EFFECT OF ANNEALING TEMPERATURE ON STRUCTURAL AND OPTICAL PROPERTIES OF CHEMICALLY DEPOSITED BISMUTH SULPHIDE THIN FILMS

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Bismuth sulphide thin films have been prepared onto amorphous glass substrates by chemical bath deposition method at bath temperature of 333K using bismuth nitrate, sodium thiosulphate and EDTA as complexing agent. The deposited films are characterized by X-ray diffraction and optical absorption. The effect of annealing on the structural and optical properties is studied.

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Keywords: Thin films; Structural properties; Optical properties; Bismuth sulphide

1. Introduction

Metal chalcogenides have shown many potential and actual applications in optoelectronic, thermoelectric and photo electric devices and solar selective coatings [1-5]. Bismuth sulphide finds special applications in photo electrochemical devices as its forbidden energy gap lies between 1.25–1.7 eV [6]. Among the different deposition techniques for thin films of Bi_2S_3 [7-13], chemical bath deposition [14] has been singled out as an inexpensive, simple and convenient technique for large area applications. Chemical deposition of Bi_2S_3 thin films has been reported earlier using different sulphide ion releasing sources such as thio sulphate, thiourea and thioacetamide [11, 13 and 15] and it is reported that the properties of Bi_2S_3 films vary from source to source.

The present work describes a chemical method for deposition of Bi_2S_3 thin films from an acidic aqueous medium using sodium thiosulphate as S^{2-} ion source. The characterization of Bi_2S_3 thin films was carried out using XRD and optical absorption. The effect of annealing on structural and optical properties of Bi_2S_3 thin films is studied.

2. Experimental details

2.1. Preparation of Bi_2S_3 thin films

For the preparation of Bi_2S_3 thin films, 12ml of 0.1M solution of disodium salt of EDTA was added in to 15ml of 0.2M ($Bi(NO_3)_3$) solution in a beaker. The solution was stirred continuously by using magnetic stirrer for few minutes. The 9 ml solution of 0.2M Sodium thiosulphate was then added in to a beaker. The pH of this reaction bath was maintained at 2. The substrates were vertically immersed in the reaction bath and the temperature of the bath was increased slowly. After attaining 333K (60^0C), the reaction beaker was kept deposition period of

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12 hours, the substrates were taken out, rinsed in distilled water and dried. The annealing of the films was done at 150^0C, 200^0C and 250^0C.

2.2. Characterization

The thickness of the films was measured by the gravimetric method. The structural characterization of the films was made using a X-ray diffractometer (Model-PHILIPS-PW3710) using Ni filtered CuKα radiation (λ=0.154nm) at 40 kV and 25 mA. Grain size of Bi_2S_3 film particles was calculated by using Scherrer's formula.

Optical absorption studies were carried out using UV-VIS-NIR Spectrophotometer (Model-V-570) in the wavelength range 190 nm to 2500 nm at room temperature using un-polarised lights from deuterium and tungsten lamps which are used at near normal incidence.

3. Results and discussion

3.1. Bismuth sulphide growth mechanism

The chemical reaction responsible for Bi_2S_3 film from an acidic bath using $Na_2S_2O_3$ as the sulphide ion source [11, 16-18] could be:

$$Na_2S_2O_3 \rightarrow 2Na^+ + S_2O_3^{-2} \quad (1)$$

$Na_2S_2O_3$ is a reducing agent by a virtue of the half-cell reaction as:

$$6S_2O_3^{-2} \rightarrow 3S_4O_6^{-2} + 6e^{-} \quad (2)$$

In acidic medium, dissociation of $S_2O_3^{-2}$ takes place as:

$$3S_2O_3^{-2} + 3H^+ \rightarrow 3HSO_3^- + 3S \quad (3)$$

The released electrons react with sulphur as:

$$3S + 6e^- \rightarrow 3S^{-2} \quad (4)$$

Bi^{3+} from Bi $(NO_3)_3$ solution or a complex of Bi^{3+} formed by EDTA react to give

