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OPTICAL AND ELECTRICAL PROPERTIES OF BISMUTH–SULFIDE (Bi_2S_3) THIN FILMS PREPARED BY THERMAL EVAPORATION

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Thin films of Bi_2S_3, of thickness in the range 300 to 500 nm, were produced by thermal evaporation technique. The reaction consisted in depositing the two elements (bismuth and sulfur) from a boat source and allowing their atoms to interdiffuse to form the compound during the deposition on quartz substrates. The material has been characterized by X–ray studies, optical and electrical measurements. When these films were annealed at 353 K, 393 K and 453 K for 5 hours, a nearly amorphous to polycrystalline transition was observed. The absorption coefficient revealed the existence of an allowed direct transition with $E_g = 1.56$ eV. The activation energies for electrical conduction in low and high temperature regions are 0.28 eV and 0.73 eV, respectively.

1. *Introduction*

Semiconducting chalcogenide thin films are important for their application in fabrication of many devices. Bismuth sulfide (Bi_2S_3) is an important member of chalcogenides because of their use to form liquid, solid-state junction solar cells and photo-conductor cells. It is a layered semiconductor that crystallizes in the

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orthorhombic system (Pbnm space group) and is isostructural to antimony sulfide (Sb_2S_3) and selenide (Sb_2Se_3) [1]. A literature survey reveals that the conventional thermal evaporation method is being widely used for the growth of binary and ternary compounds because of its simplicity. The thermal evaporation in vacuum continues to be of importance to obtain high quality, pure compound films for most thin film applications. It is observed that the compound has a tendency to dissociate on heating as well as on condensation over a heated substrate, leading to films that are non-stoichiometric in composition [2].

Kirshna Moorthy [2,3] has prepared polycrystalline stoichiometric Bi_2S_3 films by various physical deposition techniques, such as flash evaporation, conventional thermal evaporation of the compound, and the hot-wall technique. Also Lukose et al. [4] studied the physical properties of bismuth sulfide thin films and obtained a band–gap of 1.38 eV. The present work presents the results of studies of the structure and composition of the vacuum deposited bismuth sulfide thin films and the relevance of their optical and electrical characteristics.

2. *Experimental techniques*

Thin bismuth sulfide (Bi_2S_3) films were prepared by thermal evaporation in which the spec. pure elements (bismuth and sulfur) were evaporated from the source. The compound films were deposited on quartz substrate initially at 325 K because the deficiency of sulfur in the compound films increases with increasing substrate temperature. Deposition rate was maintained considerably low (about 2.5 nm/s). Tungsten boats were used as vapour sources and were aligned to provide a near-normal deposition onto substrates placed at a distance of about 7 cm. During deposition, the substrate temperature may have increased by about 25 K due to radiant heat from the bismuth-sulfur source [4]. The deposition chamber was evacuated to a residual pressure of about 10^{-4} Pa prior to all deposition experiments. The thickness of the films was measured using multiple beam interferometry [5]. The composition of the films was analysed by XRD using a Philips type PW 1390 diffractometer. Normal-incidence transmittance and reflectance spectra were recorded at room temperature in the range 200-300 nm, using a double-beam spectrophotometer, Shimadzu model 3101. The electrical resistance of the sample was measured directly by using Keithley 617 programmable electrometer having an input resistance of 10^{16} Ω. All films were given an overlayer of carbon in an attempt to minimize the possible re-evaporation of the components during annealing treatments.

3. *Results and discussion*

It is well known that the structure and properties of the evaporated thin material films are influenced greatly by deposition conditions such as deposition rate, substrate temperature and background pressure. At pressure common for evaporation, atoms travel from the source to the substrate without collision or loss of energy in transit. When incident atoms approach to within several atomic diameters of the substrate, they enter the force field of the substrate surface. After an atom has been adsorbed, or has joined another evaporant atom on the substrate surface, the atom may undergo additional processes which involve energy changes such as desorption, migration over the sufrace, or a change from physical adsorption to chemical adsorption. The energy required to cause the adsorbed atom to migrate over the surface of the substrate is less than that required to remove the atom from the substrate. Also, it is clear that the influence of deposition rate appears most predominantly at the thickness where the growth process changes from that of a discontinuous film to a continuous one.

