Structural, Transport and Optical Properties of Nanostructured Vacuum Evaporated Bi2Se3 Thin Films

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Abstract - Thin films of bismuth (III) selenide were deposited thermally onto amorphous glass substrates at a pressure of 10^{-5} torr. X-Ray diffraction analysis was used for identification of the material obtained. Surface morphology of the films was determined using scanning electron microscope (SEM) and atomic force microscope (AFM). Optical, electrical and photoluminescence properties of the films were investigated. According to the resistance–temperature measurements, Bi2Se3 thin films are typical semi-conducting materials with calculated activation energies of 0.031095 – 0.07664 eV and the majority charge carriers are electrons. As-deposited films are characterized with band gap energy of 1.4 - 2.25 eV. Fermi energy was evaluated as 0.0784 to 0.0272 eV and absorption coefficient was found to be 0.173 – 0.059. The emission peak at 598.35 nm of Bi_2Se_3 attributed the edge emission to transitions associated with donor/acceptor exciton. The peak observed at 671.48 nm shows reduction in band gap. So, this emission can be identified as radiative decay of free exciton of Bi_2Se_3.

Keywords - Thermal evaporation, Optical band gap, Activation energy, Fermi energy

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1. Introduction

Nanocrystalline semiconducting materials have opened a new chapter in the field of electronic applications, since material properties would be changed by changing grain size and thickness of the films [1]. Areas of applications that can be foreseen to benefit from small size and organization of nanoscale objects include quantum electronics, non linear optics, photonics, chemo selective sensing and information storage and processing. Semi-conducting thin film materials, which are based on selenides and tellurides, have recently attracted much interest as materials for optoelectronics technology [2]. Among these, bismuth selenide, a member of the family of V-VI semi-conducting materials, has been extensively studied due to possible application in various fields. Bismuth selenide has potential applications as: a photographic film in infrared photography [3]; optical and photosensitive devices [4]; and modern thermoelectric cooling modules [5]. The study of bismuth selenide thin films is 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].

Thin films of bismuth (III) selenide have been prepared using various techniques such as solution growth [10], the SILAR method [11], electro deposition [12] and the molecular jet method [13]. This variety in preparation leads to inconsistencies in properties of Bi_2Se_3 thin films in the literature. Also the important property of a semiconductor for particular device application is the band gap energy. Therefore, in the present investigation,

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Nanocrystalline 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 technique, TEP measurement, UV-VIS-NIR spectrophotometer, photo luminescence and EDAX for structural, optical, electrical and compositional studies.

2. Experimental

2.1 Preparation of Compound Ingot

The bulk sample 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. The optical absorption studies were carried out using Shimadzu – 2450 spectrophotometer. 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. The thermo electric power of samples was measured by TEP set up using model no. DMV – 001, "Pushpa Scientific, Hyderabad", as a function of thickness and temperature.

3. Results and Discussions

3.1 XRD characterization

Fig.1 shows the recorded XRD patterns of the bismuth (III) selenide films (on glass substrates) at substrate temperature of 305K. As can be seen, the as-deposited film has a glassy, amorphous structure. A broad 2θ peak, from 20^0 to 40^0 is characteristic of the glass substrate. The chemical composition of deposited films was identified by comparing the XRD pattern of film with the standard data [14] and it was concluded that the material is bismuth (III) selenide. A peak at $2\theta = 43.570^0$ corresponding to the reflection plane of (109) appears proving the microcrystalline nature of the film exhibit the formation of the hexagonal phase of bismuth (III) selenide. The presence of large number of peaks indicates that the films are polycrystalline in nature. The average grain size of bismuth (III) selenide thin film was determined using Debye–Sherrer's equation [15],

$$d = \frac{0.9\,\lambda}{\beta \cos\theta}$$

Where, θ is the Bragg angle, λ is the X-ray wavelength and β is full width at half maximum. Calculation based on the peak at $2\theta = 43.693^0$ gave a value of 9.8 nm. 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 bismuth

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selenium oxide (Bi_2O_5Se) that could be also formed during the deposition process. The lattice parameters a and c in the prepared thin films have been determined as 4.18, and 22.79 Å respectively and V = 345 which are in good agreement with the values listed by the American society for testing materials (ASTM).

