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STRUCTURAL AND OPTICAL PROPERTIES OF THERMALLY EVAPORATED Bi_2Se_3 THIN FILM

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Bismuth selenide thin films were deposited thermally on to well cleaned glass substrates at a pressure of 10^{-6} torr. Thickness of the samples were determined using quartz crystal monitor and it was found to be 320 nm. Structure of the samples were analyzed using Shimadzu 6000 X-ray diffractometer(XRD). The diffraction pattern revealed the microcrystalline nature of the film with hexagonal structure. From the diffractogram, microstructural and the lattice parameters were calculated. Surface morphology of the film was determined using scanning electron microscopy(SEM). on the basis of transmission spectra obtained in the wavelength range of 400 – 2500 nm, type of transition and band gap of the films were estimated.

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Keywords: Bismuth selenide, thin films, XRD, SEM, Optical devices

1. Introduction

Semiconducting binary chalcogenides of V_2VI_3 compounds have attracted wide attention in recent years due to their unique properties and potential applications in television cameras with photoconducting targets, thermoelectric devices, optoelectronic devices and IR spectroscopy [1-5]. Bi_2Se_3 an important member of these compounds is a narrow band gap semiconductor (Eg = 0.35 eV[6] and exhibits an unusual anisotropic layered structure. Studies on thin films of Bi_2Se_3 are of continued interest for investigators from the point of preparation and characterization in order to test their suitability for a particular and desired application.

Several methods have have been employed to grow Bi_2Se_3 thin films, such as chemical bath deposition [7-10] SILAR method[11] electro deposition[12] Molecular beam epitaxy[13,14] reactive evaporation[15] and thermal evaporation[16-18]. 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, it was thought interesting to determine the optical properties of the as-deposited and annealed Bi_2Se_3 thin film prepared by thermal evaporation.

2. Experimental technique

High purity Bi_2Se_3 alloy (99.999% Aldrich company, USA) thin films of different thicknesses (1500A^o ,2250 A^o and 3200 A^o) were prepared onto glass substrates kept at room

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temperature by thermal evaporation using HINDHIVAC 12" vacuum coating unit under a vacuum of 10^{-6}torr. A molybdenum boat was used as the evaporation source and the substrates were placed directly above the source at a distance of nearly 19 cm. The glass substrates were freshly cleaned with detergent solution and distilled water followed by ultrasonic agitation. Rate of deposition and thickness of the film were measured and controlled *in situ* using HIND-HIVAC quartz crystal thickness monitor. The rate of deposition were maintained ~ 1 A^o/s. Thickness of the samples were monitored by quartz crystal monitor and verified using Tolansky's method. The phases and the crystallographic structure of the films were analyzed by Schimadzu 6000 X-ray diffractometer using CuKα radiation (λ = 0.15418nm) as the incident radiation. A JEOL scanning electron microscope was used to record the micrograph of the samples.

Optical investigations were carried out using spectrophotometer (Jasco Corp, V-570) which allows measurement in the spectral range 200 -2500 nm with 1nm resolution. From the transmission spectrum absorption coefficient and band gap energy values were determined.

3. Results and discussion

3.1 Structural analysis of Bi_2Se_3 thin films from XRD spectra

X-ray diffraction pattern of thermally evaporated as-deposited Bi_2Se_3 thin film of thickness 320 nm is shown in Fig. 1. A weak peak at 2θ equal to 28.09^{o}corresponding to the reflection plane of (015) appears proving the microcrystalline nature of the film, as shown in Fig. 2. Improvement in crystallinity were observed upon annealing the film for 1 hour at 373 K. XRD pattern of annealed film shown in figure 1b exhibits peak at 2θ equal to 18.36^o, 29.26^o 43.65 ^{o},

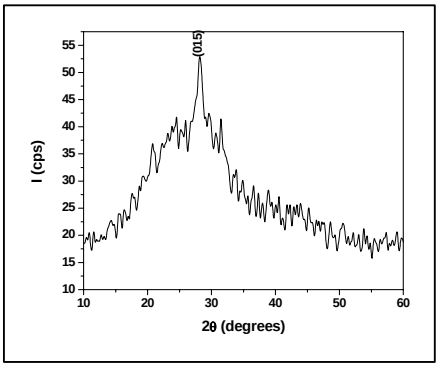

Fig. 1. XRD spectrum of as-deposited Bi_2Se_3 thin film

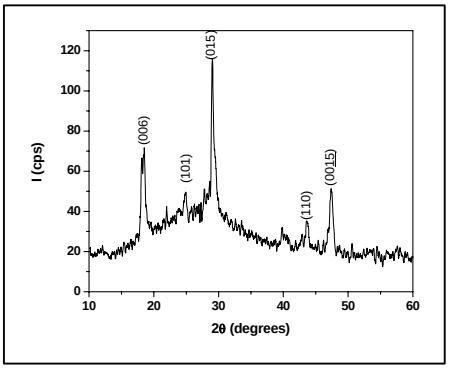

Fig. 2. XRD spectrum of annealed Bi_2Se_3 thin film

47.35 ^{o} corresponding to weak reflections from (006), (015), (110), (00$\underline{15}$) plane are in agreement with the standard JCPDS data(card No ; 33-0214)values confirming the formation of hexagonal Bi_2Se_3 thin films. From the observed 'd' spacings and hkl values the lattice constants were evaluated using the relation [19].

