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Structural and optical properties of Chemical bath deposited Bi_2S_3 thin films

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Abstract: Thin films of Bi_2S_3 of different thickness have been prepared on glass substrates in various temperatures by Chemical bath deposition. The thickness of the deposited film is measured by employing quartz crystal monitor method. The micro structural parameters such as grain size, dislocation density and strain have been evaluated. The lattice parameter values 'a' and 'c' have been determined and is found to be 4.101Å and 6.68 Å respectively. The optical properties have been studied. The variation of band gap values of Bi_2S_3 thin film samples were found to be in the range of 2.16 to 2.45 eV

Keywords: Structural property, Optical property, Chemical bath deposition, Bi_2S_3 thin films.

Introduction

Chemical bath deposition is a well known deposition process for Chalcogenides such as Bi, Zn, Cd, Co, Hg, Pb sulphides and selenides[1-3]. The Chemical Bath Deposition (CBD) method, being less expensive than other thin film deposition methods allows for the manufacture of relatively low cost devices especially light detectors, light energy conversion cells and thin films field effect transistor[4-6]. Bi_2S_3 in an important semiconductor material with very narrow band gap (2.10 to 2.40eV). The Bi_2S_3 material exhibits hexagonal structure with a preferred orientation along (002), (116,312) and (316,332) directions[7-10]. In this paper we present the results of our studies on structural and optical studies of Chemical Bath Deposited Bi_2S_3 thin film.

Materials and Methods

Bi_2S_3 thin films were deposited on quartz, Si and glass substrates using a chemical bath deposition (CBD) method in an aqueous solution containing ethylene diamine tetra acetic acid disodium salt as the complexing agent for Bismuth ions and thioacetamide as the sulfide source at temperatures ranging from 60 to 80 °C. Bi_2S_3 thin films with thicknesses ranging from 80 to 400 nm were synthesized at various Bi^{2+}molar ratios ranging from 1 to 4. Time taken for the growth of the Bismuth Sulfide on the glass substrates varied from 30 minutes to 45 minutes. Substrate cleaning plays an important role in the deposition of thin films[11-12]. Commercially available glass micro slides were submerged into the chromic acid for upto 2 to 3 hours. Then the glass substrates are washed with detergent and finally rinsed with acetone before use. The films with different thickness were obtained by varying the deposition time period. The thickness of the Bi_2S_3 thin films are measured by using gravimetric method[13-14]. The thickness variation of successive film is in the range of 90 Å in Bi_2S_3 combination. The structural characteristics were found by using x-ray diffractometer (Model-SHIMADZU XRD-2000). The arrangement consists of PID controlled oven (Model PID-2000, Scientific Equipment and services, Roorkee, India).

Result and Discussion

Structural analysis of Bi_2S_3 thin films

XRD analysis is carried out on Bi_2S_3 films and typical diffraction patterns of as-grown Bi_2S_3 thin films prepared by CBD technique on glass substrates with different thicknesses are shown in Fig. 1, Fig. 2 & Fig.3. The spectra are obtained by scanning 2θ in the range 10° to 80° with grazing angle equal to 1.5°.

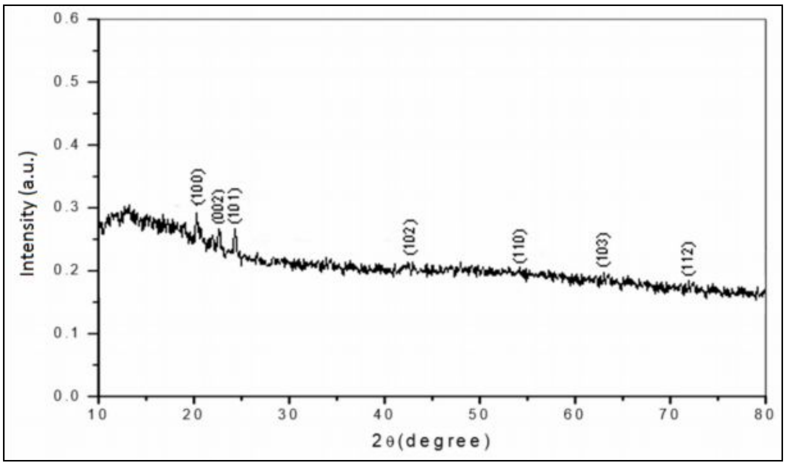

Figure 1. X-ray diffractogram of Bi_2S_3 thin film of thickness 550 Å.