The dislocation density (δ), defined as the length of dislocation lines per unit volume, has been estimated using the equation

$\delta = 1 / D^2$

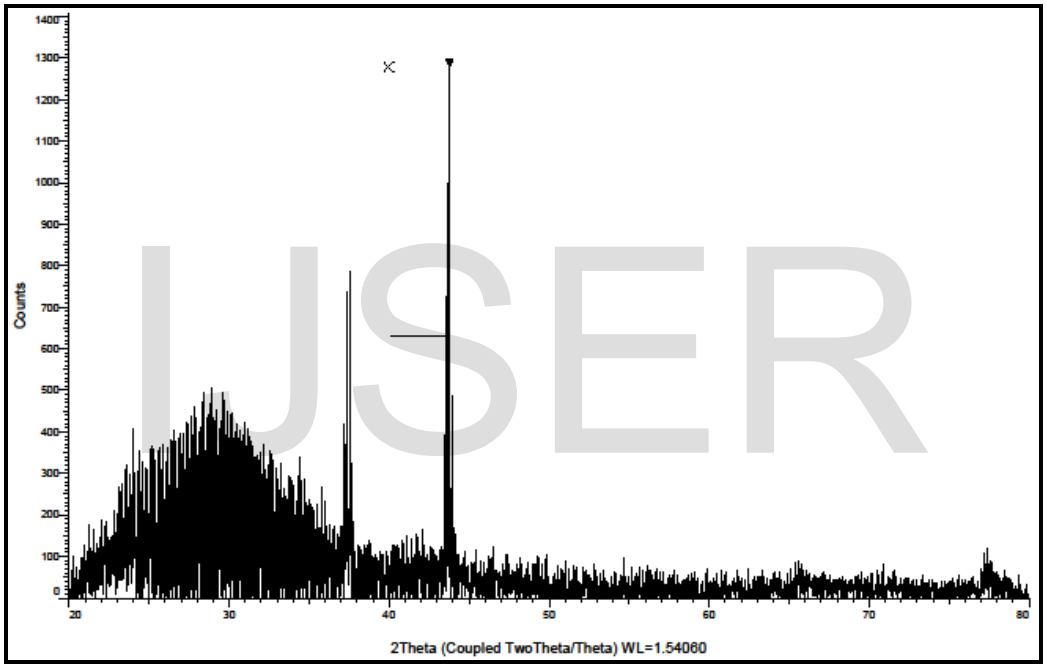
Where δ being the measure of amount of defects in a crystal.

The number of crystallites per unit area (N) and the strain (ε) of the films were determined with the use of the following formulae:

$N = t / D^3$

$\varepsilon = \beta \cos \theta / 4$

Where, t is the thickness of the film. The calculated structural parameters are $\delta = 10.37 \times 10^{15}$ lines / cm^2, $N = 1.0626 \times 10^{17}$, $\varepsilon = 2.44 \times 10^{-3}$. The small values of δ obtained in the present study confirm the good crystallinity of the thin films fabricated by the thermal evaporation technique.



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3.2 Surface morphological and Micro structural studies

Surface morphology of the synthesized bismuth selenide thin films was studied by using scanning electron microscope (SEM). Microphotographs of Bi_2Se_3 thin films at magnifications 200 K X and 300 K X are shown in Fig. 2 (a) and (b), respectively. The cross sectional micro structure was observed by high resolution scanning electron microscope with compositional contrast detectors (Fig. - 3). The films are dense, smooth and of compact structure of as synthesized Bi2Se3 films. The image clearly demonstrates granular particles and free from microscopic defects. It is seen that substrate is well covered by Bi_2Se_3. The average grain sizes calculated from SEM images was 10 – 12 nm. However from SEM studies one cannot conclude about surface structure or roughness of the films. Fig. 4 (a) and (b) shows 2D and 3D images of Bi_2Se_3 in nanometric range. 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. This observation infers that the film surface is smooth.

