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EFFECT OF SUBSTRATE TEMPERATURE ON THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF NEBULISED SPRAY PYROLYSED Bi_2S_3 THIN FILMS

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Thin films of Bi_2S_3 are deposited by nebulised spray pyrolysis technique at different substrate temperatures. The films are characterised by X-ray diffraction, Scanning electron microscopy, Atomic force microscopy, Energy dispersive X-ray analysis,UV-Vis.-NIR spectrophotometry and Four probe resistivity measurement. The effect of substrate temperature on the structural, optical and electrical properties of the films is analysed and it is found that the substrate temperature had a profound effect on the stoichiometry, morphology, optical band gap and resistivity of the films. The optical band gap of the films deposited at different substrate temperatures is in the range of 1.71 -2.1 eV. d.c. electrical resistivity of the films is in the range of 20-120 Ω m.

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Keywords : Bi_2S_3, Nebulised spray pyrolysis, Substrate temperature, Optical bandgap, Resistivity, stoichiometry.

1. Introduction

Identification of potential materials for photoelectrochemical solar energy conversion has always been a challenging task. The prospective materials should possess a suitable band gap (1.4-1.7eV), high absorption coefficient, low resistivity and should be non-toxic and available at low cost. Metal chalcogenides are suitable materials for photovoltaic applications. In particular bismuth trisulphide (Bi_2S_3) which belong to V-VI group of semiconductors is a potential material for photoelectrochemical solar energy application. Bi_2S_3 possess an optical band gap of 1.7 eV, absorption coefficient of the order of 10^5 and is non-toxic. Bi_2S_3 thin films are deposited by a number of techniques such as chemical bath deposition[1], SILAR[2], electrodeposition[3], vacuum evaporation[4] and spray pyrolysis [5]. It was found that the properties of Bi_2S_3 thin film varies with the method of deposition, deposition parameters and post deposition treatments. It is essential to deposit Bi2S3 thin films by an appropriate technique and to optimize the deposition parameters to obtain thin films with reproducible properties. In the previous work authors have reported a deposition and characteristics of Bi2S3 thin film by a novel method known as nebulised spray pyrolysis. The properties of spray pyrolysed films depend on spray parameters such as substrate temperature, substrate-nozzle distance, precursor concentration, geometry of the spray gun, size and shape of the droplets. Substrate temperature is the important parameter that influences the characteristics of the films the most. It is essential to optimise the temperature of the substrate to deposit device quality thin film. And hence in the present work an attempt has been to study the effect of substrate temperature on the structural, optical and electrical properties of the

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films and to optimize the substrate temperature for the deposition uniform, stoichiometric Bi_2S_3 thin films with desired electrical and optical properties.

2. Experimental

Bismuth sulphide thin films are deposited by nebulised spray pyrolysis technique. Custom made spray pyrolysis unit consisting of a spray gun, nebulizer and compressor is used for the deposition of thin films. In the present study conventional atomizer is replaced by a nebulizer which produces uniform and very fine droplets of the spray solution. Bismuth nitrate ($Bi(NO_3)_2.5H_2O$) and thiourea ($CS(NH_2)_2$) are used as the precursors for 'Bi' and 'S' ions respectively. Molar solutions of the precursors are prepared by dissolving appropriate amount of materials in deionized water. The spray solution is prepared by mixing equimolar solutions of the precursors in suitable volumes. Magnetic stirrer was used to obtain homogeneous solution. Chemically cleaned microscope glass slides are used as the substrates. The substrates are preheated to desired temperature using a hot plate coupled with a digital temperature controller. Films are deposited at different substrate temperatures (523,573 and 623K). Other deposition parameters such as substrate-nozzle distance and carrier gas pressure are optimized to obtain good quality films. The substrate-nozzle distance is optimized as 5 cm. Compressed air at a pressure of 1 bar is used as the carrier gas and the spray rate is 0.5 cc/ min. The solution is sprayed intermittently with a time interval of 2 min after each spray process in order to avoid excessive cooling of the substrates. The substrate was allowed to cool down to room temperature naturally. Thickness of the films is measured using Mitutuyo Suface profilometer (Surf Test 330) and the thickness of the films is in the range of 1-2μm. The as-deposited samples are annealed at 573 K for an hour.

