

STRUCTURAL AND OPTICAL PROPERTIES OF CHEMICALLY DEPOSITED CuBiS_2 THIN FILMS

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Thin films of Copper bismuth sulphide prepared on well cleaned glass substrates by chemical deposition showed polycrystalline in nature with monoclinic structure. The average grain sizes as calculated from Scherrer's formula were found to be within the range 237 Å to 752 Å. The films are oriented in the (403) direction. In addition, optical studies revealed that variation of optical band gap with thickness: 2.62 to 2.19 eV.

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1. Introduction

A large amount of work has been devoted to the study of ternary semiconductors of the type V-VI in view of their potential applications in the field of optoelectronic devices, photo sensitivity and thermo electronic power [1-8]. Thin films can be prepared by various techniques [9-12]. Amongst them, chemical deposition method has a special significance, as this method has been proved to be the least expensive, non-polluting and low temperature method.

Copper bismuth sulphide (CuBiS_2) is a ternary compound semiconducting material. Sonawane et al. [13] have deposited CuBiS_2 thin films from chemical bath deposition method using Sodium thio sulphate as a sulphur ion source. The optical band gap of that film was found to be 1.8 eV. Pawar et al. [14] have deposited CuBiS_2 thin films from spray-pyrolytic deposition method using thiourea as a sulphur ion source and reported that CuBiS_2 thin films are polycrystalline.

The present work describes a chemical method for deposition of CuBiS_2 thin films from acidic bath on a glass substrates using $\text{Na}_2\text{S}_2\text{O}_3$ as a sulphur ion source. The characterization of CuBiS_2 films was carried out by XRD and optical studies. The effect of deposition time at 60°C on structural and optical properties of CuBiS_2 thin films is studied.

2. Experimental details

2.1 Preparation of thin films

0.2M Copper nitrate solution was added into 0.2M Bismuth nitrate solution in a beaker. To the above mixture 0.2M Sodium thiosulphate was added. The resultant solution was stirred for few minutes and pH of this reaction bath was maintained between 2 and 3. Ultrasonically cleaned glass substrates were dipped in the reaction bath and the temperature of the bath was increased slowly. After attaining 333K, the reaction beaker was kept at room temperature

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for further deposition. After a deposition period of 1h, 3h and 5h, the substrates were taken out, rinsed in distilled water and dried. To enhance uniformity and quality of the films, di sodium salt of EDTA was used as complexing agent [15].

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 CuK α radiation ($\lambda=0.154\text{nm}$) at 40 kV and 25 mA. Grain size of CuBiS₂ 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 unpolarised lights from deuterium and tungsten lamps which are used at near normal incidence.

3. Results and discussion

3.1 CuBiS₂ growth mechanism

The chemical reaction responsible for CuBiS₂ film from an acidic bath using Na₂S₂O₃ as the sulphur ion source [13, 15-17] could be:



Na₂S₂O₃ is a reducing agent by a virtue of the half-cell reaction as:



In acidic medium, dissociation of S₂O₃²⁻ takes place as:



The released electrons react with sulphur as:



Finally metal sulphide film was formed as:



3.2 X-Ray diffraction analysis

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 CuBiS₂ films was carried out with X-ray diffraction in the range of angle 2 θ between 20 and 60. Fig.1, 2 and 3 shows the XRD pattern of CuBiS₂ thin films with thickness 100 nm, 160 nm and 240 nm (deposited at 60°C for 1h, 3h and 5h time periods). The film having thickness 100, 160 and 240 nm is polycrystalline nature with monoclinic structure. Table 1 Summarises the crystallographic data of these films compared with ASTM data file (JCPDS 170320) [18]. The Structural parameters of the deposited CuBiS₂ 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 film thickness.

It was found that crystallite size increases from 237 Å to 752 Å as film thickness increases from 100 to 224 nm. This significant improvement in crystallite size is due to controlled slow

release of copper and bismuth ions from its complex in the solutions which give probability of growth of larger particles [13].