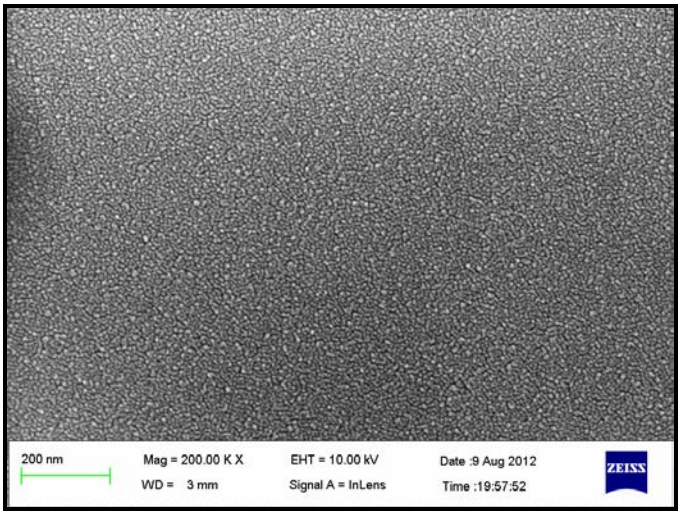

Fig: 2(a) SEM image of Bi_2Se_3 thin film

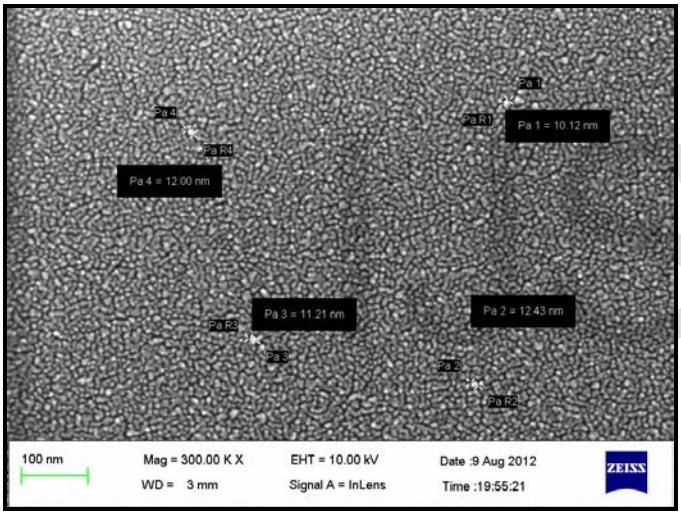

Fig: 2(b) SEM image of Bi_2Se_3 thin film

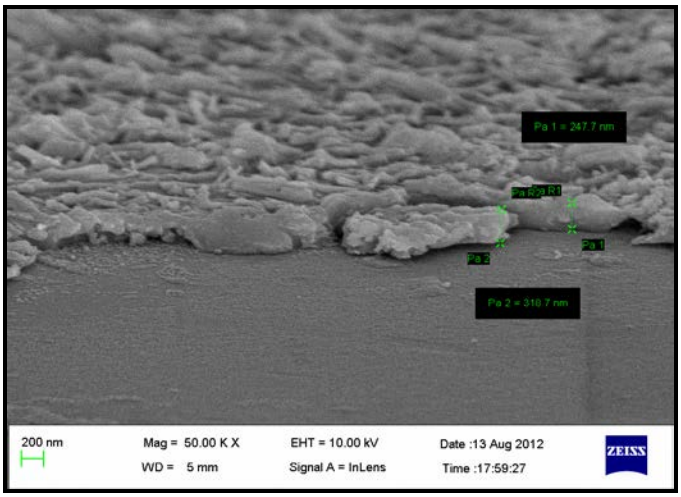

Fig: 3 Cross sectional view of Bi_2Se_3 thin film

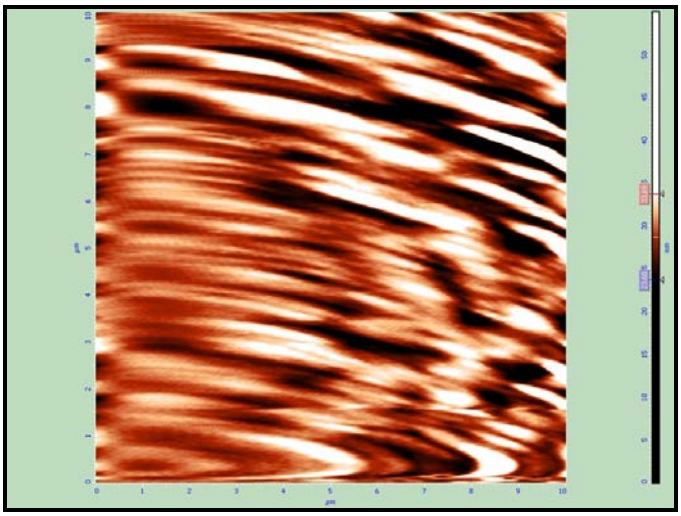

Fig: 4 (a) AFM 2-D image of Bi_2Se_3 film