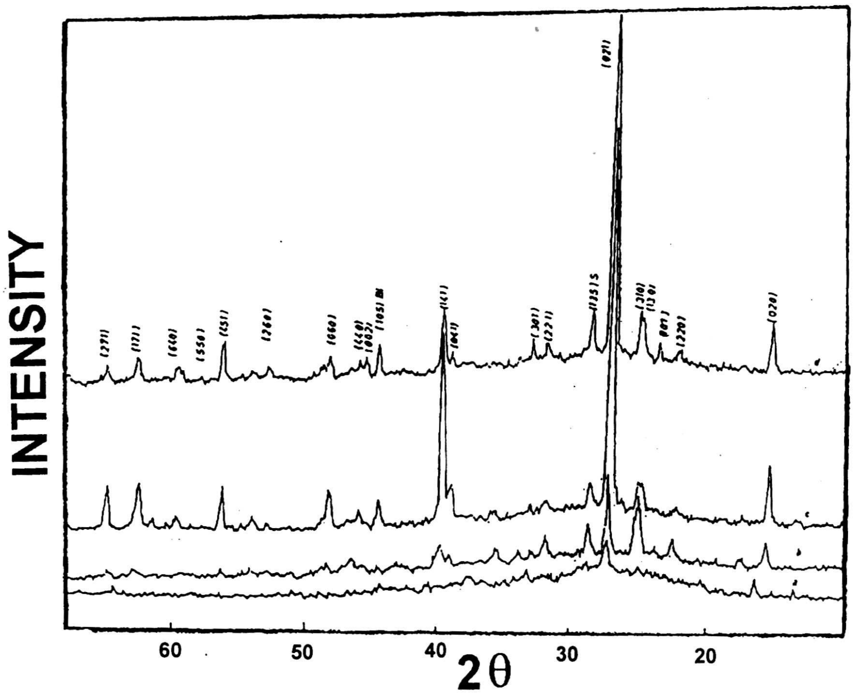


Fig. 1. X–ray diffractograms of Bi_2S_3 *thin films at different heat–treatment. a) as deposited, b) annealed at* 353 K, *for* 5 h, *c) annealed at* 393 K, *for* 5 h, *d) annealed at* 453 K, *for* 5 h.

Typical X–ray diffractographs of the film substrate systems prepared at the substrate temperature of about 325 K are shown in Fig. 1(a-d). The as-deposited film (Fig. 1a) showed weak reflections corresponding to the compound Bi_2S_3. When the film is deposited onto the substrate kept at about 325 K, effectively the film forming atoms or molecules are being quenched from the high temperature source to the substrate at low temperature (325 K). Though chemical reaction can take place to form Bi_2S_3, there is not sufficient energy for the arrangement of molecules in a regular crystalline array [4]. Hence, weak reflections are observed (Fig. 1a).

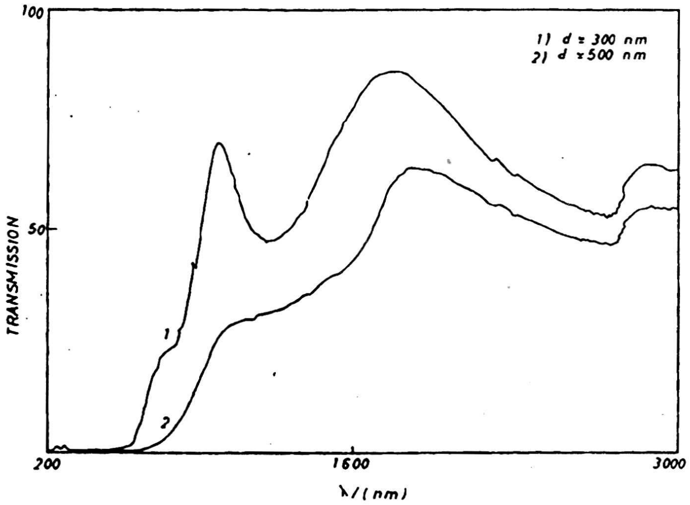
TABLE 1.
X-ray diffraction of thermally deposited Bi_2S_3 *layers on quartz substrate. d is interplanar distance expressed in* 10^{-10} m.

