Microscopy (AFM) were employed to study the films. The structural properties of thin films were investigated by XRD using CuKα (λ = 1.5418 Å) radiation. Surface morphological studies of were done using the Scanning Electron Microscope (Zeiss EVO 50) operating with an accelerating voltage 10 KV and Atomic Force Microscopy (AFM). The quantitative compositional analysis of the CdS films was carried out by EDAX (Energy dispersive X-ray Analyzer) technique attached with the SEM. Electrical and magnetic properties were studied with the help of four probe and Hall effect setup respectively.

3. RESULTS AND DISCUSSIONS:

3.1 STRUCTURAL STUDY:

X-ray diffraction patterns of the Bi_2Se_3 thin film having thickness 2000Å (on glass substrates) recorded in the range of 20–80_ at room temperature on Brucker D8 advance powder diffractometer (Cu Ka radiations k = 1.5416 Å) shown in Fig. 1.

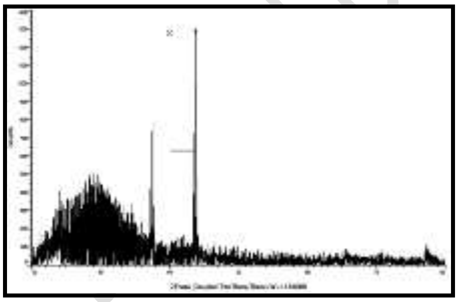

Fig. 1: XRD pattern of Bi_2Se_3 of thickness 2000 Å

The dominating peak at 43.570^0 corresponding to the reflection plane of (109) reveals the microcrystalline nature of the film with hexagonal structure and it is good agreement with literature data [15]. The presence of large number of peaks indicates that the films are polycrystalline in nature. The degree of purity of the material obtained is relatively high. Thus, the recorded XRD patterns do not show peaks due to the various forms of Bi_2O_3 or Bi_2O_5Se that could be also formed during the deposition process. The lattice parameters 'a' & 'c' were calculated by the formula given in eq. (1) and it is determined as 4.18 Å and 22.79Å respectively. Using Debye Scherrer's formula [16] given in eq. (2), the crystalline size (D) was calculated from full width half maxima (FWHM) of major XRD peak at 2θ = 43.693°.

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \text{ ---------(1)}$$

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ ---------------(2)}$$

Here, λ is the wavelength of the X-ray radiation (k = 1.5416 Å), K is the shape factor (0.9), β is the FWHM in radians; θ is the Bragg's angle in degree. It is found that the average grain size is 9.8 nm. . The volume of unit cell also calculated by the formula [17] and it is found that volume of unit cell is 345 which is in good agreement with the values listed by the American society for testing materials (ASTM)

$$V = 0.866\, a^2 c \text{ ---------------(3)}$$

3.2. MICROSTRUCTURAL STUDY

The morphology of prepared sample was done with the help of scanning Electron Microscopy (SEM) shown in Fig. 2 (a). The SEM images of Bi_2Se_3 thin film of thickness 2000Å with magnifications 120KX is shown in Fig. 2(a). From SEM image it is observed that the nano rods are uniformly distributed over smooth substrate and it is well agreement with literature data [15]. It is seen that substrate is well covered by Bi_2Se_3. The average particle sizes were calculated from SEM images was 330.4 nm. The cross sectional micro structure was observed by high resolution scanning electron microscope with compositional contrast detectors of magnifications 50 KX as shown in Fig. 2(b).