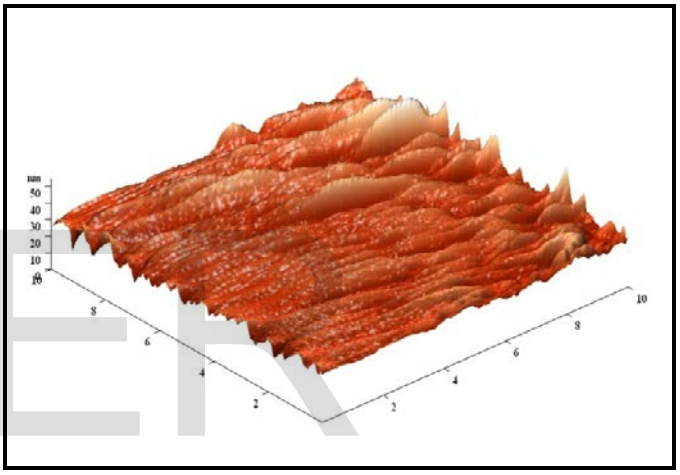

Fig: 4 (b) AFM 3-D image of Bi_2Se_3 film

The quantitative analysis was performed by EDAX for Bi_2Se_3 film. A typical EDAX spectrum for Bi_2Se_3 is shown in fig. 5. The average ratio for atomic percentage of Bi: Se was 53.02: 46.98 showing the sample is in good stoichiometric ratio.