3. Results and discussion

3.1 Crystalline Structure

As-deposited Bi_2S_3films are amorphous in nature (figure not shown). X-ray diffraction pattern of annealed Bi_2S_3 thin films deposited at different substrate temperatures are shown in figure 1 which shows that the films are polycrystalline in nature. The film deposited at a substrate temperature of 573 K exhibited better crystallinity when compared to the films deposited at 523 and 623 K. At 623 K amount of material deposited on the substrate is decreased as consequence of which the films are comparatively thinner. This may be attributed to the re-evaporation of the volatile species in the reacting mixture which is sulphur in the present case. Crystal structure of the deposited material is identified by comparing the peak positions with the standard data (JCPDS card no. 75-1306). The material is crystallized in orthorhombic crystal structure. No peaks corresponding to metallic 'Bi' or 'S' are found there by indicating that material is of single phase.

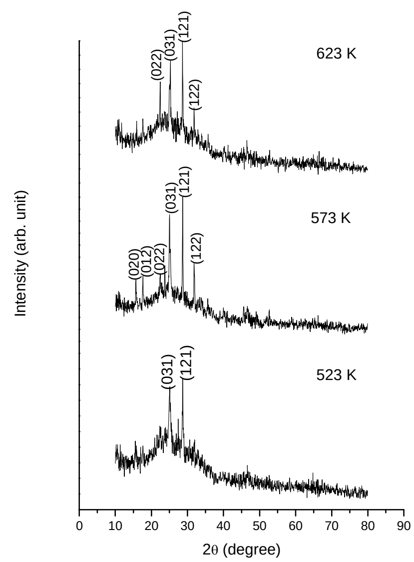


Fig. 1 XRD Pattern of Bi_2S_3 thin films deposited at different substrate temperatures

The lattice constants a,b and c are calculated using the following relation and the values are in good agreement with the standard value.

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

where d is inter planar spacing and h,k,l are Miller indices. The crystallite size is calculated from the diffraction peak broadening using Scherrer relation [6].

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \quad (2)$$

where λ is the wavelength of the X-rays used, β is the peak width at half maximum intensity in radian, θ is the Bragg angle of the diffraction peak. Microstrain is calculated from β values using the relation [7]

$$\varepsilon = \beta \cot\theta / 4 \quad (3)$$

Dislocation density is calculated using the relation [8]

$$\delta = n / D^2 \quad (4)$$

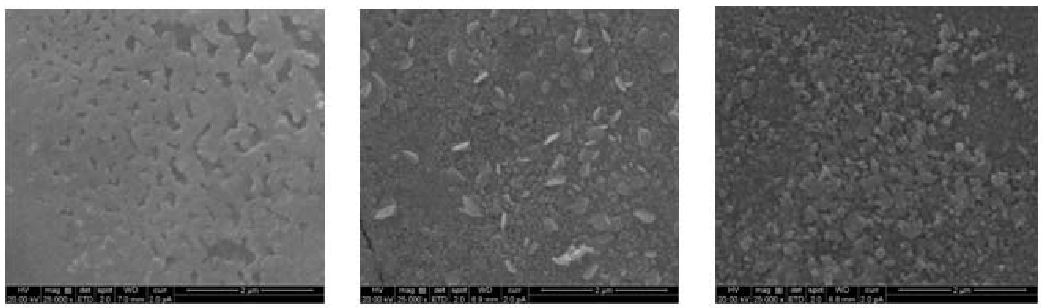
where n is the factor which is equal to unity for minimum dislocation density. The calculated values of microstructural parameters are given in table-1. XRD results show that the crystalline properties of the film deposited at a substrate temperature of 573 K is superior to those deposited at 523 K and 623 K.