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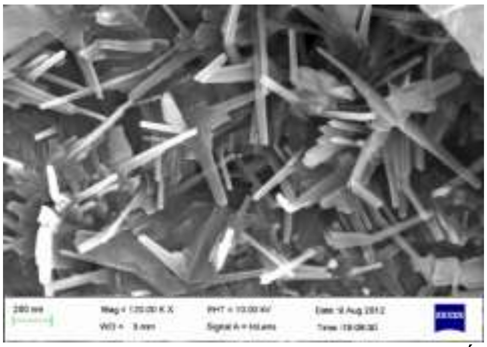


Fig. 2**:** (a) SEM image of thickness 2000Ǻ

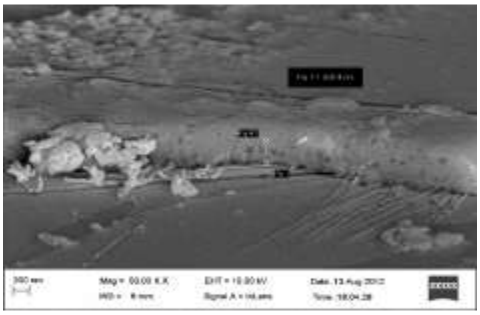


Fig. 2**:** (b) Cross sectional area of thickness 2000Ǻ

The EDAX elemental analysis of Bi and Se has been carried out EDAX in the binding energy region between 0 to 10 KeV of Bi_2Se_3 thin film having thickness 2000Ǻ shown in Fig. 2 (c).

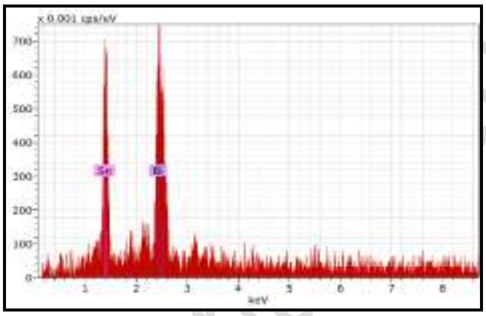
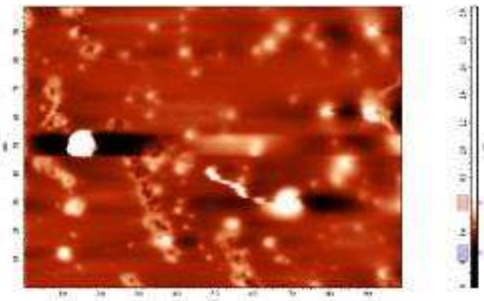
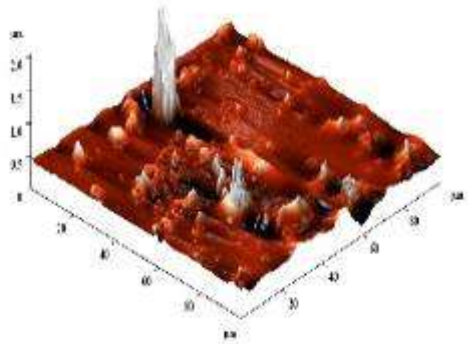


Fig. 2 (c): EDAX spectrums of Bi_2Se_3thin film of thickness 2000Ǻ

The spectrum peak reveals presence of Bi and Se at 1.2 and 2.3KeV which confirms the presence of Bi and Se and there was no evidence for the appreciable amounts of impurities. The atomic percentage of Bi and Se were found to be 53.02% and 49.98% respectively [18]. The 2D and 3D images of Bi_2Se_3 thin film having thickness 2000Ǻ in nano-metric range is shown in Fig. 3.



(a)



(b)

Fig. 3**:** AFM photograph of Bi_2Se_3 (a) 2D image and (b) 3D image

The samples were scanned in 100 x 100 μm^2 area. The film is appearing to be made up of small granular cluster. It should be noted that both height and diameter of islands are of the order of same size. The root mean square value of the surface roughness of the films from different area of the film was calculated. It was observed that the surface roughness of the film is 6 nm[18]. This observation infers that the film surface is smooth. This roughness of the films is unavoidable since particles are in spherical shape which shows semi rounded hills on the upper surface [18]. These observations show that Bi_2Se_3 films deposited at room temp have the device quality surface which will be suitable for developing magneto resistance devices.

3.3 RESISTIVITY MEASUREMENT:

The resistivity of Bi_2Se_3 films of different thickness (1000-3000Ǻ) was measured by Four-probe set up at room temperature. The graphical representation of probe voltage Vs. probe current for different thickness is as shown in Fig. 4 (a).