The copper bismuth sulphide thin films are having the preferential orientation along (403) plane. The intensity of the peak (403) increases significantly faster than other peaks ((202), (112), (113), (113), (311), (514) and (020)) indicating a relatively preferred structural orientation in the (200) plane. Similar had been reported earlier for CdS thin films [11]. 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 [11]. According to this method the preferred orientation factor f (403) of the (403) plane for the CuBiS_2 thin films has been calculated by evaluating the fraction of (403) plane intensity over the sum of intensities of all peaks within a given measuring 2θ range $[10^\circ\text{--}80^\circ]$. Similarly the orientation of all other peaks has been evaluated for all the films. In CuBiS_2 films prepared at 60°C of 1 hour deposition time period (Fig.1) $f(202) = 0.1893$, $f(112) = 0.1796$, $f(403) = 0.2008$, $f(113) = 0.1732$, $f(113) = 0.1310$, $f(311) = 0.1216$, $f(514) = 0.0917$, $f(020) = 0.0702$. In CuBiS_2 films prepared at 60°C of 3 hours deposition time period (Fig.2) $f(202) = 0.1987$, $f(112) = 0.1735$, $f(403) = 0.2077$, $f(113) = 0.1684$, $f(113) = 0.1288$, $f(311) = 0.1175$, $f(514) = 0.0924$, $f(020) = 0.0708$. In CuBiS_2 films prepared at 60°C of 5 hours deposition time period (Fig.3) $f(202) = 0.1673$, $f(112) = 0.1458$, $f(403) = 0.3300$, $f(113) = 0.1458$, $f(113) = 0.1177$, $f(311) = 0.1241$, $f(514) = 0.0830$, $f(020) = 0.0654$. Since $f(403)$ is greater compared to other orientation in all the three films, it can be concluded that CuBiS_2 thin films have the preferential orientation along (403) plane. The enhancement of (403) plane and in-turn the improved crystallinity with bath deposition time is remarkable irrespective of the chemical bath. The predicted peaks (202), (112), (403), (113), (113), (311), (514) and (020) are reported as the characteristic peaks for CuBiS_2 thin films. Table 3 shows the calculated preferential orientational factor of CuBiS_2 thin films with different thicknesses (100nm, 160nm and 240 nm) for peaks (202), (112), (403), (113), (113), (311), (514) and (020).