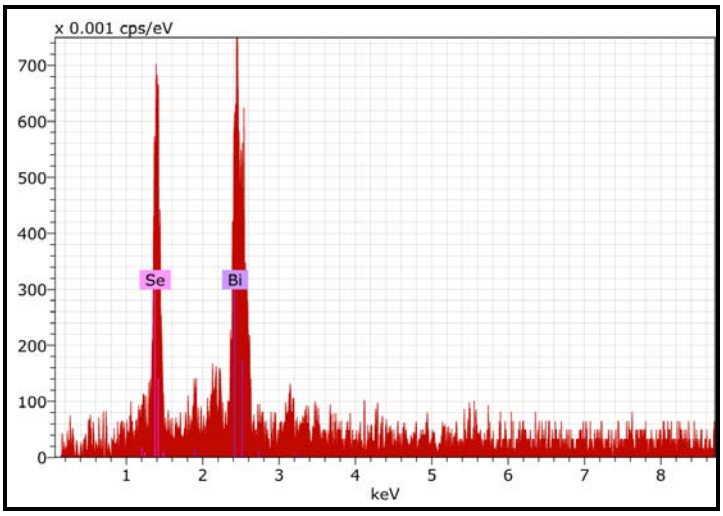

Fig: 5 EDAX spectrum of Bi_2Se_3

3.3 Optical studies

Optical absorption spectra of the bismuth (III) selenide films were recorded in the spectral range from 300 to 1100 nm. Fig. 6 shows the absorbance spectra of as-deposited bismuth (III) selenide films. The band gap energy (E_g) was estimated on the basis of the recorded optical spectra using the following relation:

$$\alpha h\nu = A (h\nu - E_g)^n$$

Where, A is constant, α is the absorption coefficient, $h\upsilon$ is photon energy, and n depends on the nature of the transition. For direct transitions n =1/2 or 3/2, while for the indirect case n = 2 or 3, depending on whether they are allowed or forbidden, respectively. The best fit to the experimental data was obtained for n = 1/2. This is in agreement with the literature data according to which Bi_2Se_3 is a semi-conducting material with a direct band gap [16].In Fig. 7, the dependence of $(\alpha h\upsilon)^2$ on $h\upsilon$ for as-deposited bismuth (III) selenide thin films is presented. The Bi_2Se_3 films are characterized by band gap energy of 1.4 - 2.25 eV. The value of band gap energy goes on increasing with increase in thickness. The literature reported values for band gap energy of bulk Bi2Se3 are 0.35 [17] and 0.16 eV [18].The higher calculated values of the band gap in our case are presumably due to the quantum size effect [19]. In particular, it is well known that the optical band gap of thin film materials, which are characterized by a length scale less than 10 nm, is higher than that of bulk material.