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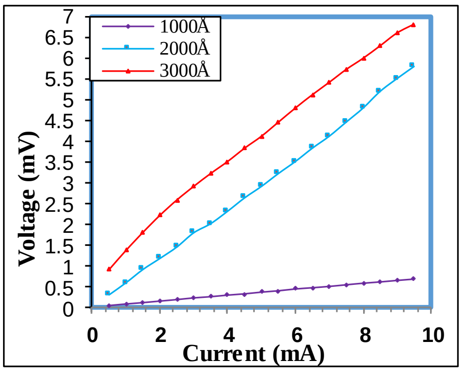

Fig. 4: (a) Resistivity measurement of Bi_2Se_3 films of different thickness (1000-3000Å)

The plot of resistivity as a function of thickness shown in Fig. 4 (b). The Fig. 4 (b) indicates that resistivity of film increases as thickness increases [19]. This is due to obeying size effect theory and shows the semiconducting nature of the deposited films [5]. This fact is further confirmed from the plot ρ against 1/d and plot of ρd against d shown in Fig. 4 (c & d) respectively. From these graphs bulk resistivity (ρ_0), mean free path and charge carrier concentration were calculated and tabulated in table 1. The estimated resistivity was 3.174 x 10^{-5} to 16.439 x 10^{-5} Ω - cm and the carrier concentration was 4.37 x 10^{20} cm^{-3}.

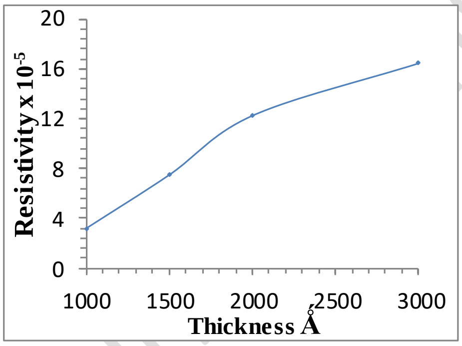

Fig. 4: (b) The plot of resistivity as a function of thickness.

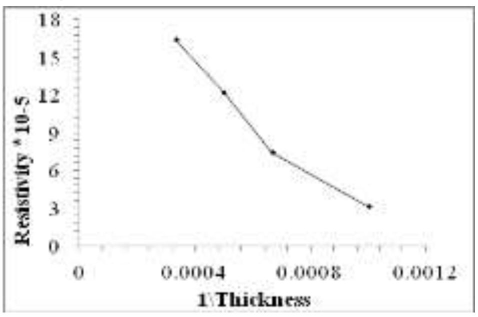

Fig. 4: (c) plot ρ against 1/d

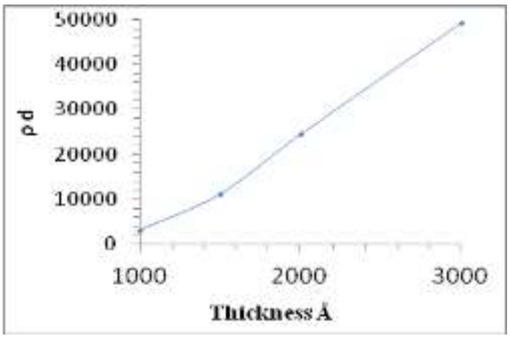

Fig. 4: (d) plot of ρd against d

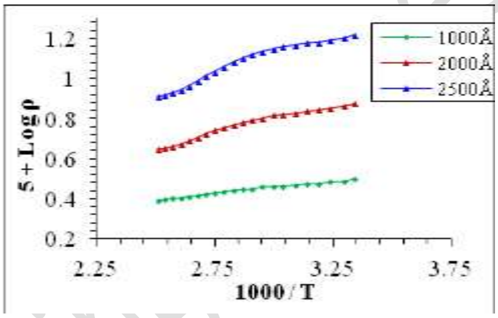

Fig. 4 (e): Plot of log of resistivity Vs. reciprocal of temperature

Table 1: Bulk Resistivity ρ_0, Mean free path λ_0, Carrier concentration η, Mobility μ of thin films