Table 1 Microstructural parameters of Bi_2S_3 thin films deposited at different substrate temperatures.

Substrate Temperature (K)	Grain Size D (nm)	Microstrain (10^{-3})	Dislocation density (10^{15} m^{-2})
523	19	8.23	5.69
573	50	6.63	3.88
623	21	7.72	5.277

3.2 Surface Morphology and Elemental Composition

Figure 2 presents the SEM micrographs of the Bi_2S_3 thin films deposited at different substrate temperatures. The film is discontinuous when deposited at 523 K. Novel slice like structures are observed in the case of film deposited at 573 K. No unique morphology is observed in the case of films deposited at 523 K and 623 K. As evidenced by XRD pattern, the films deposited at 623 K consisted of smaller grains than the films deposited at 573 K. EDAX spectra of the films are shown in figure 3. No remarkable deviation from stoichiometry is observed in the case of Bi_2S_3 thin films deposited by nebulised spray pyrolysis technique. Elemental composition of the films deposited by nebulised spray pyrolysis are given in table 2 . The substrate temperature of 573 K yielded stoichiometric films and the film deposited at 523 K and 623 K are slightly sulphur rich and sulphur deficient respectively.



(a) (b) (c)

Fig. 2 SEM Micrograph of Bi_2S_3 thin films deposited at different substrate temperatures (a) 523K (b) 573K (c) 623K

