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Structural, optical and electrical properties of Bi_2Se_3 thin films prepared by spray pyrolysis technique

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Abstract: Bismuth selenide thin films were prepared onto the glass substrates by spray pyrolysis technique at different substrate temperatures (523 K, 573 K and 623 K). The structural, optical and electrical properties of the thin films were studied using X-ray diffraction (XRD), scanning electron microscopic (SEM), UV-visible spectroscopic techniques and four-point probe method. X-ray diffraction pattern revealed microcrystalline nature of the films. The crystallite size of the film prepared at 573 K is 23.87 nm and 27.38 nm at 623 K. The SEM image shows increase of grain size with the substrate temperature. From the optical spectra the transmittance range and the direct allowed band gap energy were evaluated. The band gap energy decreased and the electrical conductivity increased with increase of substrate temperature and the sheet resistances of the films is in the order of megaohms.
Keywords: Bi_2Se_3 thin film, Spray Pyrolysis, XRD, SEM, Optical properties, Electrical properties.

Introduction

Binary Bi_2Se_3 thin film belongs to group V-VI finds applications in photosensitivity, photoconductivity and thermoelectric power. It is a narrow band gap semiconductor ($E_g = 0.2$ eV, $\Delta E = 0.35$ eV) and has received considerable attention because of its desirable thermoelectric and Hall effect applications [1-4]. They can be considered environmentally friendly since no ozone depleting chlorofluorocarbons (CFCs) are produced [5]. These compounds and their alloys have a high thermoelectric figure of merit (ZT) and their electronic properties are strongly influenced by their structure which in turn depends on the preparation technique and deposition condition [6-10]. Several methods such as Thermal evaporation [11], chemical bath deposition (CBD) [12-15], successive ionic layer absorption and reaction (SILAR) [16], solvothermal [17], electrodeposition [18,19], molecular beam epitaxy [20,21], reactive evaporation [7], metalorganic chemical vapour deposition (MOCVD) [22,23] and magnetron sputtering [24] were employed to deposit bismuth selenide thin films. However, no attempt has been made for deposition of Bi_2Se_3 thin films by spray pyrolysis technique. Owing to simplicity and inexpensiveness, the spray pyrolysis technique can be used to prepare thin films with a larger area. Also, it provides an easy way to dope any element in a ratio of required proportion through the solution medium [25]. Therefore, attempts were made to deposit and investigate the properties of Bi_2Se_3 thin films at different substrate temperature using spray pyrolysis technique.

Experimental

Bismuth Selenide films were prepared using Bismuth nitrate (Merck) and Selenium dioxide (Merck) as precursors. Bismuth nitrate ($Bi_2(NO_3)5H_2O$) was dissolved in concentrated nitric acid and then diluted by deionized water to prepare 0.1 M solution. Selenium dioxide (SeO_2) was dissolved in deionized water and 0.1 M solution was prepared. The equimolar (0.1 M) solutions of bismuth nitrate and selenium dioxide in volume ratio of 6:4 were mixed to prepare the precursor solution. This solution was sprayed onto glass substrates at different substrate temperatures (523 K, 573 K and 623 K). The carrier gas (air) pressure is kept constant as 25 kg/cm^{-2}. The distance between the nozzle and the substrate was 30 cm. The Bi_2Se_3 thin films deposited on glass substrates were dark grey in color, well adherent to the substrates, and uniform in appearance. The thickness of the deposited film was determined by a weight difference method and is 156 nm.

The structural studies of the spray deposited Bi_2Se_3 thin film samples were done by using Schimadzu XRD-6000 X-ray diffractometer with a CuKα radiation □□□□□□□□□ Å□□□The morphological analysis of the film was carried out using JEOL mode JSM 6390 SEM and optical studies of the samples were done using spectrophotometer Jasco corp. V-570 in the spectral range 200-2500 nm with 1 nm resolution. Electrical resistivity was measured by the four-point probe method.