Bulk Resistivity ρ_0(ohm- cm)	3.174 x 10^{-5}
Mean free path λ_0(Å)	5.0784
Carrier concentration η (cm^3)	9.758 x 10^{20}
Mobility μ (cm^2/Volt-Sec)	1.986 x 10^4

The resistivity of Bi_2Se_3 (Thickness 1000-3000 Å) thin films were measured by using the high temperature Four- probe resistivity set up in the temperature range 298-403 K. Fig. 4 (e) shows the graph between log ρ Vs. reciprocal of temperature. From Fig. 4 (e), it is observed that the resistivity decreases with increase in temperature. This indicates the semiconducting nature of Bi_2Se_3 thin films and suggests that the resistivity of material is temperature dependent. The activation energy of Bi_2Se_3 thin films of thickness 1000-3000 Å are tabulated in table 2.

Table 2: Experimental values of activation energy for Bi_2Se_3 thin films

Thickness (Å)	Activation Energy(eV)
1000	0.031095
1500	0.05525
2000	0.06041
3000	0.07664

From table 2, it is observed that the activation energies go on increasing with increase in thickness. It is well known that the activation energy is related to the conductivity of sample. Higher the conductivity, lower is activation energy [20, 21].

3.4 THERMOELECTRIC POWER MEASUREME : The thermal properties of Bi_2Se_3 (Thickness 1000-3000 Å) thin films were measured by using thermoelectric Power (TEP) Measurement set up. Fig. 5 (a & b) show the graphical representation of thermo e.m.f. Vs. 1000/T and Seebeck coefficient Vs. 1000/ΔT

Thickness (Å)	Fermi Energy (eV)	Scattering parameter
1000	0.0784	0.173
1500	0.08	0.169
2000	0.0288	0.062
3000	0.0272	0.059

for different thicknesses (1000-3000Å) of Bi_2Se_3 thin films respectively.

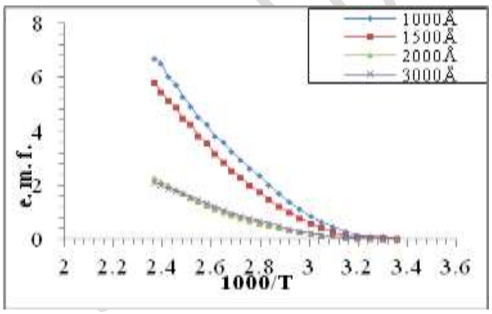

Fig. 5: (a) Plot of Thermo e.m.f. Vs. 1000/T

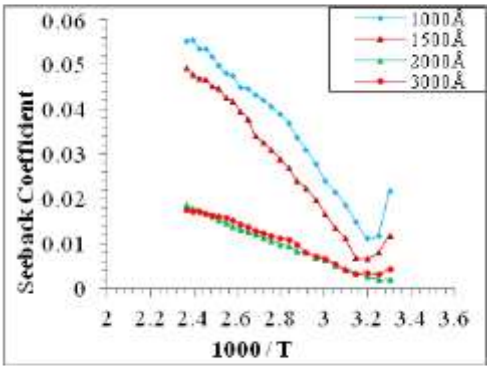

Fig. 5: (b) Plot of Seeback coefficient Vs. 1000/T

From this graph the fermi energy was calculated using the relation,

$$E_F = eST - AKT \text{---------------(4)}$$

Where, K is Boltzmann's Constant, e is electronic charge, S is Seeback coefficient and T is absolute temperature. A is a dimensionless constant related to the kinetic energy of charge carrier and has value ranging from 0 – 2. From Fig. 5 (a & b), the Fermi energy and absorption coefficient were calculated and tabulated in table 3. From table, it is observed that the Fermi energy decreases with increase in thickness. This shows that the Fermi energy of Bi_2Se_3 thin films is thickness dependent. From this one may say that the Bi_2Se_3 is N – type material [22, 23].