$$2Bi^{3+} + 3S^{-2} \rightarrow Bi_2S_3 \quad (5)$$

3.2. Structural properties of Bi_2S_3 films

X-ray diffraction is a powerful non-destructive method for material characterization, by which the crystal structure, grain size and orientation factor can be determined. Structural identification of Bi_2S_3 films was carried out with X-ray diffraction in the range of angle 2θ between 20 and 60. Fig.1, 2 and 3 shows the XRD pattern of annealed Bi_2S_3 thin films with thickness 100 nm, 78 nm and 62 nm (deposited at 60^0C). The film having thickness 100, 78 and 62 nm is polycrystalline nature with orthorhombic structure. Table 1 Summaries the crystallographic data of these films compared with ASTM data file (JCPDS 653884) [19]. The Structural parameters of the deposited Bi_2S_3 films like grain size, dislocation density and strain have been evaluated in Table 2. It was observed that grain size increases but the strain and dislocation density decreases with increase of annealing temperature.

It was found that crystallite size increases from 235 Å to 728 Å as annealing temperature increases from 150^0C to 250^0C. This significant improvement in crystallite size is due to controlled slow release of bismuth ions from its complex in the solutions which give probability of growth of larger particles [18].

The bismuth sulphide thin films are having the preferential orientation along (102) plane. The intensity of the peak (102) increases significantly faster than other peaks ((022), (110), (013), (122), (130), (132), (104) and (142)) indicating a relatively preferred structural orientation in the (102) plane. Similar had been reported earlier for CdS thin films [14]. A method that evaluates the magnitude of the preferred orientation factor '*f*' for a given plane (peak) relative to other planes (peaks) in material was employed [14]. According to this method the preferred orientation factor *f* (102) of the (102) plane for the Bi_2S_3 thin films has been calculated by evaluating the fraction of (102) plane intensity over the sum of intensities of all peaks within a given measuring 2θ range [10°-80°]. Similarly the orientation of all other peaks has been evaluated for all the films. In Bi_2S_3 films prepared at 60°C of annealing at 150^0 C (Fig.1) *f* (022) =0.1388, *f* (110) =0.1575, *f* (013) =0.1678, *f (102)* =0.2189, *f* (122) =0.1254, *f* (130) =0.1115, *f* (132) =0.0898, *f* (104) =0.0749, *f(*142*)=0.0685,*. In Bi_2S_3 films prepared at 60°C of annealing at 200^0 C (Fig.1) *f* (022) =0.1388, *f* (110) =0.1444, *f* (013) =0.1582, *f (102*) =0.2110, *f* (122) =0.1223, *f* (130) =0.1142, f (132) =0.0950, *f* (104) =0.0780, *f(*142*)=0.0755,*. In Bi_2S_3 films prepared at 60°C of annealing at 250^0 C (Fig.1) *f* (022) =0.1501, *f* (110) =0.1544, *f* (013) =0.1590, *f (102*) =0.2031, *f* (122) =0.1221, *f* (130) =0.1147, f (132) =0.0969, *f* (104) =0.0812, *f(*142*)=0.0778,*. Since *f* (102) is greater compared to other orientation in all the three films, it can be concluded that Bi_2S_3 thin films have the preferential orientation along (102) plane. The enhancement of (102) plane and in-turn the improved crystallanity with annealed temperature is remarkable irrespective of the chemical bath. The predicted peaks (022), (110), (013), (102), (122), (130), (132), (104) and (142) are reported as the characteristic peaks for Bi_2S_3 thin films. Table 3 shows the calculated preferential orientational factor of Bi_2S_3 thin films with different annealed temperature (150^0C, 200^0C and 250^0C) for peaks (022), (110), (013), (102), (122), (130), (132), (104) and (142).