Result and discussion

X-ray diffraction pattern

XRD pattern of Bi_2Se_3 thin films prepared at different substrate temperatures are shown in Fig. 1(a-c). It is clear that the substrate temperature play an important role in determining the structure of the films. The XRD peaks appear super imposed on the XRD profile of the glass substrate, which is indicated by broad signal in the range 20^o to 35^o. The XRD pattern also reveals that the intensity of the peak is significantly increased with the increase of substrate temperature. The film prepared at 523 K (Fig.1a) reveals nanocrystalline nature with smaller peaks. The XRD pattern of the film (Fig.1b) prepared at 573 K shows improvement in peaks corresponding to the planes (006), (015) and (110). On further increase of temperature to 623 K, improved the intensity of (006), (015) and (110) peaks and other weak peaks corresponding to the planes (10<u>10</u>), (00<u>15</u>) and (205) are also observed (Fig.1c). The standard and observed values along with their hkl planes are presented in the table 1. The grain size (D) of the films is estimated using Debye Scherer's formula

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where, λ is the wavelength of the X-ray, β is the full width at half maximum (FWHM) in radians and θ is the Bragg angle. The dislocation density (δ) can be evaluated from the particle size (D) by the following equation

$$\delta = \frac{1}{D^2}\,\frac{\text{lines}}{m^2} \qquad (2)$$

The micro strain (ε) developed in the thin films can be calculated from the following relation

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad (3)$$

The total number of crystallites can also be calculated using the relation

$$N = t / D^3 / \text{unit area} \qquad (4)$$

where, t is the thickness of the film. The lattice parameter values 'a' and 'c' were found to be a=0.4160 nm and c=2.9032 nm for 573 K and a=0.4145 nm and c=2.8620 nm for 623 K. The observed results are in good agreement with the standard JCPDS data (Card No.33-0214) thus confirms that Bi_2Se_3 belongs to hexagonal structure.

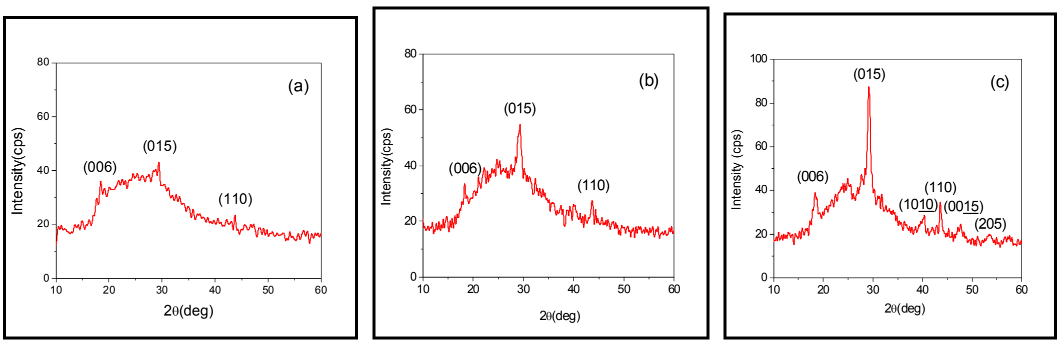


Fig. 1. XRD spectra of Bi_2Se_3 thin films of deposited at temperature a) 523 K b) 573 K c) 623 K

Table. 1. XRD data of Spray Pyrolysed Bi_2Se_3 thin films

Substrate temperature (K)	Standard JCPDS values		Observed values		hkl planes
	2θ (Degree)	d-Spacing (A^o)	2θ (Degree)	d-Spacing (Å)	
573	18.55 29.37 43.72	4.78 3.04 2.07	18.41 29.35 43.65	4.82 3.04 2.07	0 0 6 0 1 5 1 1 0
623	18.55 29.37 40.25 43.72 47.60 53.58	4.78 3.04 2.24 2.07 1.91 1.71	18.43 29.25 40.27 43.66 47.68 53.54	4.81 3.05 2.24 2.07 1.90 1.71	0 0 6 0 1 5 1010 1 1 0 0015 2 0 5

The intensity of preferred growth orientation increases with increase in the substrate temperature. Thus the film prepared at the substrate temperature of 623 K shows better crystalline quality, as indicated from the XRD spectra. The grain size of the films increases from 23.87 nm to 27.38 nm with increasing substrate temperature from 573 K to 623 K. Thus, increase in the substrate temperature results in large grains [26]. Further the micro strain and dislocation density of the film prepared at the substrate temperature 623 K decrease when compared to the value of the film prepared at 573 K. The decrease may be due to the movement of interstitial Bi atoms from its grain boundary to the crystallites, which may be leading to the reduction in the concentration of lattice imperfections [27]. The lattice parameter, dislocation density, crystallite size, strain and number of crystallites/unit area calculated in this work are presented in the Table 2.