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

where 'd' is the d spacing and 'a' and 'c' are lattice parameters. The values were found to be a = 0.438 nm and c = 2.88 nm which are in close agreement with the values reported for bulk(a=.4138 and c= 2.8623 nm) and to those reported by Saji etal [18]and Wang et al[20] and the value available in JCPDS data. The slight variation in the lattice constant 'a' for the as-deposited film over the bulk clearly suggests that the film grains are strained and this may be owing to the change of nature and concenteration of lattice imperfection. The film density is therefore expected to change in accordance with the change in lattice constant. values are in agreement with the standard data and also the earlier reporters The crystallite size of the film were calculated using Scherer's formula

$$D = k\lambda/(\beta\cos\theta) \tag{2}$$

Where k is the Scherer's constant ,λ is the wavelength of the X-ray used, β is the full width half maximum and θ is the Bragg angle. Dislocation density and strain were also evaluated using standard expressions [21,22]. The grain size of the as-deposited and annealed film were found to be 13.86 nm and 17 nm respectively. The increase in grain size may be due to the reorientation of grain boundaries when subjected to heat treatment. The microstrain and dislocation density of the as-deposited film were found to be 2.105×10^{-3} and $4.8 \times 10^{5} cm^{-2}$ and for annealed film the values are 1.916×10^{-3} and $4.1 \times 10^{5} cm^{-2}$ The decrease in microstrain and dislocation density may be due to the movement of interstitial bismuth atoms from the grain boundary to crystallites leading to reduction in the concentration of lattice imperfections.

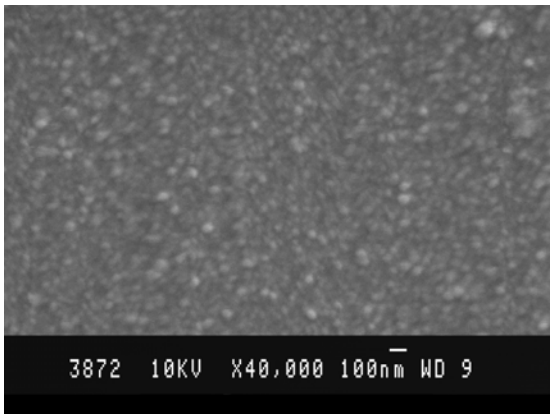

Fig. 3. Scanning electron micrograph of as-deposited Bi_2Se_3 thin film

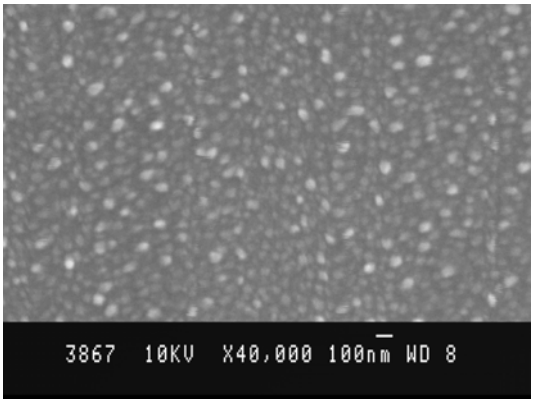

Fig. 4. Scanning electron micrograph of as-deposited Bi_2Se_3 thin film.

From the SEM micrographs shown in fig. (3) and (4) taken at a magnification of 40,000×, 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. It was also observed that the sizes of the grains increases with increasing film thickness, 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