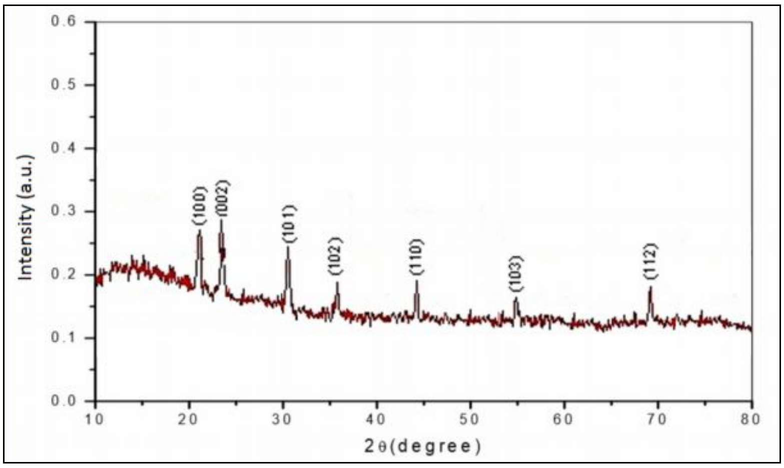

Figure 2. X-ray diffractogram of Bi_2S_3 thin film of thickness 1060 Å.

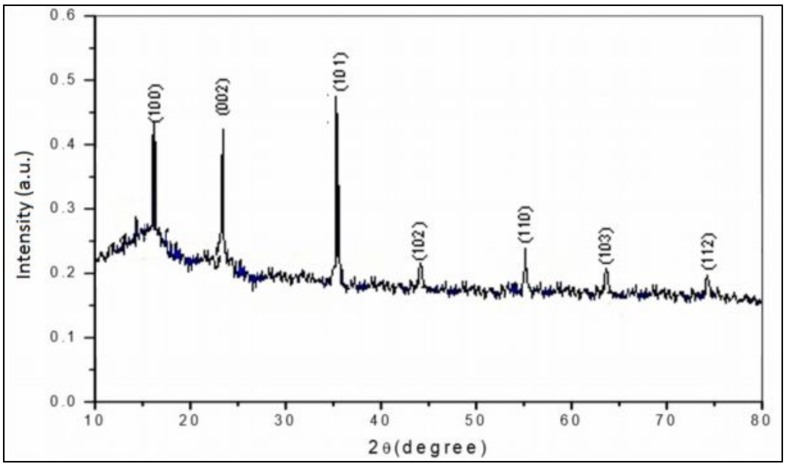

Figure 3. X-ray diffractogram of Bi_2S_3 thin film of 1750 Å.

From the diffraction patterns, it can be seen that the diffraction peaks are sharp and well defined, indicating that the film is polycrystalline in nature. From the diffraction peaks, it is found that the material exhibits cubical structure with orientations along (100), (002), (101), (102), (110), (103) and (112) directions. Also, it is clear from the high intensity peaks which indicate a significant increase in crystallite size with the cubical modification. This behaviour shows a phase transformation from the metastable amorphous cubic phase to stable polycrystalline cubic phase, which increases with increase of film thickness. The crystallinity of the films increased further by decreasing the cadmium content in the precursor solution.

The diffraction direction is solely determined by the structure and size of the unit cell. The calculated 'd' values for Bi_2S_3 sample coincides fairly with those of bulk material reported in ASTM tables on cubic Bi_2S_3. All these data showed a clear evidence for a cubic Bi_2S_3. The interplanar distance (d), lattice parameter (a), grain size (D), dislocation density (ρ) and microstrain (ε) are shown in Table 1.