Table. 2. Structural parameters of spray pyrolysed Bi_2Se_3 thin films

Substrate temperature (K)	Lattice parameter (Å)		Crystalline size (D) (nm)	Dislocation density δ (10^{15} lines /m^2)	Strain ε (10^{-3})	Number of crystallites/unit area ($10^{15}m^{-2}$)
	JCPDS	Observed				
573	a=4.13 c=28.63	a=4.16 c=29.03	23	1.7550	1.4526	11.4701
623		a=4.14 c=28.62	27	1.3339	1.2662	7.6001

SEM analysis

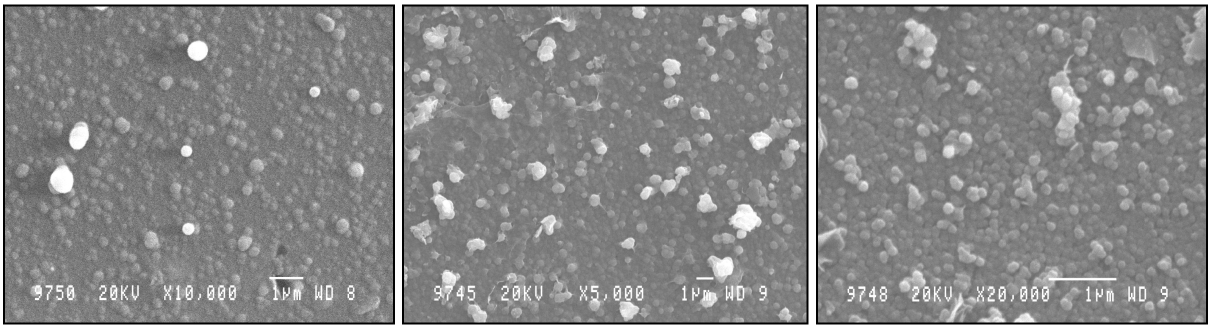


Fig. 2. SEM images of Bi_2Se_3 thin films of deposited at temperature a) 523 K b) 573 K c) 623 K

The SEM images of Bi_2Se_3 thin films prepared at different substrate temperatures are shown in Fig. 2(a-c). From the SEM micrographs it is observed that the size of the grain on the surface increases with increase in substrate temperature as evinced by the XRD spectra. As the substrate temperature increases surface morphology of the films becomes more homogeneous.

Optical analysis

The optical transmittance and absorbance of Bi_2Se_3 thin films prepared at different substrate temperature (523 K, 573 K and 623 K) are shown in Fig. 3(a-c). Sharp fall in transmission near the fundamental absorption edge and well defined absorption edge shifted towards red region are noticed on increasing the substrate temperature. This may be due to well developed crystallinity at higher temperature leading to reduction in absorption edges. Similar behavior was reported by earlier workers [14,18] for chemical bath deposited and electrodeposited thin films. The variation of optical absorption coefficient 'α' a function of photon energy hν is presented in Fig. 4. The optical absorption coefficient is of the order of 10^{6} m^{-1} supporting the allowed and direct band transition of the material [28,29].

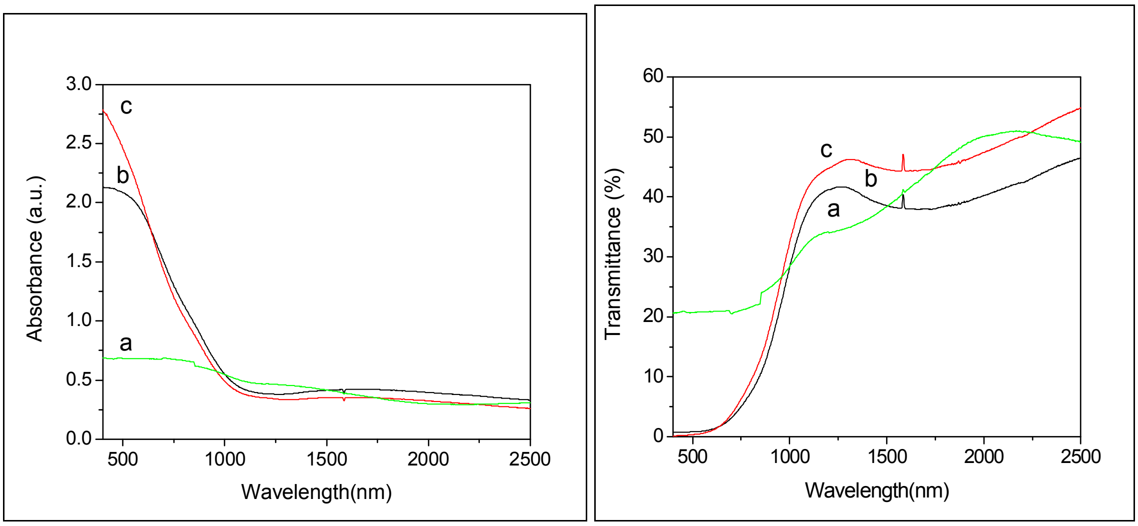


Fig. 3. Wavelength Vs Absorbance and Transmittance of Bi_2Se_3 thin films deposited at temperature a) 523 K b) 573 K c) 623 K