Table 3: Estimated Parameters from TEP for Bi_2Se_3 thin films.

4 MAGNETIC STUDY:

The magnetic properties of Bi_2Se_3 (Thickness 1000-3000 Å) thin films were measured by using Hall effect set up in the magnetic field range 0KG to 10KG. The graphical representation of Hall voltage versus probe current at different magnetic field of 0KG, 5 KG and 10 KG for different thicknesses is shown in Fig. 6 (a, b & c) respectively. From graph, the hall mobility, hall coefficient and carrier concentrations were calculated and tabulated in table 4. It is observed from table 4 that the hall mobility, hall coefficient and carrier concentrations increase with increasing the thickness as well as magnetic field. The values of magneto resistance were been also evaluate and was found to be in the range of 1601 ohm, 2298

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ohm and 9011 ohm for magnetic field of 0 KG, 5 KG a10 KG [24].

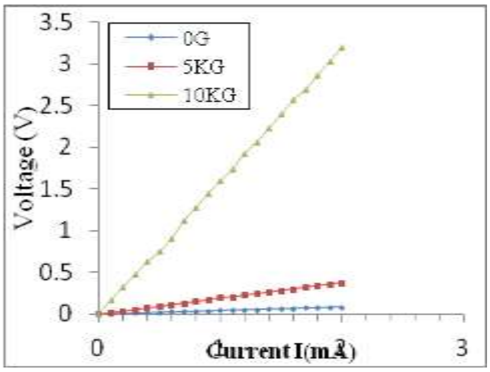

Fig. 6(a)**:** Plot of Probe voltage Vs. probe current for thickness 1000Å,

Table 4: Estimated Parameters R_{H}, μ_{H} **&** **ή** for Bi_2Se_3 thin films.

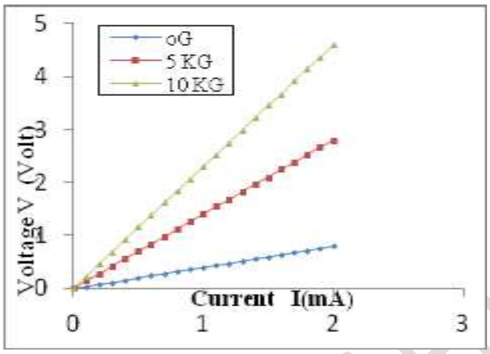

Fig. 6(b)**:** Plot of Probe voltage Vs. probe current for thickness 2000Å,

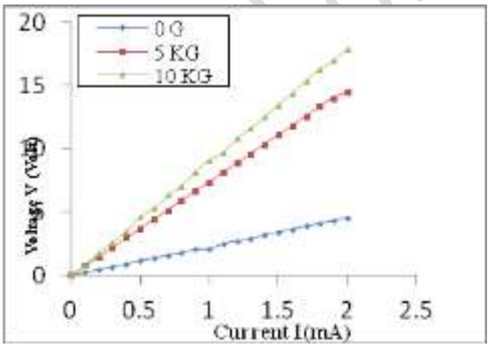

Fig. 6(c)**:** Plot of Probe voltage Vs. probe current for thickness (c) 3000Å

CONCLUSIONS:

The Bi_2Se_3 thin films of different thickness have been deposited successfully on glass substrate with different thicknesses. XRD confirms that the structure of the film is polycrystalline in nature and having hexagonal structure. From SEM study it is observed that deposited Bi_2Se_3 film were homogenous and rod like structure with nano crystalline in nature. The particle size varying from 10 to 12 nm.

From AFM study it is observed that surface image is homogeneous and well connected grains. The resistivity study shows that the Fermi energy of Bi_2Se_3 thin films is thickness dependent. It is observed from magnetic study that the hall mobility, hall coefficient and carrier concentrations increases with increasing the thickness as well as magnetic field.

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