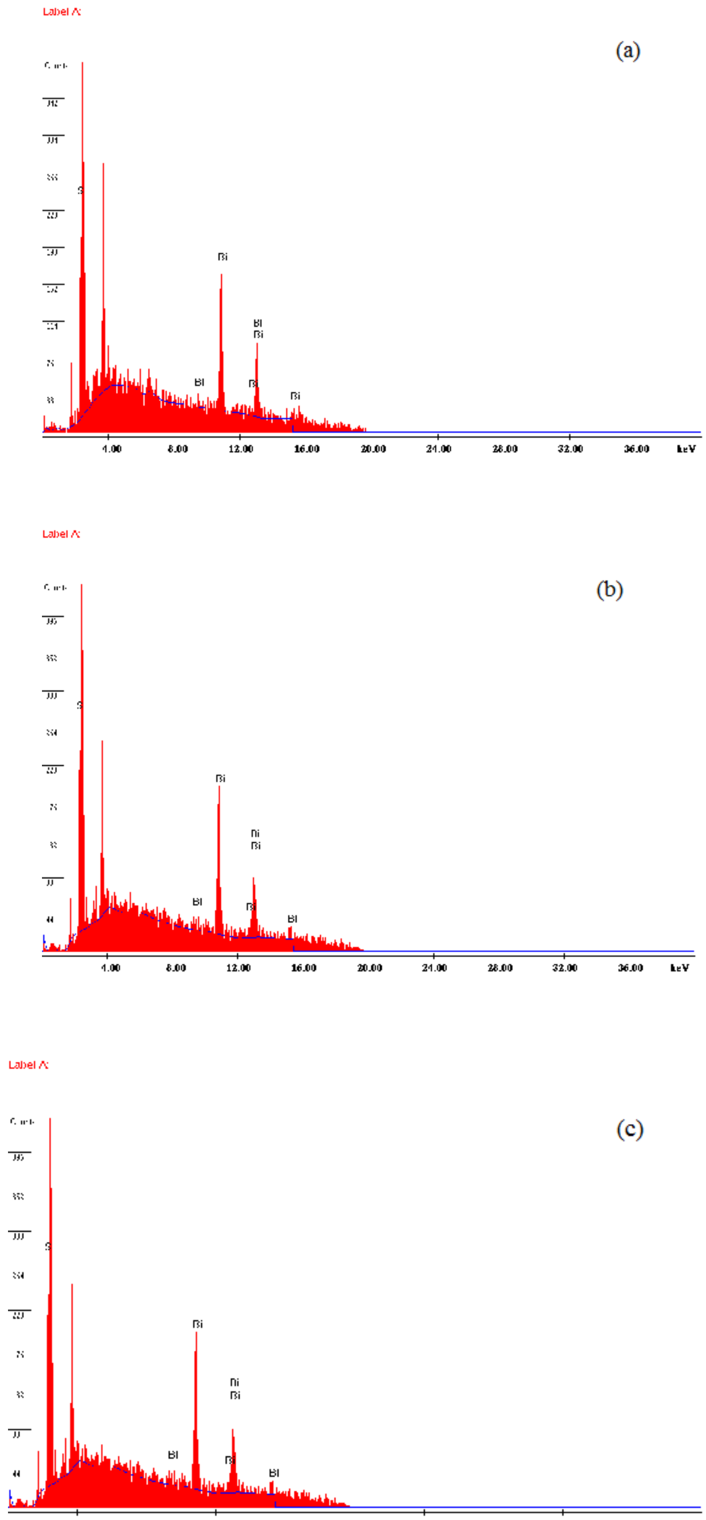


Fig. 3 EDAX Spectra of Bi_2S_3 thin films deposited at different substrate temperatures
(a) 523K (b) 573K (c) 623K

Table 2 Elemental composition of Bi_2S_3 thin films deposited at different substrate temperatures.

Substrate Temperature (K)	Weight Percentage of elements	
	Bi	S
523	79.68	20.32
573	81.02	18.98
623	88.21	11.79

3.3 Optical Properties

Optical transmittance spectra of the Bi_2S_3 films are shown in figure 4. Films exhibited higher transmittance (T) at longer wavelengths and transmittance decreases with decrease in wavelength. The films exhibited 50% transmittance in visible region.

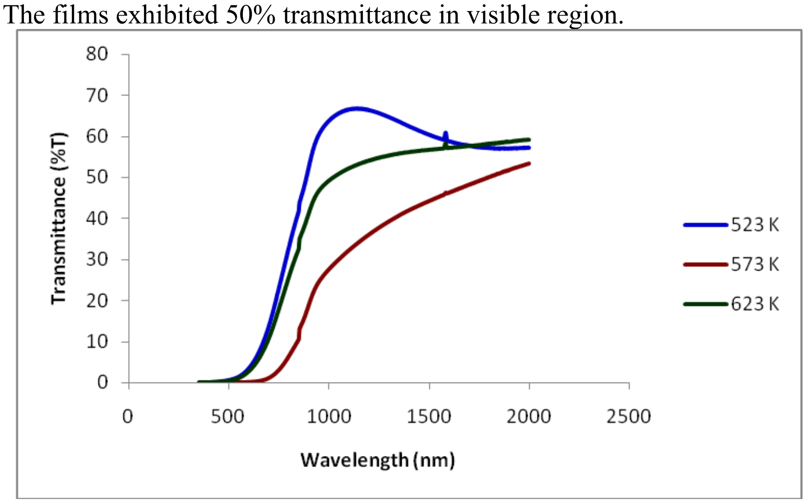


Fig. 4 Transmittance spectra of Bi_2S_3 thin films deposited at different substrate temperatures

Absorption coefficient is calculated from the transmittance data using the relation [9]

$$\alpha = (1/t)*\ln(1/T) \tag{5}$$

where 't' is the thickness of the film. Absorption spectra of the films are shown in figure 5.