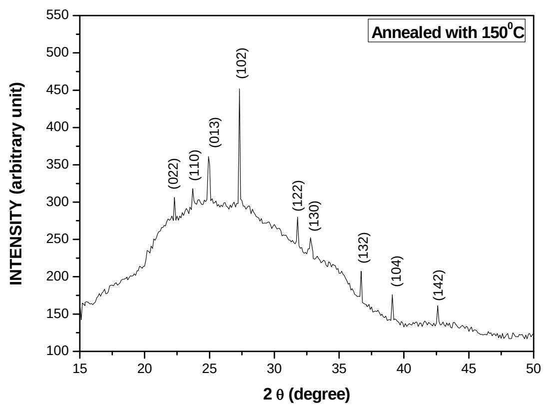

Fig. 1. X-ray diffraction pattern of Bi_2S_3 thin films annealed at 150^0C

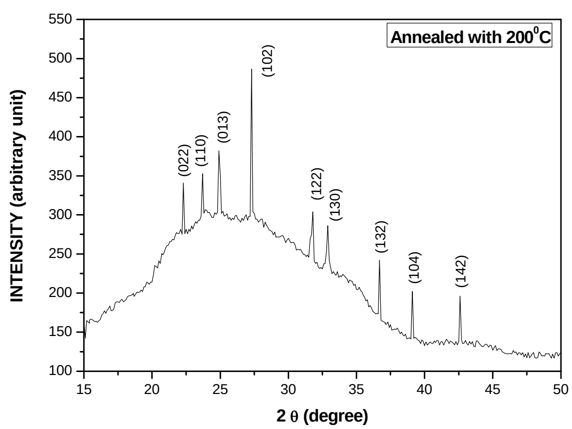

Fig. 2. X-ray diffraction pattern of Bi_2S_3 thin films annealed at 200^0C

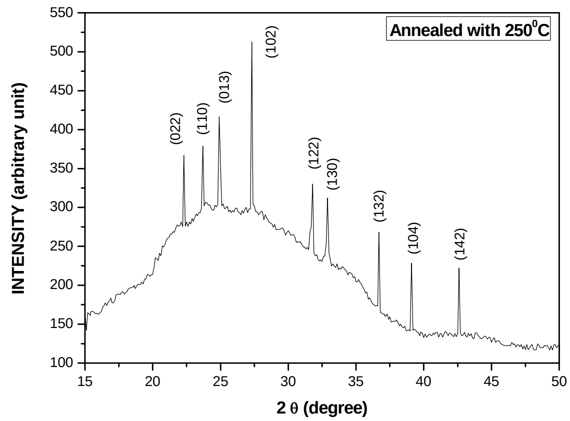

Fig. 3. X-ray diffraction pattern of Bi_2S_3 thin films annealed at 250^0C

Table 1 Comparison of XRD data for Bi_2S_3 thin films with the JCPDS card

Annealed Temperature (^{0}C)	Thickness (nm)	Planes (hkl)	2θ values (degree)		d-spacing values d (Å)	
			JCPDS	Experiment	JCPDS	Experiment
150	100	022	22.38	22.34	3.968	3.942
		110	23.71	23.70	3.749	3.741
		013	24.92	24.91	3.569	3.576
		102	27.38	27.34	3.254	3.246
		122	31.81	31.79	2.810	2.833
		130	32.94	32.78	2.176	2.133
		132	36.67	36.70	2.448	2.456
		104	39.05	39.10	2.304	2.311
		142	42.67	42.60	2.116	2.122
200	78	022	22.38	22.34	3.968	3.942
		110	23.71	23.70	3.749	3.741
		013	24.92	24.91	3.569	3.576
		102	27.38	27.34	3.254	3.246
		122	31.81	31.79	2.810	2.833
		130	32.94	32.78	2.176	2.133
		132	36.67	36.70	2.448	2.456
		104	39.05	39.10	2.304	2.311
		142	42.67	42.60	2.116	2.122
250	62	022	22.38	22.34	3.968	3.942
		110	23.71	23.70	3.749	3.741
		013	24.92	24.91	3.569	3.576
		102	27.38	27.34	3.254	3.246
		122	31.81	31.79	2.810	2.833
		130	32.94	32.78	2.176	2.133
		132	36.67	36.70	2.448	2.456
		104	39.05	39.10	2.304	2.311
		142	42.67	42.60	2.116	2.122