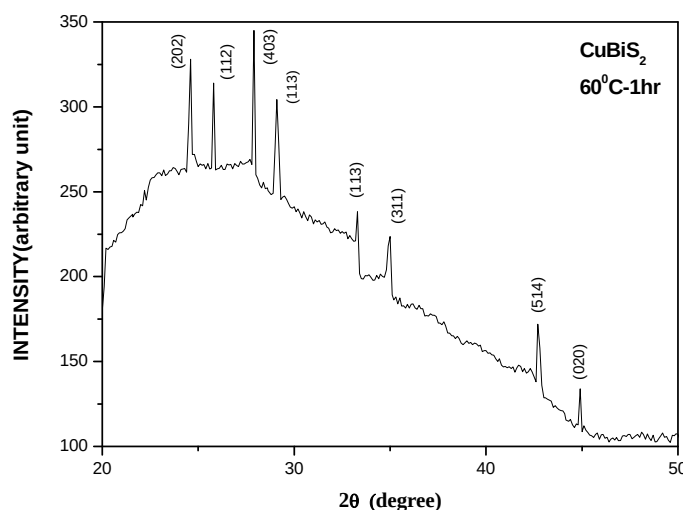


Fig. 1. X-ray diffraction pattern of CuBiS_2 thin films of thickness 100 nm

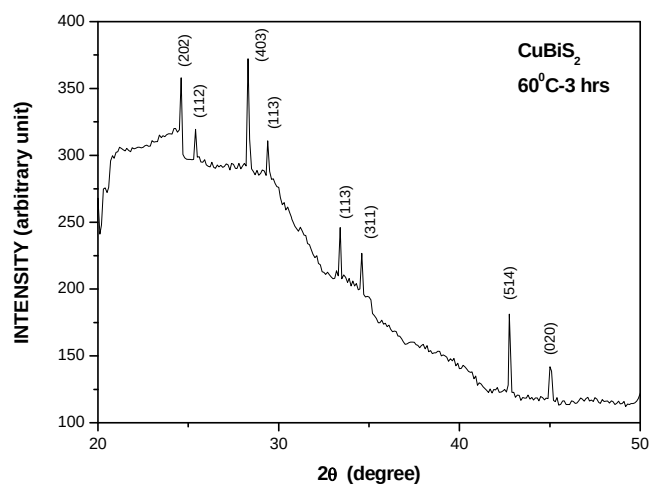


Fig. 2. X-ray diffraction pattern of CuBiS_2 thin films of thickness 160 nm

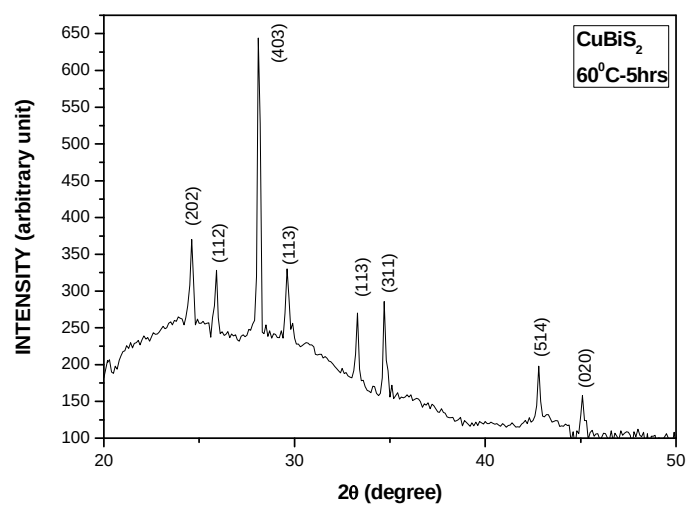


Fig. 3. X-ray diffraction pattern of CuBiS_2 thin films of thickness 240 nm.

Table 1 Comparison of XRD data for CuBiS₂ thin films with the JCPDS card

Deposition time period (hours)	Thickness (nm)	Planes (hkl)	2 θ values (degree)		d-spacing values (Å)		FWHM (β) (degree)
			JCPDS	Experiment	JCPDS	Experiment	
1	100	202	24.48	24.52	3.632	3.686	0.3621
		112	25.50	25.65	3.489	3.444	0.2929
		403	28.18	28.02	3.163	3.171	0.2328
		113	29.24	29.49	3.051	3.015	0.2693
		113	33.70	33.37	2.656	2.693	0.2860
		311	34.52	34.82	2.595	2.576	0.4188
		514	42.63	42.67	2.118	2.112	0.2647
		020	45.00	44.99	2.012	2.009	0.2500
3	160	202	24.48	24.61	3.632	3.621	0.2672
		112	25.50	25.38	3.489	3.450	0.1672
		403	28.18	28.10	3.163	3.157	0.1342
		113	29.24	29.42	3.051	3.031	0.1562
		113	33.70	33.44	2.656	2.649	0.1860
		311	34.52	34.69	2.595	2.586	0.3141
		514	42.63	42.83	2.118	2.111	0.1561
		020	45.00	45.01	2.012	2.014	0.1564
5	240	202	24.48	24.6	3.632	3.615	0.1657
		112	25.50	25.77	3.489	3.482	0.1471
		403	28.18	28.10	3.163	3.150	0.1246
		113	29.24	29.65	3.051	3.041	0.1345
		113	33.70	34.77	2.656	2.645	0.1714
		311	34.52	34.69	2.595	2.583	0.2896
		514	42.63	42.75	2.118	2.119	0.1342
		020	45.00	45.08	2.012	2.006	0.1207

Table 2 The Structural parameters of the deposited CuBiS₂ films

Deposition time period (hrs)	Thickness (nm)	Planes (hkl)	Grain size d (Å)	Dislocation Density X10 ¹⁵ lines/m ²	Strain ϵ X10 ⁻³
1	100	202	237.01	1.7800	1.5431
		112	293.65	1.1596	1.2455
		403	372.10	0.7222	0.9829
		113	322.02	0.9643	1.1357
		113	306.12	1.0671	1.1947
		311	209.86	2.2704	1.7427
		514	340.13	0.8643	1.0753
		020	363.08	0.7585	1.0073
3	160	202	321.24	0.9689	1.1385
		112	514.16	0.3782	0.7113
		403	644.23	0.2409	0.5677
		113	555.13	0.3244	0.6588
		113	470.81	0.4511	0.7768
		311	279.72	1.2780	1.3075
		514	577.12	0.3002	0.6337
		020	580.41	0.2968	0.6301
5	240	202	518.04	0.3726	0.7060
		112	584.87	0.2923	0.6253
		403	693.89	0.2076	0.5271
		113	645.03	0.2403	0.5670
		113	512.73	0.3803	0.7133
		311	303.38	1.0864	1.2055
		514	671.10	0.2220	0.5450
		020	752.33	0.1766	0.4861