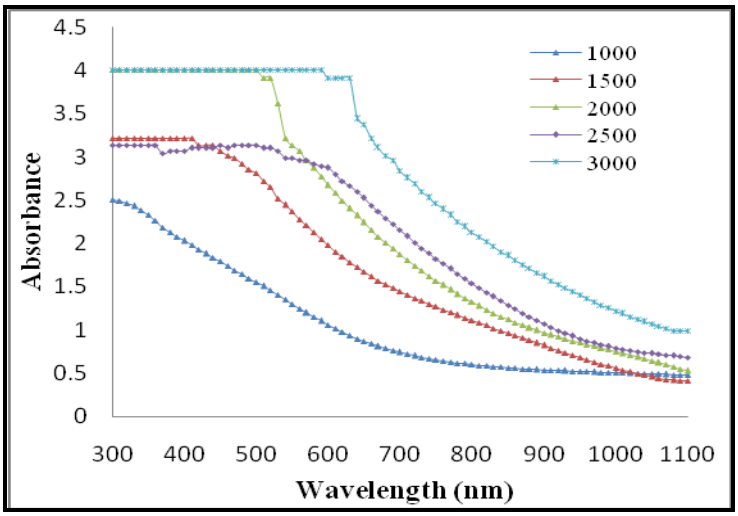

Fig: 6 Plot of absorbance vs. wavelength

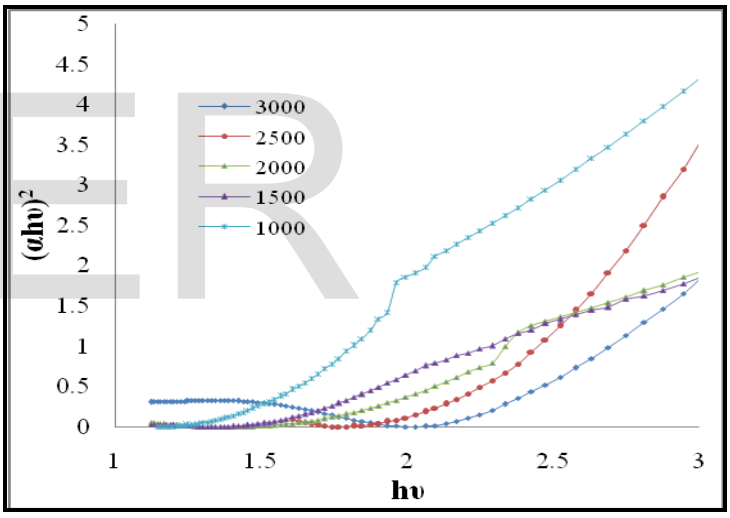

Fig: 7 Plot of $(\alpha h\upsilon)^2$ vs. hυ

Fig.-8 shows PL emission spectra of Bi_2Se_3 film. The emission spectrum of Bi_2Se_3 shows two peaks. The emission peak at 598.35 nm of Bi_2Se_3 corresponds to band gap 2.07 eV and so it can be assumed to be the edge emission of Bi_2Se_3 attributed the edge emission to transitions associated with donor/acceptor exciton complexes. The peak observed at 671.48 nm shows reduction in band gap. So, this emission can be identified as radiative decay of free exciton of Bi_2Se_3.

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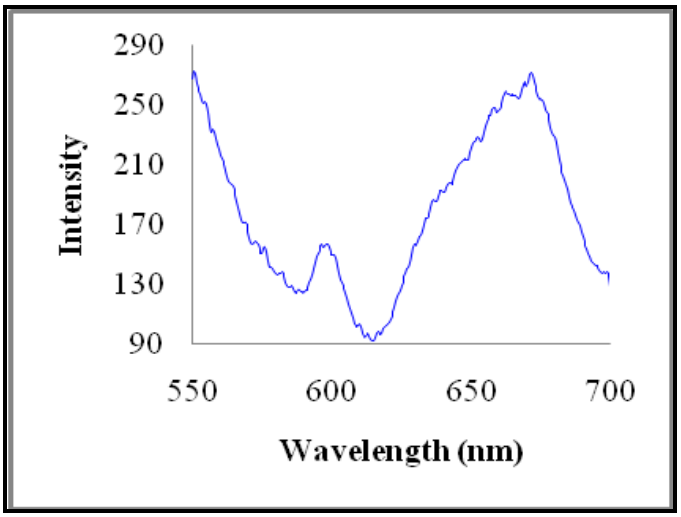

Fig. 8 Emission spectra of Bi_2Se_3 thin film under 516 nm excitation

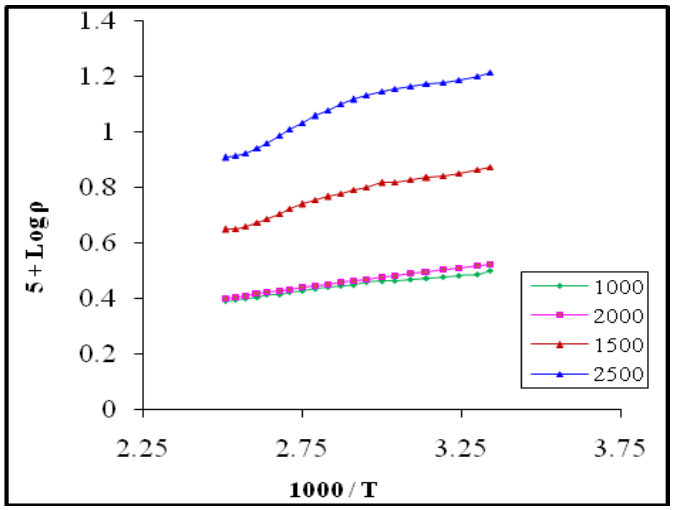

Fig. 9 Plot of log of resistivity vs. reciprocal of thickness

3.4 Electrical Properties

The resistivity of bismuth (III) selenide films of thicknesses 1000 – 2500 Á was measured in the temperature range 298 – 398 K. Fig. 9 shows variation in logarithm of conductivity with inverse of temperature for different thicknesses. The resistivity decreases with increase in temperature indicating the semiconducting nature of Bi_2Se_3 thin films. Moreover, resistivity increases with increase in thickness of the films. Increase in resistivity with increase in thickness, may be due to lower atomic % of Bi.