Table 1. Structural parameters for Bi_2S_3 thin films

Thickness	(h k l)	d (Å) Exp	d (Å) ASTM	2 θ	a (Å)	Grain size (D) Å	Dislocation density (ρ)cm^2	Strain (ε) 10^{-3}
550 Å	(100)	1.67	1.67	33	5.6081	5.0735	5.5897	7.4581
	(002)	3.39	3.53	18	5.6459	5.2584	4.5637	7.4241
	(101)	1.73	1.95	32	5.6566	4.6603	14.5056	13.5682
	(102)	3.58	3.56	16	5.5937	4.3312	8.5765	9.6486
	(110)	1.68	1.62	32	5.5779	4.3523	5.4675	8.075
	(103)	2.59	2.64	24	5.6043	5.1958	8.3899	9.3103
	(112)	1.72	1.93	30	5.6566	2.6442	14.2743	13.4023
1060 Å	(100)	3.5	3.46	16	5.5336	5.3537	5.3212	6.9055
	(002)	1.8	1.85	27	5.5809	5.6118	4.4269	6.7397
	(101)	2.48	2.45	21	5.5213	4.8533	8.0632	6.8629
	(102)	1.8	1.82	29	5.627	5.2602	8.2732	7.8693
	(110)	3.31	3.37	17	5.5969	5.2934	4.4884	7.3079
	(103)	1.85	2.02	28	5.6353	5.5299	8.1645	8.6527
	(112)	3.43	3.39	14	5.5858	4.4673	11.7157	11.5416
1750 Å	(100)	1.67	1.64	32	5.593	5.9258	4.5286	6.2665
	(002)	2.99	3.09	21	5.6251	5.8271	3.4768	6.3672
	(101)	1.72	1.94	31	5.6566	5.033	7.3899	6.4852
	(102)	3.54	3.51	16	5.5572	5.5924	7.2488	7.277
	(110)	1.74	1.73	29	5.5794	5.4821	4.0472	6.9073
	(103)	2.54	2.55	23	5.5628	6.0245	6.7265	6.5866
	(112)	1.76	1.88	30	5.612	4.9522	8.5737	7.6358

Table. 2. Variation of film thickness with deposition time.

Sl.No.	Deposition Time Allowed (Mins)	Thickness observed in Å
1.	20	550
2.	30	1060
3.	40	1750

From the Table 1, it is found that the grain size of the film increases with film thickness and the dislocation density and microstrain is found to decrease. It can be attributed to the decrease in the imperfections and dislocations of the films with increasing film thickness. From the table 2, thickness of the film is gradually increased with increasing deposition time.

Optical properties of Bi_2S_3 thin films.

Transmission spectra of films were recorded as a function of wavelength in the range of 250-500nm. The transmittance spectra of the Bi_2S_3 films in the visible region for the different thickness films are shown in the Fig.4. It reveals that the transmittance decreases with the increase of film thickness.

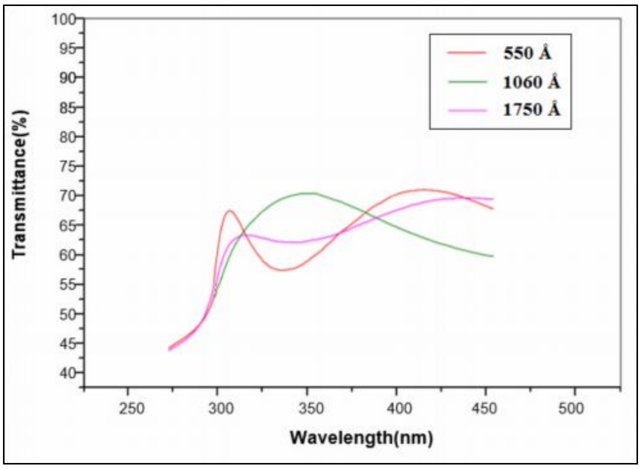

Figure 4. Transmittance Spectra of Bi_2S_3 thin films for various thickness.

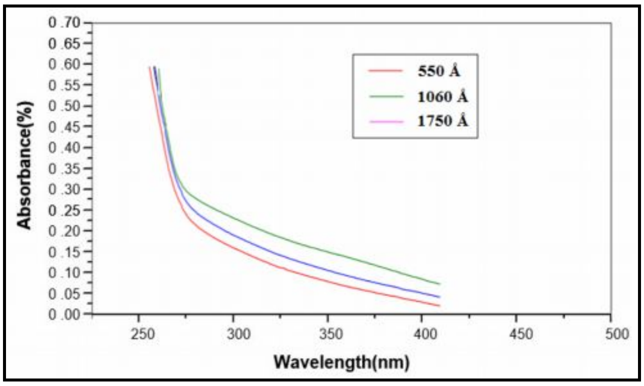

Figure 5. Absorbance Spectra of Bi_2S_3 thin films for various thickness.

From the Fig.5. Optical properties of Bi_2S_3 thin films are determined from absorbance measurements in the range of 250-500nm. The absorption coefficient can be written in terms of the incident radiation energy.

$\alpha = A(h\gamma - Eg)$ ------------------- (1)

Where 'h' is the Planck's constant and 'γ' is the frequency of the incident radiation.