Table 3 Preferential orientational factor of CuBiS₂ thin films

Deposition time period (hours)	Thickness (nm)	Plane (hkl)	Orientation factor (f)
1	100	202	0.1893
		112	0.1796
		403	0.2008
		113	0.1732
		113	0.1310
		311	0.1216
		514	0.0917
		020	0.0702
3	160	202	0.1987
		112	0.1735
		403	0.2077
		113	0.1684
		113	0.1288
		311	0.1175
		514	0.0924
		020	0.0708
5	240	202	0.1673
		112	0.1458
		403	0.3300
		113	0.1458
		113	0.1177
		311	0.1241
		514	0.0830
		020	0.0654

3.3 Optical Analysis

The optical properties of the chemically deposited CuBiS₂ 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 CuBiS₂ films of three different thicknesses are shown in fig. (4-9). It can be observed that in general a decrease in film thickness improves the transmission.

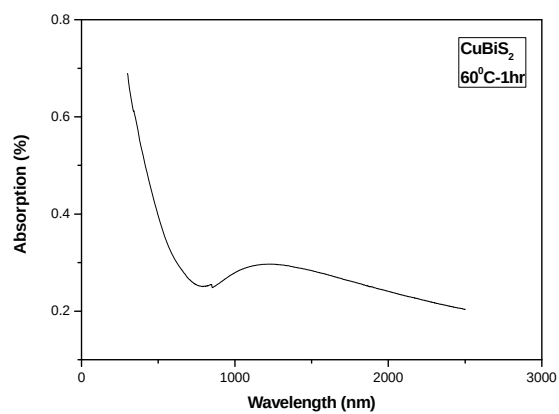


Fig. 4. Absorption spectra of CuBiS₂ thin films of thickness 100 nm

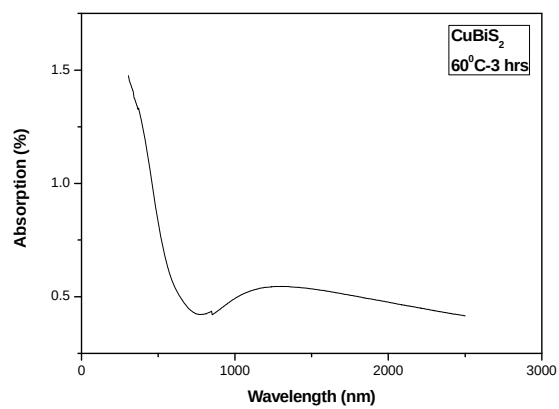


Fig. 5. Absorption spectra of CuBiS₂ thin films of thickness 160 nm

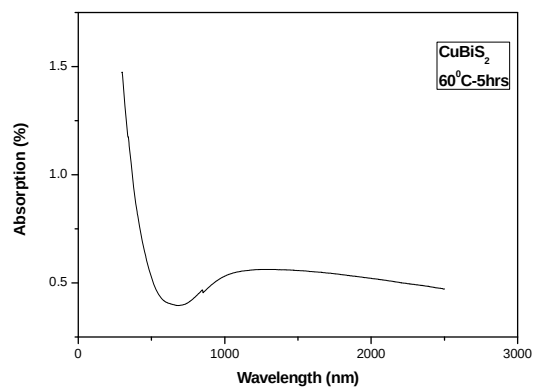


Fig. 6. Absorption spectra of CuBiS₂ thin films of thickness 240 nm

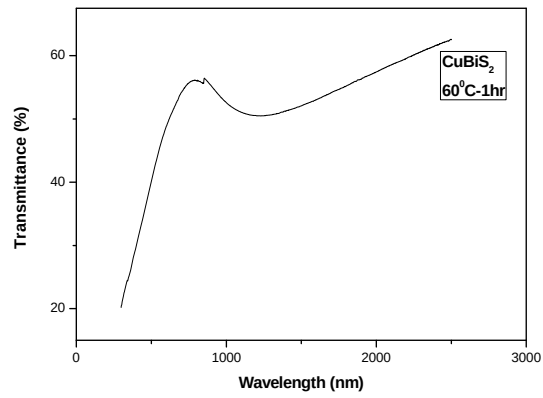