	JCPDS 17–320			As deposited a		Annealed at 353 K, 5 h b		Annealed at 393 K, 5 h c		Annealed at 453 K, 5 h d	
n	d	$\frac{I}{I_0}$	hkl	d	$\frac{I}{I_0}$	d	$\frac{I}{I_0}$	d	$\frac{I}{I_0}$	d	$\frac{I}{I_0}$
1	5.654	20	020	-	-	5.639	40	5.604	22	5.639	23
2	5.040	20	120	-	-	5.092	25	5.006	8	5.006	10
3	3.969	40	220	-	-	3.948	28	3.965	9	3.969	40
4	3.748	18	101	-	-	3.735	34	3.719	9	3.735	16
5	3.569	100	130	3.558	60	3.558	76	3.558	17.6	3.558	25
6	3.530	60	310	-	-	3.530	60	3.530	17	3.530	27
7	3.253	16	021	3.252	100	3.275	100	3.252	100	3.263	100
8	3.118	80	230	-	-	3.143	25	3.161	11	3.161	15
			221	-	-						
9	2.824	14	040	-	-	2.802	-	2.802	11	2.802	17
10	2.812	50	221	-	-	2.811	43	-	-	-	-
11	2.717	30	301	-	-	2.720	29	2.752	8	2.760	8
12	2.641	18	311	2.664	56	2.649	27	2.657	7	2.664	12
13	2.305	20	041	-	-	2.301	25	2.301	16.8	2.301	13
14	2.258	30	141	-	-	2.262	35	2.262	66	2.268	27
15	2.188	6	510	-	-	2.188	17	-	-	2.164	7.9
16	2.130	8	241	-	-	2.139	14	2.134	4	2.134	8
17	1.990	18	002	-	-	-	-	1.963	8	1.967	7
18	1.985	16	440	-	-	1.979	19.5	-	-	1.987	7
19	1.884	25	060	-	-	1.880	20.6	1.882	15	1.882	13
20	1.857	14	600	-	-	1.853	14	-	-	1.857	10
			160	-	-			-	-		
21	1.785	4	260	-	-	1.782	14	1.782	3	1.782	6
22	1.606	4	451	-	-	1.614	11	1.635	16	1.637	17
23	1.587	2	550	-	-	1.535	11	1.598	1	1.587	6
24	1.552	8	640	-	-	1.557	6.3	1.554	5.3	1.554	9.2
25	1.482	12	171	-	-	-	-	1.489	15.5	1.489	12
26	1.445	6	271	-	-	-	-	1.445	15	1.445	10.5

After heating the as-deposited film to higher temperatures (353 K, 393 K and 453 K) for 5 hours (Fig. 1b-d), more peaks appeared which contained all prominent reflections corresponding to the Bi_2S_3 compound. This means that the thin film tended to form the compound more readily. The enhanced probability for the formation of the compound results from the combined effect of the diffusion of bismuth and sulfur atoms. On the other hand, the film forming particles acquire enough energy to form regular crystalline structures and hence the formation of polycristalline films with no preferred orientation. The X–ray diffraction patterns of all films match well with the bismuth sulfide card (JCPDS – Joint Commitee on Powder Diffraction Standards 17–320). The data on these conditions are illustrated in Table 1. The crystallite size S, can be calculated from the formula [6]

$$S = \frac{K\lambda}{D\cos\theta}, \tag{1}$$

where D is the angular width of the diffraction line at the half–maximum of its intensity, λ is the wavelength of X-rays $\lambda = 1.5404 \times 10^{-10}$ m), θ is the Bragg angle and K is the constant known as the Scherrer constant and is equal to 0.94. It is observed that the crystallite size values of the as-deposited film is 3.72 nm and at the annealing temperatures, the values are constant (4.97 nm).