Table 2 The Structural parameters of the deposited Bi_2S_3 films

Annealed Temperature (^0C)	Thickness (nm)	Planes (hkl)	Grain size d (Å)	Dislocation Density X10^{15} lines/m^2	Strain ε X10^{-3}
150	100	022	235.2	1.8076	1.5549
		110	291.3	1.1784	1.2552
		013	368.0	0.7384	0.9937
		102	318.7	0.9845	1.1475
		122	302.5	1.0928	1.2088
		130	207.0	2.3337	1.7665
		132	330.4	0.9160	1.1067
		104	351.9	1.0020	1.0392
		142	277.4	1.2995	1.3181
200	78	022	319.07	0.9822	1.1463
		110	510.41	0.3838	0.7165
		013	637.11	0.2463	0.5740
		102	549.50	0.3311	0.6656
		122	465.34	0.4618	0.7859
		130	276.20	1.3108	1.3240
		132	560.40	0.3184	0.6526
		104	562.56	0.3159	0.6501
		142	354.60	0.7952	1.0314
250	62	022	514.01	0.3784	0.7115
		110	580.18	0.2970	0.6304
		013	685.72	0.2126	0.5333
		102	638.19	0.2455	0.5731
		122	504.98	0.3921	0.7242
		130	299.54	1.1145	1.2210
		132	651.84	0.2353	0.4488
		104	728.98	0.1881	0.5017
		142	624.57	0.2563	0.5856

Table 3 Preferential orientational factor of Bi_2S_3 thin films

Annealed Temperature (^0C)	Thickness (nm)	Plane (hkl)	Orientation factor (f)
150	100	022	0.1388
		110	0.1575
		013	0.1678
		102	**0.2189**
		122	0.1254
		130	0.1115
		132	0.0898
		104	0.0749
		142	0.0685
200	78	022	0.1388
		110	0.1444
		013	0.1582
		102	**0.2110**
		122	0.1223
		130	0.1142
		132	0.0950
		104	0.0780
		142	0.0755
250	62	022	0.1501
		110	0.1544
		013	0.1590
		102	**0.2031**
		122	0.1221
		130	0.1147
		132	0.0969
		104	0.0812
		142	0.0778

3.3 Optical Analysis

The optical properties of the chemically deposited Bi_2S_3 films were characterized by optical absorption and transmittance measurements. The measurements have been taken in the wavelength range 190-2500 nm. The optical absorption and transmittance spectra of Bi_2S_3 films of three different thicknesses are shown in fig. (4-9). It can be observed that in general a increase in annealing temperature improves the transmission.