Fig. 5(a-c) show the plot of $(\alpha h\upsilon)^2$ Vs energy (hν) of the Bi_2Se_3 films prepared at various substrate temperatures. Extrapolation of the straight line part in each of the plots to the abscissa gives the value of direct band gap. Optical bandgap values distinct from that of the bulk crystalline material are known to exist in polycrystalline thin films. The variation is ascribed to very small crystallites constituting a thin film which results in the quantum confinement of charge carriers in the crystallites. The resultant effect is an increase in the bandgap in thin films, as compared with its value in bulk crystalline material, when crystallite size is typically less than 10 nm [14]. For example, in the case of chemically deposited Bi_2Se_3 thin films, optical band gaps in the range 1.7 to 2.3 eV have been reported, depending on the deposition condition [12,14] and for thermally evaporated films the values are found to be in the range 0.6 to 0.9 eV [30,31]. In the case of spray deposited Bi_2Se_3 film, the optical band gap value was found to vary from 1.22 eV to 1.03 eV on increasing the substrate temperature from 523K to 623K. The shift in the longer wavelength region upon increasing the substrate temperature of spray deposited thin films is associated with an improvement in the crystallinity of the films [32,33]. In the literature, Bi_2Se_3 is reported as a semiconductor material with a direct band gap. Two different values for the minimum energy gap are reported for bulk Bi_2Se_3 : 0.35 eV [34] and 0.16 eV [35].

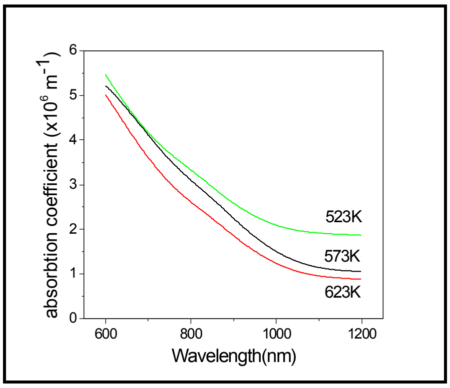


Fig. 4. Plot of α Vs λ for Bi_2Se_3 thin films at different substrate temperature

In the case of chemically deposited thin films of Bi_2Se_3, the presence of two absorption edges have been reported [15,36], one at 3500 nm corresponding to 0.354 eV and the other at 1200 nm corresponding to 1.03 eV. The latter value is close to value obtained in this work for the film deposited at 623 K.

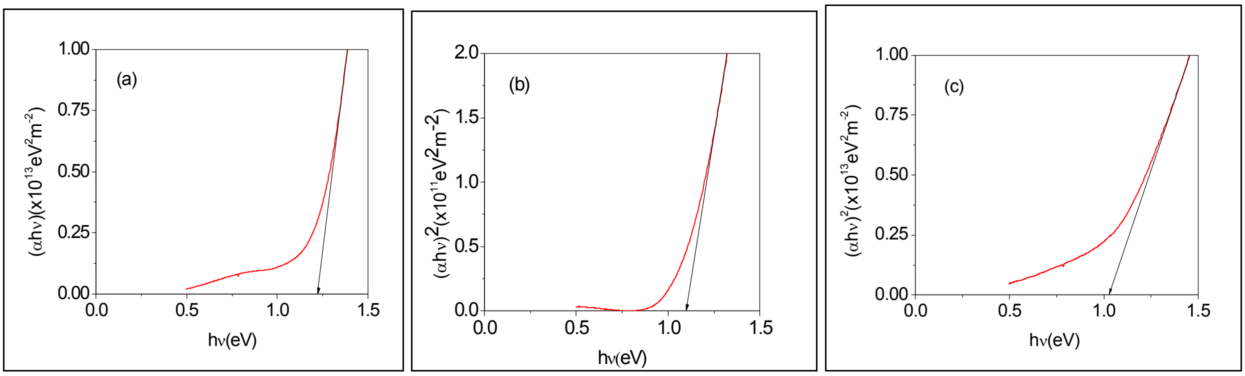
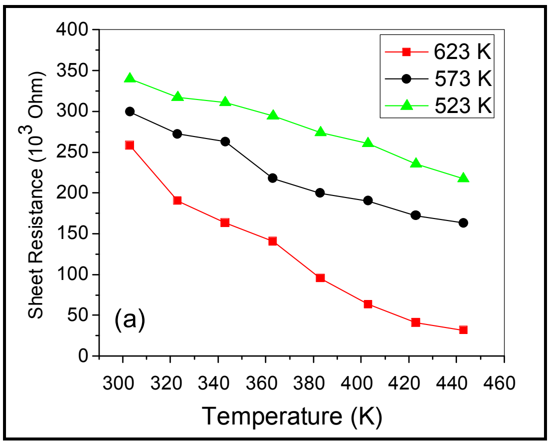
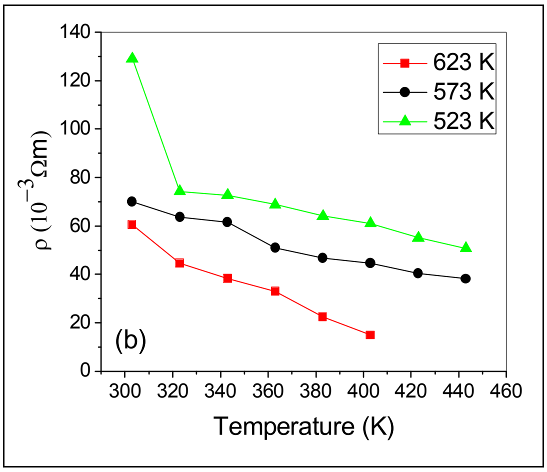