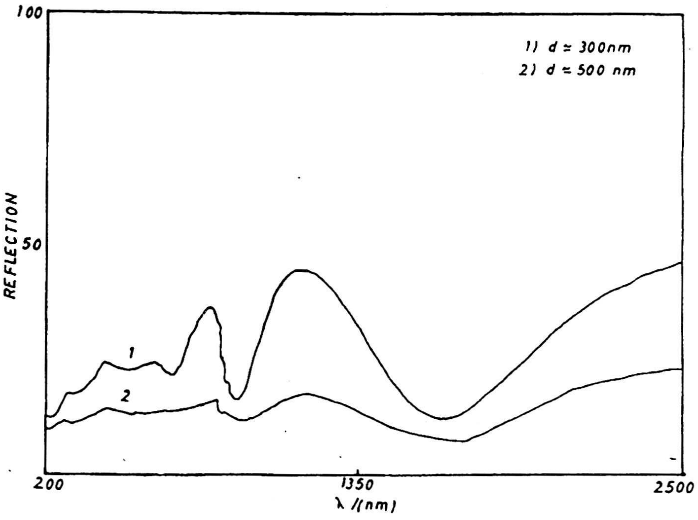


Fig. 2a. Transmission spectrum of a typical Bi_2S_3 *thin film heated at* 453 K *of different thicknesses.*

Fig. 2b. Reflection spectrum of a typical Bi_2S_3 *thin film heated at* 453 K *of different thicknesses.*

The optical properties and the possible electronic transitions were investigeted by measuring the transmission and reflection spectra recorded for the heated Bi_2S_3 films of different thicknesses (300 nm and 500 nm). The spectra are shown in Fig. (2a-b). The transmission curves demonstrate two maxima, at 1720 nm and 940 nm. A similar behaviour of the transmission spectrum was obtained by Lukose and Pradeep [4] for Bi_2S_3 films prepared by reactive evaporation. The absorption coefficient α at different wavelengths was deduced from the transmission spectra of two different film thicknesses using the relation

$$\alpha = \frac{2.303 \Delta T}{\Delta d}, \tag{2}$$

where ΔT and Δd are the differences in the transmission and thicknesses of the films, respectively. The dependence of the optical absorption α on the incident photon energy $h\nu$ is plotted in Fig. 3. The sharp rise in the absorption coefficient is observed for $E_g > 1.5$ eV. Normally, this rise in the absorption coefficient is attributed to the fundamental absorption edge. The absorption coefficient α of the order of 10^4 cm^{-1}, indicating that the material is of the direct–band–gap type and that transitions are allowed [7–10]. In order to deduce the gap of these transitions, α^2 vs. $h\nu$ was represented in Fig. 4. Extrapolation of the linear portion of the