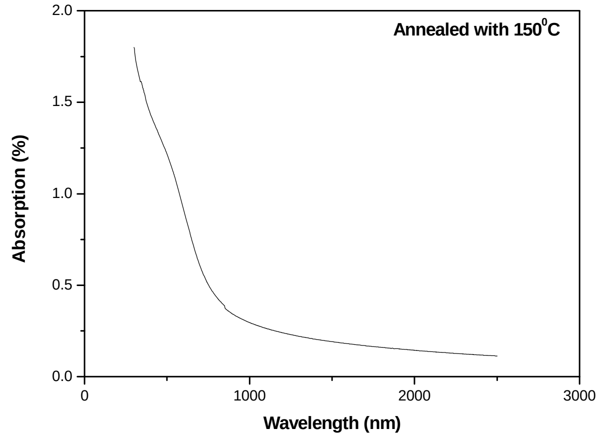

Fig. 4. Absorption spectra of Bi_2S_3 thin films annealed at 150^0C

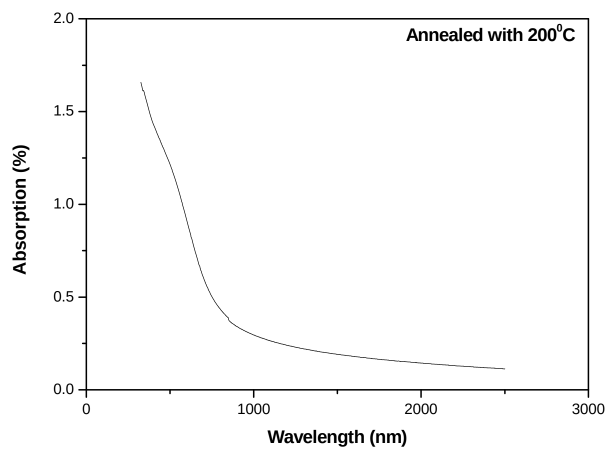

Fig. 5. Absorption spectra of Bi_2S_3 thin films annealed at 200^0C

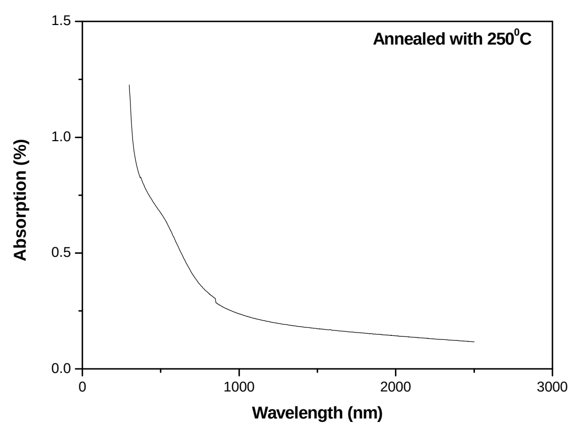

Fig. 6. Absorption spectra of Bi_2S_3 thin films annealed at 250^0C

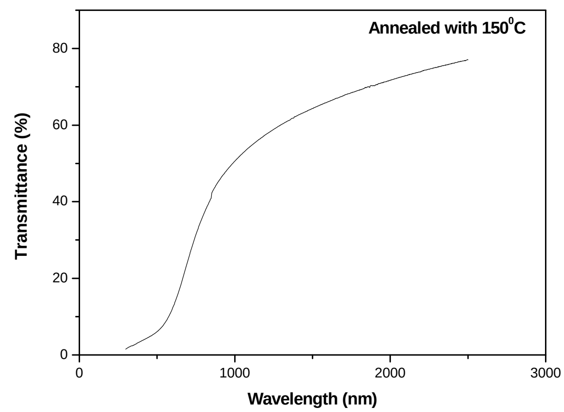

Fig. 7. Transmittance spectra of Bi_2S_3 thin films annealed at 150^0C

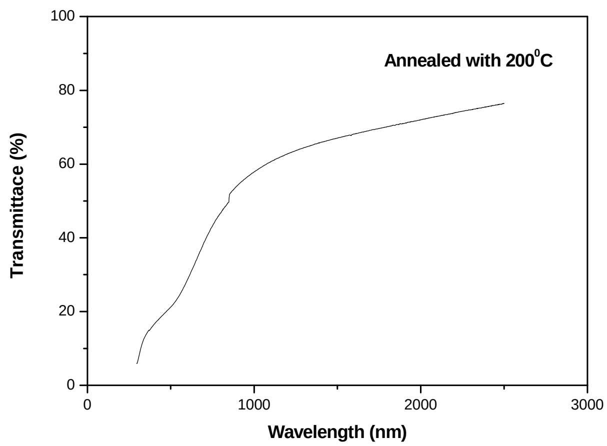

Fig. 8. Transmittance spectra of Bi_2S_3 thin films annealed at 200^0C

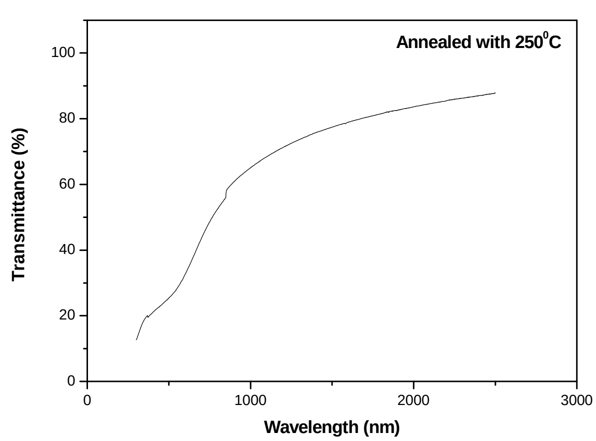

Fig. 9. Transmittance spectra of Bi_2S_3 thin films annealed at 250^0C

The relationship between the absorption coefficient α and the incident photon energy can be written as [20, 21]

$$\alpha = a\,(h\nu - E_g)^n / h\nu \quad (6)$$

Where "a" is a constant, Eg is the band gap, n is a constant equal to ½ for direct bad gap semiconductor and 2 for indirect bad gap semiconductor. The value of α is obtained from the relation [22]

$$\alpha = 2.303\ A / t \quad (7)$$

where 'A' is the absorbance and 't' is the thickness of the film.