Fig .5. Plot of $(\alpha h\upsilon)^2$ Vs (hν) for Bi_2Se_3 thin films of temperature a) 523 K b) 573 K c) 623 K

Resistivity studies





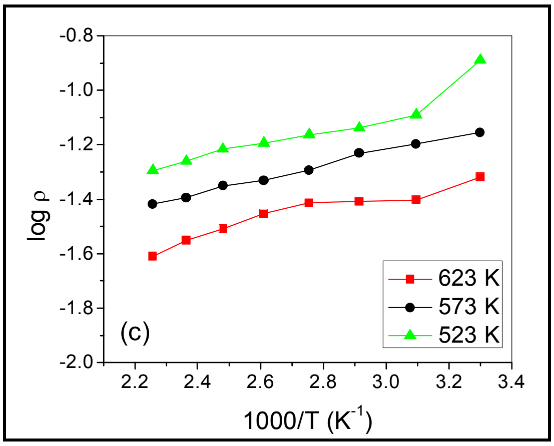


Fig. 6. a)Variation of sheet Resistance with Temperature b) Variation of Resistivity with temperature and c) plot of Logρ against 1000/T for Bi_2Se_3 thin films at different substrate temperatures.

Fig.6 a shows the plot between sheet resistance and temperature for the Bi_2Se_3 samples at 523 K, 573 K and 623 K. The decrease in sheet resistance with increase in temperature indicates the semiconductor behavior of the material. The resistivity of the films also decreases with increase in temperature and agrees fairly with the earlier reporters [11,14,31,37]. The high resistivity of thin films could be attributed to the lattice defects and dislocations developed in the thin films and can be explained on the basis of Sondheimer's theory [38] that the scattering of carriers at the surface of the films effectively reduces the mean free path of the carriers, so that the resistivity decreases with increase in substrate temperature. It is well known that the thermal activation energy can promote an electron into the conduction band of a semiconductor. Both the electrons and the accompanying hole are mobile and thereby leading to electrical conductivity and hence the temperature dependence of the resistivity as shown in Fig.6 b. From the plot of Ln (ρ) against 1000/T (Fig.6c), the activation energy of the film could be determined. The activation energies are calculated from the slopes and the summary of the activation energy obtained for various substrate temperature of the samples are presented in Table 4. The decrease of activation energy with increase in the substrate temperature is due to the increase in grain size of Bi_2Se_3 thin films.

Table. 3. Band gap and activation energy with substrate temperature for Bi_2Se_3 thin films

Deposited temperature (K)	Band gap energy (eV)	Activation energy (eV)
523	1.22	0.319
573	1.10	0.282
623	1.03	0.261

Conclusion

Bismuth selenide thin films were successfully prepared by spray parolysis technique onto the glass substrates at different substrate temperatures. The films formed are nanocrystalline with hexagonal crystal structure. XRD studies revealed that the crystallinity and grain size of the films increases with increase of substrate temperature. Morphological analysis shows that films are homogeneous and well covered to the substrate. The bandgap and activation energy decreases with increasing substrate temperature. 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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