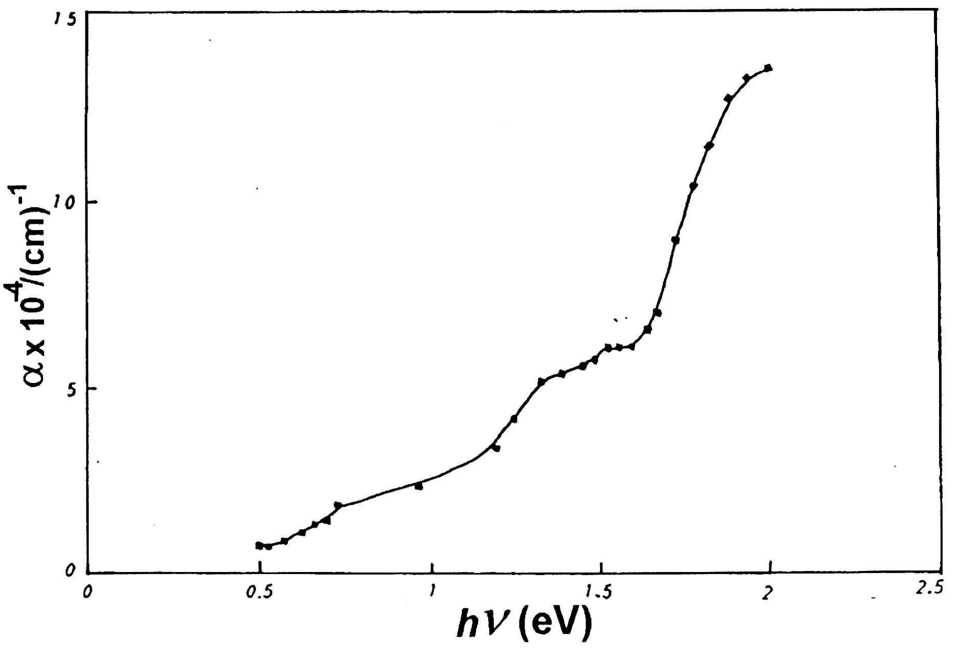


Fig. 3. Variation of optical absorption coefficient (α) with photon energy ($h\nu$).

curve to $\alpha^2 = 0$ gives the band–gap which is 1.56 eV. The estimated band–gap seems to be higher than from observations on single-crystals. The difference may be due to the interference by diffuse reflectance within the material itself [11] and the anisotropy of the film-formation process [12].

The resistance of thin films is generally high compared with the single crystal. The higher resistance may be due to the grain boundary, discontinuity and thickness of the films. Moreover, the grain boundary and discontinuity of the samples depend on the deposition conditions [7]. Figure 5 is a representative example for $\log R$ vs. $1/T$ for a layer of about 500 nm thick heated at 453 K. This relation is divided into two distinct regions corresponding to two activation energy. The activation energies of electrical conduction, calculated from the slope of the curve in both low and high temperature regions, are found to be 0.28 eV and 0.73 eV, respectively. The activation energy of 0.73 eV, in the high temperature region, is an intrinsic activated process. This value agrees well with the value reported by many authors [5,7,12], but it is higher than that of the crystalline Bi_2S_3 which is 1.3 eV [1,13–15]. The value of the conductivity activation enegy of the Bi_2S_3 films above 399 K is nearly equal to half the optical band–gap. This leads us to believe that the Fermi level is near the middle of the gap.

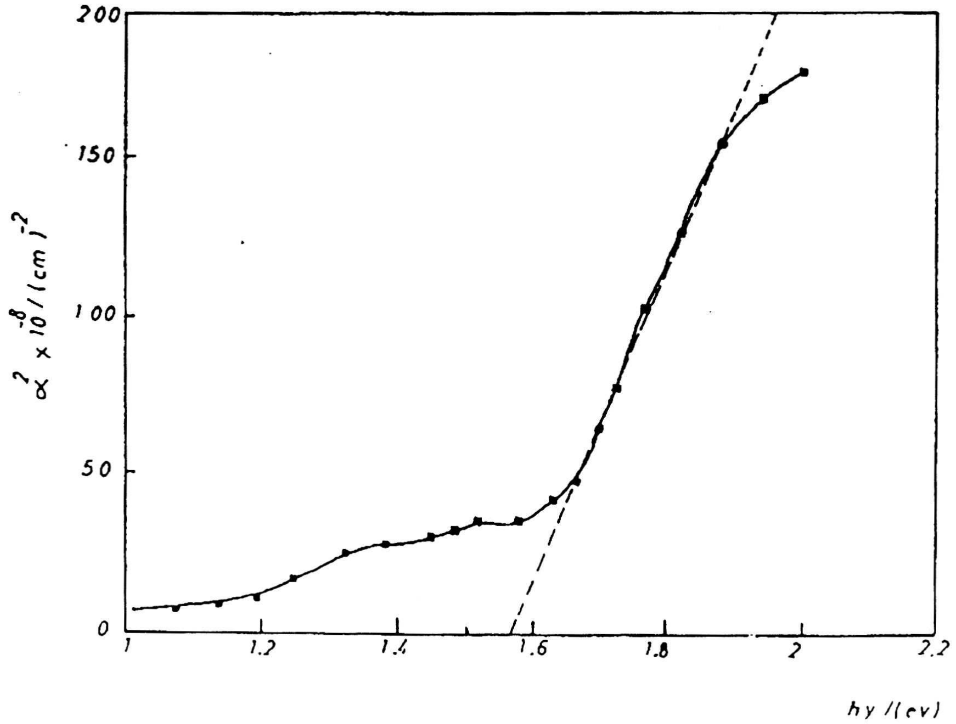


Fig. 4. Variation of α versus hν.