The variation of $(\alpha h\nu)^2$ versus (hν) plot (Fig.10-12). The linear extrapolation of this curve to the energy axis gives the value of band gap of Bi_2S_3 as 2.73 eV, 2.41 eV and 2.34 eV which agrees with the reported value [18]. Table 4 gives the optical band gap of Bi_2S_3 thin films of different annealed temperature. The optical band gap decreases from 2.73 eV to 2.34 eV as annealed temperature varied from 150^0C to 250^0C.

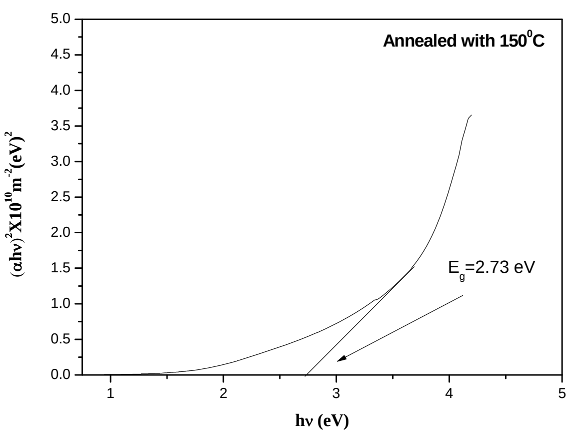

Fig. 10. Band gap plot of Bi_2S_3 thin films annealed at 150^0C

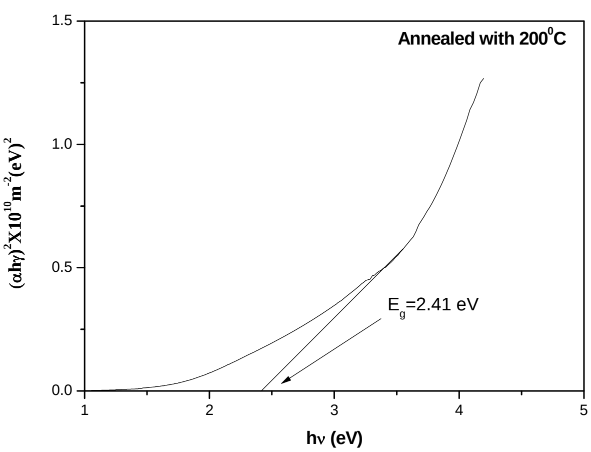

Fig. 11. Band gap plot of Bi_2S_3 thin films annealed at 200^0C

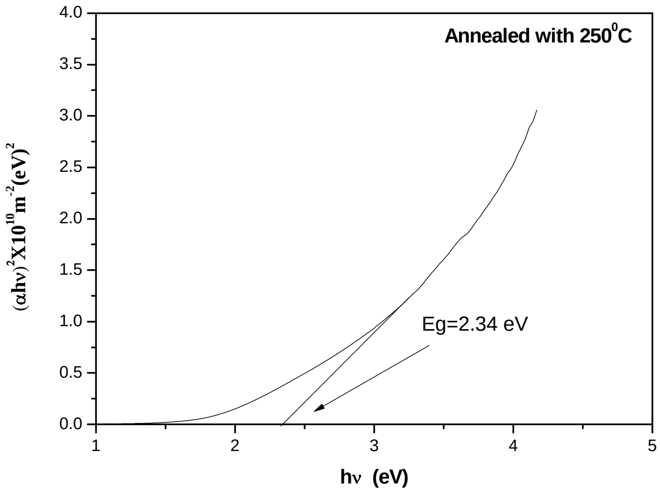

Fig. 12. Band gap plot of Bi_2S_3 thin films annealed at 250^{0}C

Table 4 Optical band of Bi_2S_3 thin films of different annealed temperature

Thickness (nm)	Annealed Temperaure (^{0}C)	Band gap (eV)
100	150	2.73
78	200	2.41
62	250	2.34

4. Conclusions

From the above study, it is concluded that Bi_2S_3 thin films of three different annealed temperature prepared by CBD are found to be polycrystalline with grain size within the range 235 Å to 728 Å. The grain size of Bi_2S_3 thin films are found to increase with increase in annealed temperature. The films are oriented in the (102) direction. Consequently, optical band gap energy was decreased with increase in annealed temperature.

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