The activation energy were calculated using the relation,

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{KT}\right)$$

The activation energy goes on increasing with increase in thickness. The activation energy is related to the conductivity of sample. Higher the conductivity, lower is activation energy. Charge carrier need lower energy of activation in case of material having higher conductivity.

In a semiconductor, temperature gradient yield thermo electric effect, in which phonons travel preferentially from hot end to cold end due to electron – phonon interaction. During TEP measurements, thermal gradient established changes of the density of charge defect state by capturing electrons and holes. The motion of the electrons and holes can takes place through the process of diffusion. The graphical representation of thermo electric voltage verses change in temperature for different thickness of Bi_2Se_3 thin films are shown in Figure 10 and the graphical representation of Seebeck coefficient versus 1000/T for different thicknesses of the same thin film are as shown in Fig 11. Thermo electric power data were utilized to determine Fermi energy. The Fermi energy was calculated using the relation,

E_F = eST – AKT; where K, e, S and T are Boltzmann's Constant, electronic charge, Seeback coefficient and absolute temperature respectively. A is a dimensionless constant related to the kinetic energy of charge carrier and has value ranging from 0 – 2.

From this graph the Fermi energy and absorption coefficient are calculated and represented in table 1. The Fermi energy of Bi2Se3 thin films is thickness dependant. It shows that Bi_2Se_3 is a n type material.

Table 1 Fermi energy and Scattering Parameters

Thickness	Fermi Energy (eV)	A
1000	0.0784	0.173
1500	0.08	0.169
2000	0.0288	0.062
2500	0.0272	0.059