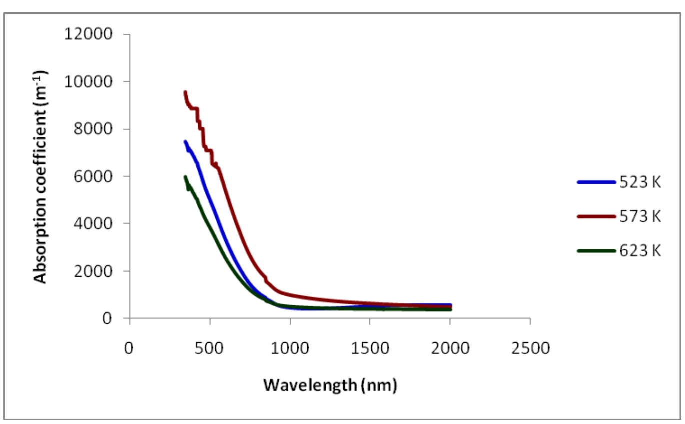


Fig. 5 Variation of absorption coefficient of Bi_2S_3 thin films deposited at different substrate temperatures with wavelength

Film deposited at 573 K exhibits higher absorption when compared to the films deposited at 523 K and 623 K which may be attributed to the higher thickness of the film. The optical band gap energy of the films is calculated using the classical relationship [10] for near edge optical absorption in semiconductors

$$\alpha h\nu = K\,(h\nu - E_g)^{n/2} \quad (6)$$

where K is a constant, hν is photon energy, E_g is the optical band gap and 'n' is a constant equal to 1 for direct band gap and 4 for indirect band gap compounds. Figure 6 shows the $(\alpha h\nu)^2$ vs. hν plot of of Bi_2S_3 thin film deposited at different substrate temperatures. Optical band gap values of films are listed in table 3. Film deposited at 573 K°C recorded minimum band gap of 1.7 eV.

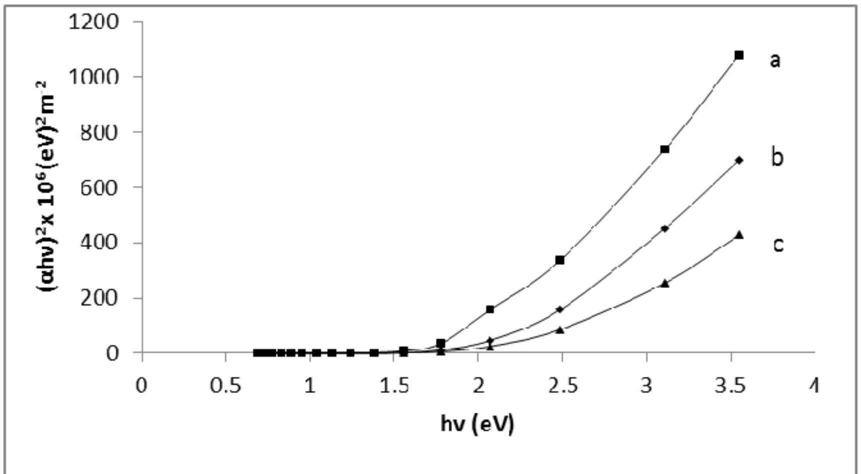


Fig. 6 Plot of $(\alpha h\nu)^2$ vs. hν of Bi_2S_3 thin film deposited at different substrate temperatures (a) 523K (b) 573K (c) 623K

Table 3 Optical Band gap values of Bi_2S_3 thin films deposited at different substrate temperatures

Substrate Temperature (°C)	Band gap, E_g (eV)
250	2.10
300	1.71
350	1.87

The sulphur deficient films had higher band gaps. Similar behaviour is observed by Sonawane and Patel [11] for Bi_2S_3 thin films deposited by chemical bath deposition technique. They obtained a band gap of 1.71 and 2.26 eV respectively for stoichiometric and sulphur deficient films.

3.4 Electrical Resistivity

Dark electrical resistivity of Bi_2S_3 thin films is measured in the temperature range of 300 K- 423 K using four probe method. Room temperature resistivity of the films is in the range of 20-120 Ω-m. Effect of substrate temperature on the resistivity of the films is depicted in figure 7.