3.2 Optical properties

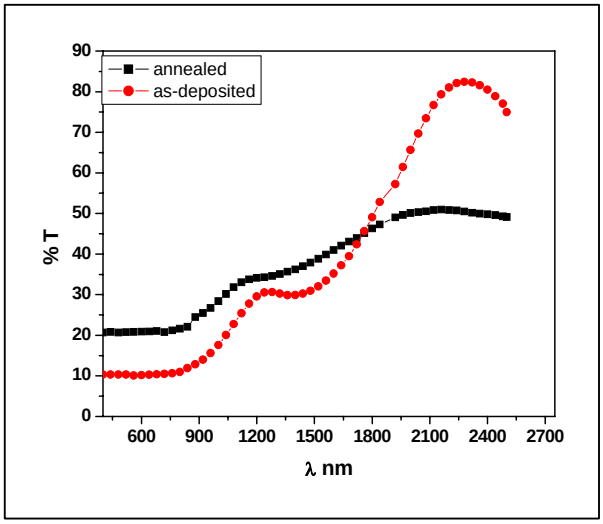

Fig. 5. Transmission Vs wavelength for Bi_2Se_3 thin films

The optical band gap energy(E_g) of Bi_2Se_3 thin film was obtained on the basis of recorded absorption spectra from 400 to 2500 nm range using double beam spectrophotometer. Figure (5)shows the transmittance spectra, obtained at room temperature and near normal incidence for as-deposited and annealed film sample of thickness 320 nm. From the figure, it was observed that the transmittance decreases upon annealing and the absorption onset is shifted towards the red region and this may possibly be attributed to improvement in crystallinity as evinced by the structural studies of the present work. For both the films the transmittance was almost constant up to 900 nm and thereafter increases 1200 nm slightly decreases and then increases. Maximum

transmittance of nearly 80% was observed for annealed film in the IR region. At a wavelength of 633 nm the optical transmittance of the films were found to be les than 20% and these values are highly suitable for studying their optical recording characteristics[17].

From the absorbance data, the absorption coefficient was calculated using Lambert law [23]

$$\text{Ln } (Io/I) = 2.303\ A = \alpha d. \tag{5}$$

Where Io and I are the intensities of the incident and the transmitted light respectively, A is the optical absorbance and d is the thickness of the film. The absorption coefficient was found to follow the relation

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \tag{6}$$

Where A is a constant which is related to the effective masses associated with the bands and Eg is the band gap energy. The index n depends on the type of electronic transitions, For direct transitions n = ½ or 3/2 while for the indirect case n = 2 or 3, depending on whether the transitions are allowed or forbidden. [19]. The linear dependence of $(\alpha h\upsilon)^n$ Verses hυ was obtained for n=2 and this is in correlation with the fact that Bi_2Se_3 is a direct allowed transition type of semiconductor and that the fundamental electronic transitions do not involve phonons

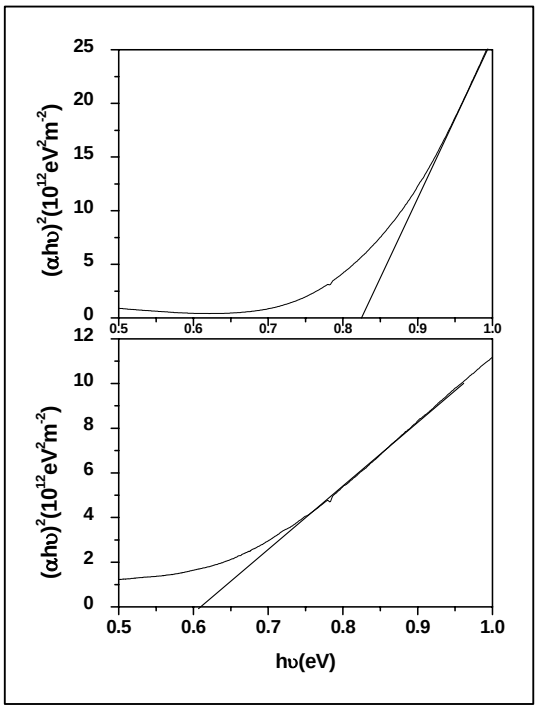

Fig. 6. Variation of $(\alpha h\upsilon)^2$ verses hυ for as deposited and annealed Bi_2Se_3 thin films.

The variation of $(\alpha h\upsilon)^2$ verses hυ for Bi_2Se_3 thin films is shown in figure (6). From the figure it was observed that the optical absorption coefficient α is a function of energy hυ. The optical absorption coefficient is found to be greater than $10^6\ m^{-1}$ supporting the allowed direct band transition of the material [24,25]. This value of absorption coefficient finds best use for optical recording devices. The optical band gap energy is estimated by extrapolating the linear portion near the onset of absorption edge to the energy axis and the values were found to be .825 eV for as

deposited film and .61 eV for annealed films. The value of the band gap energy estimated for the annealed film is in good agreement with that of the earlier reported values. The value of absorption coefficient were found to be 2.98 $\times 10^6$ and 1.06 $\times 10^6$ m^{-1}.

4. Conclusion

Bismuth selenide thin films were successfully prepared by thermal evaporation. X-ray diffraction and Scanning electron microscope studies reveal that the as-prepared films are microcrystalline and hexagonal polycrystalline nature was observed on annealing the film in air for one hour. The grain size and dislocation density were found to be dependent on post deposition heat treatment. The possible optical transitions in these films were found to be direct and allowed. The energy band gap decreases on annealing the film. The value of the absorption coefficient was found to be greater than 10^6 m^{-1} which shows the suitability of the material in optical recording devices.

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