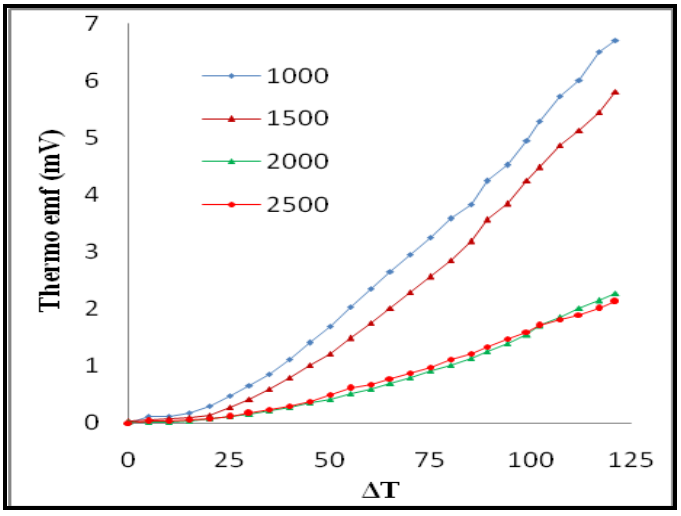

Fig. 10 Plot of thermo emf vs. Del T

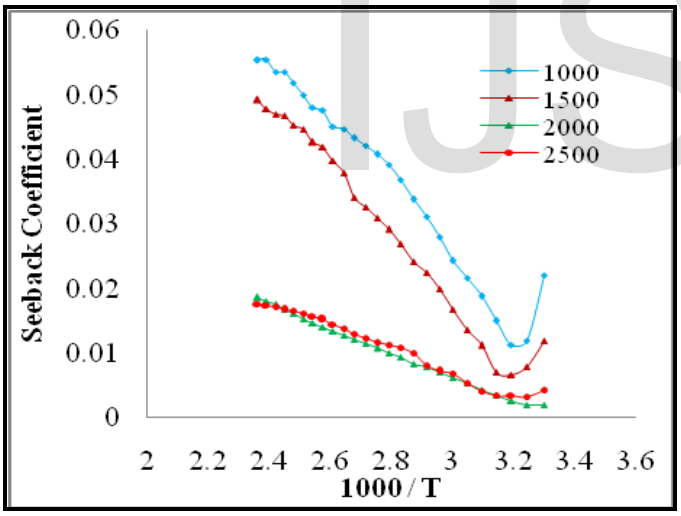

Fig. 11 Plot of Seeback Coefficient vs. 1000 / T

4. Conclusion

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 Bi2Se3 film were homogenous and granular 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. Analysis of the optical data for Bi_2Se_3 thin films, deposited at RT, showed the absorption coefficient, a = 10^{-4} cm^{-1}, and the energy band gap, Eg, in the range of, 1.4 - 2.25 eV. The emission peak at 598.35 nm of Bi_2Se_3 attributed the edge emission to transitions associated with donor/acceptor exciton complexes. The peak observed at 671.48 nm shows reduction in band gap. So, this emission can be identified as radiative decay of free exciton of Bi_2Se_3. The activation energy goes on increasing with increase in thickness and found to be 0.031095 – 0.07664 eV. Thermo electric power was negative throughout temperature range suggesting that samples were n type. Fermi energy was evaluated as 0.0784 to 0.0272eV and absorption coefficient was found to be 0.173 – 0.059.

5 References:

[1] G. A. Ozin, Adv. Mater. **4** 612 (1992).

[2] R. N. Bhattacharya, P. Pramanik, J. Electro chem. Soc. 129 (1982) 332.

[3] C.W. Bates, L. England, Appl. Phys. Lett. 14 (1996) 390.

[4] D. B. Hyun, J. S. Hwang, T. S. Oh, J. D. Shim, N. V. Kolomoets, J. Phys. Chem. Solids 59 (1998) 1039.

[5] P. Pramanik, R. N. Bhattacharya, A. Mondal, J. Electrochem. Soc. 127 (1980) 1857.

[6] Giani, Bayaz A. Al, Foucaran A, Pascal - Delannoy F and Boyer A, J. Cryst. Growth, 236 (2002) 217.

[7] R. N. Bhattacharya, P. Pramanik, J. Electrochem. Soc.129 (1982) 332.

[8] Bates C W, England L, Appl. Lett, 14 (1996) 390.

[9] Hyun D. B., Hwang J. S., Oh T. S., Shim J. D., Kolmotes N. V., J. Phys Chem. Solids 59 (1998) 1039.

[10] V. M. Garcia, M. T. S. Nair, P. K. Nair, R. A. Zingaro, Semicond. Sci. Technol. 12 (1997) 645.

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[11] B. R. Sankapal, R. S. Mane, C. D. Lonkhande, Mater. Chem. Phys. 63 (2000) 230.

[12] A. P. Torane, C. D. Lokhande, P. S. Patil, C. H. Bhosale, Mater. Chem. Phys.55 (1998) 51.

[13] A. Boyer, E. Charles, Le Vide Couches Minces 47 (1991) 99.

[14] JCPDS-International Centre for Diffraction Data set no.33 – 0214

[15] M.T. Wellller, Inorganic Materials Chemistry, Oxford Science, Oxford, 1994, p.25.

[16] T. E. Manjuvalli, T. Balasubramanian, D. Nataraj, Chalcogenides Lett. Vol.5 no. 11 (2008) 297 – 302.

[17] O. Madelung (Ed.), Semiconductors: other than Group IV Elements and III–V Compounds (Data in Science and Technology), Springer, Berlin, 1992, p.51.

[18] D. R. Lide, CRC Handbook of Physics and Chemistry, 71st edition, CRC press, Boca Raton, FL, 1990–1991, p.12.

[19] S. Gorer, G. Hodes, J. Phys. Chem. 98 (1994) 5338.

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