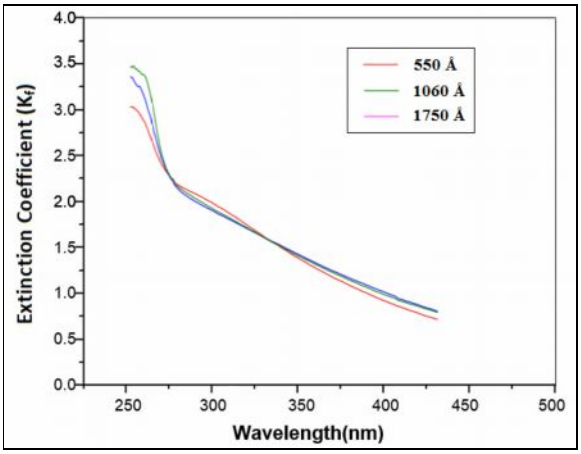

Figure 6. Thickness dependence of Extinction Coefficient (K_f).

From the Fig. 6. the value of Extinction Coefficient (Kf) decreases with the increases in the film thickness. Absorption coefficient (α) associated with the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using the relation.

$A = 2.3026\ A/t$ ------------------ (2)

The Extinction coefficients are calculated using the equation.

$K_f = 2.303\ \lambda \log(1/T_0) / 4\pi d$ ----------------- (3)

The extinction coefficient (K_f) is directly related to the absorption of light. In the case of polycrystalline films, extra absorption of light occurs at the grain boundaries[15]. This leads to non-zero value of (K) for photon energies smaller than the fundamental absorption edge[16-17].

The optical band gab can be obtained by extra plotting the linear portion of the plot $(\alpha h\gamma)^2$ Versus hγ. From the plot, the variation of $(\alpha h\gamma)^2$ Versus photon energy for different thickness (550 Å, 1060 Å, 1750 Å) Bi_2S_3 thin films are shown in Fig. 7. The presence of a single slope in the curves suggests that from thermal evaporation are of single phase in nature and the type of transition is direct and allowed.

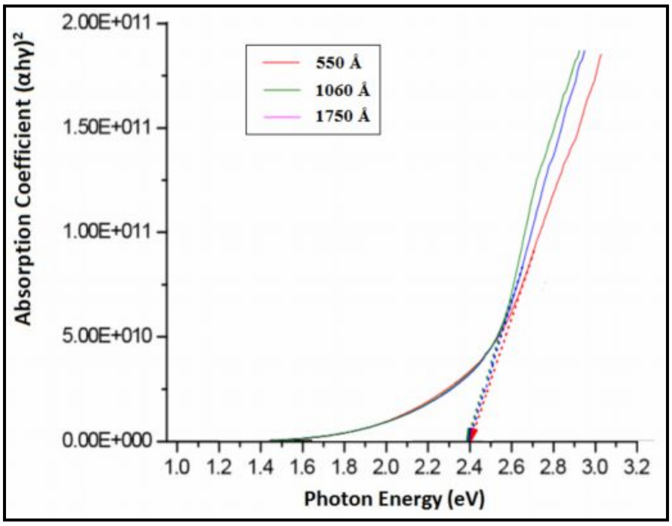

Figure 7. A plot of $(\alpha h\gamma)^2$ Vs. (hν) for Bi_2S_3 thin film of thickness 550 Å, 1060 Å &1750 Å.

From these absorption peaks, the direct and allowed band gap energy is evaluated from the plot $(\alpha h\gamma)^2$ Versus hγ are shown in table 3.

Table 3. Variation of energy gap, Absorption coefficient and Extrinsic coefficient with thickness.

Thickness Å	Band gap energy (eV)	Absorption coefficient	Extrinsic coefficient
550	2.40	1.72	0.46
1060	2.39	1.98	0.32
1750	2.38	2.68	0.30

The observed decrease in the band gap energy with increases in thickness is due to the changes in the barrier height to the size of the grain in crystalline film and large density of dislocation.

Conclusion

Bi_2S_3 bulk material is obtained by taking 99.999% of pure material. Bi_2S_3 thin film has been deposited on a well cleaned glass substrate by chemical bath deposition technique. X-ray diffraction reveals that the films are polycrystalline in nature with hexagonal phase. Variations of particle size, strain, dislocation density and full width half maxima with substrate temperature have been studied. The Bi_2S_3 has very narrow band gap (2.10 to 2.40 eV) at visible region. Carrier concentration is found to improve with Cd concentration in bath. Bi_2S_3 exhibits characteristics compatible with window material for solar cells.

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