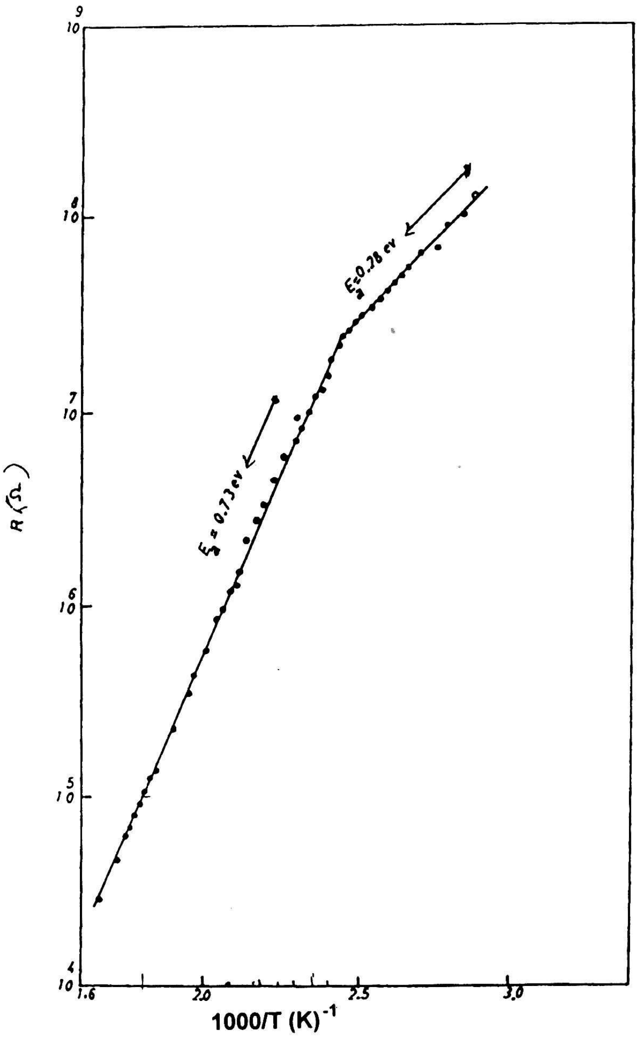


Fig. 5. $\log R$ *versus* $1/T$ *for a layer of about* 500 nm *thick heated at* 453 K *for* 5 h.

4. Conclusion

Bi_2S_3 thin films have been prepared by thermal evaporation technique and their optical and electrical properties were investigated. On the basis of X-ray analysis, it was found that the Bi_2S_3 films are nearly amorphous when the film was grown onto the substrate kept at about 325 K. After annealing at various temperatures, the deposits obtained were polycrystalline with an estimated crystallite size of about 4.97 nm and they exhibited all the prominent reflections corresponding to the compound with no indication of extra phases. The optical band–gap of Bi_2S_3 thin film is found to be 1.56 eV. The thermal activation energy calculated from the slope of resistivity measurements of Bi_2S_3 polycrystalline in the range 353 – 573 K, is 0.28 eV and 0.73 eV.

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OPTIČKA I ELEKTRIČNA SVOJSTVA TANKIH SLOJEVA BISMUT SULFIDA (Bi_2S_3) NAČINJENIH TERMIČKIM ISPARAVANJEM

Tanke slojeve Bi_2S_3, debljine 300 do 500 nm, pripremali smo isparavanjem u vakuumu. Ispitivali smo ih difrakcijom rentgenskog zračenja, te mjerenjima njihovih optičkih i električnih svojstava. Toplinskim otpuštanjem na temperaturama 353 K, 393 K i 453 K u vremenima od 5 sati, u slojevima smo opazili prijelaz iz približno potpuno amorfne u polikristaliničnu strukturu. Apsorpcijski koeficijent pokazuje prisustvo izravnog dozvoljenog prijelaza sa $E_g = 1.56$ eV. Aktivacijske energije za električnu vodljivost u području nižih i viših temperatura iznose 0.28 eV odnosno 0.73 eV.