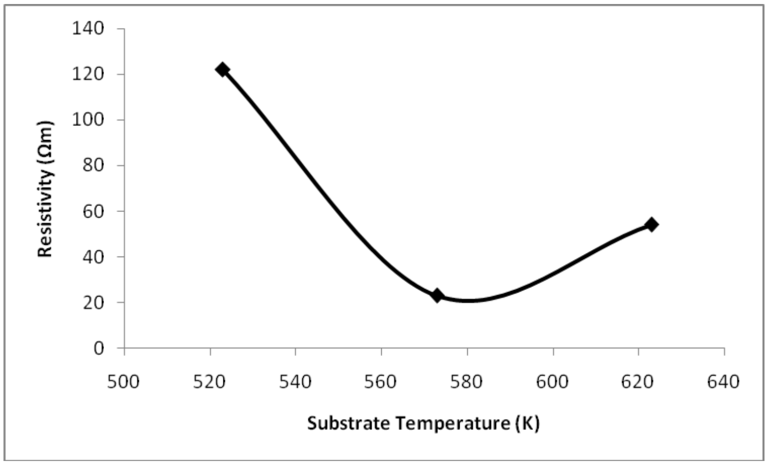
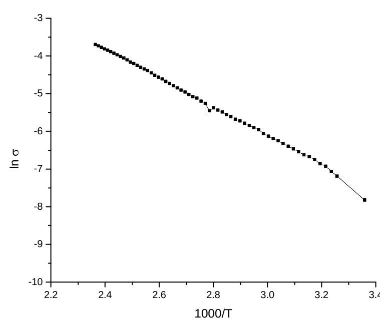


Fig. 7 Electrical resisitivity of of Bi_2S_3 thin films deposited at different substrate temperatures

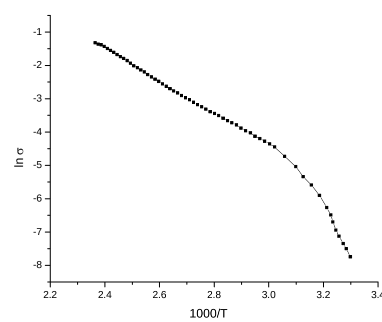
Resistivity of the films decreases with increase in temperature there by indicating the semiconducting nature of the films. d.c. conductivity is expressed by the Arrhenius relation,

$$\sigma_{d.c.} = \sigma_0 \, e^{-Ea/kT} \tag{7}$$

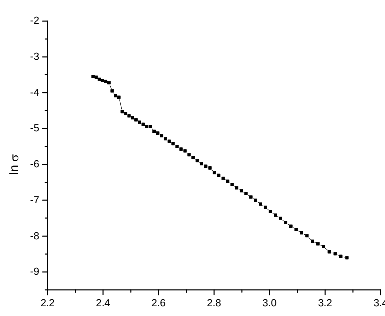
where E_a is the activation energy for d.c. conduction, k is the Boltzmann constant and σ_0 is the pre-exponential factor. The value of activation energy and pre-exponential factor for the film deposited at 573 Kare 0.154 eV and 4.97 respectively which are calculated by fitting a straight line for the resistivity data. A smaller value of the pre-exponential factor indicates wide range of localized states and conduction by hopping [12].



(a)



(b)



(c)

Fig. 8 Arrhenius plot of Bi_2S_3 thin film deposited at different substrate temperatures (a) 523K (b) 573K (c) 623K

4. Conclusions

Polycrystalline Bi_2S_3 thin films are deposited by nebulised spray pyrolysis technique at different substrate temperatures. The films deposited at a substrate temperature of 573 K exhibited better crystallinity. Novel slice like structures are observed in the case of films deposited at 573 K and these films are stoichiometric. Direct optical band gap of the films is in the range of 2.1-1.7 eV. Electrical resistivity of the films is in the range of 20-120 Ω-m. Substrate temperature is found to have pronounced effect on the structural, optical and electrical properties of the films and a substrate temperature of 573 K is found to be optimum for the deposition of Bi_2S_3 films with good structural, optical, electrical properties.

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