Fig. 7. Transmittance spectra of CuBiS_2 thin films of thickness 100 nm

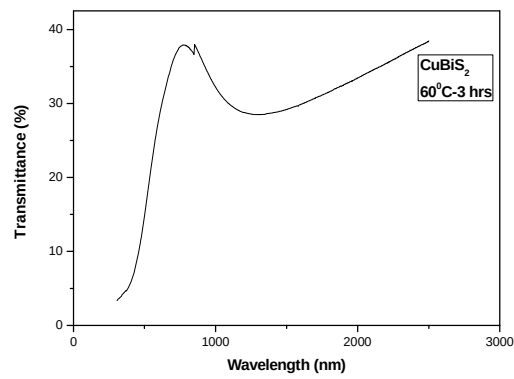


Fig. 8. Transmittance spectra of CuBiS_2 thin films of thickness 160 nm

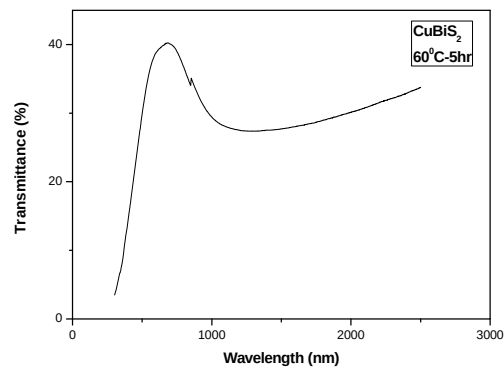


Fig. 9. Transmittance spectra of CuBiS_2 thin films of thickness 240 nm

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, E_g is the band gap, n is a constant equal to $\frac{1}{2}$ for direct band gap semiconductor and 2 for indirect band 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 $(h\nu)$ plot (Fig.10-12). The linear extrapolation of this curve to the energy axis gives the value of band gap of CuBiS_2 as 2.62 eV, 2.35 eV and 2.19 eV which agrees with the reported value [13]. Table 4 gives the optical band of CuBiS_2 thin films of different thicknesses. The optical band gap increases from 2.19 eV to 2.62 eV as thickness varied from 240 nm to 100 nm.

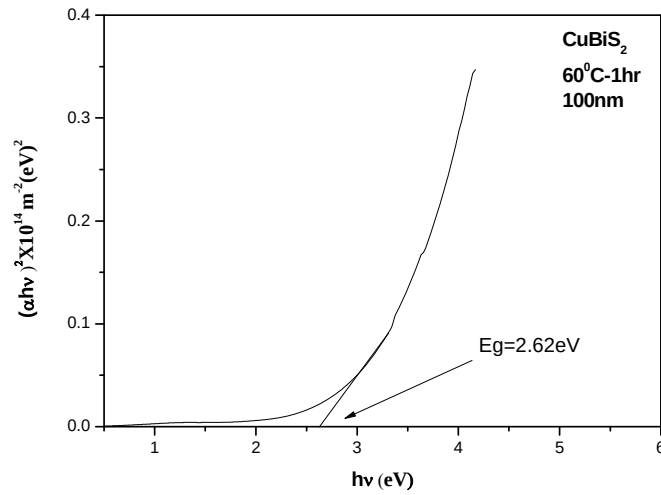


Fig. 10. Band gap plot of CuBiS_2 thin films of thickness 100 nm

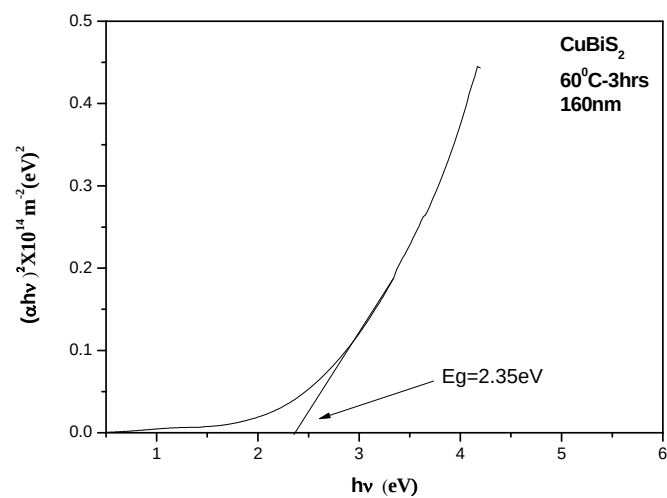


Fig. 11. Band gap plot of CuBiS₂ thin films of thickness 160 nm

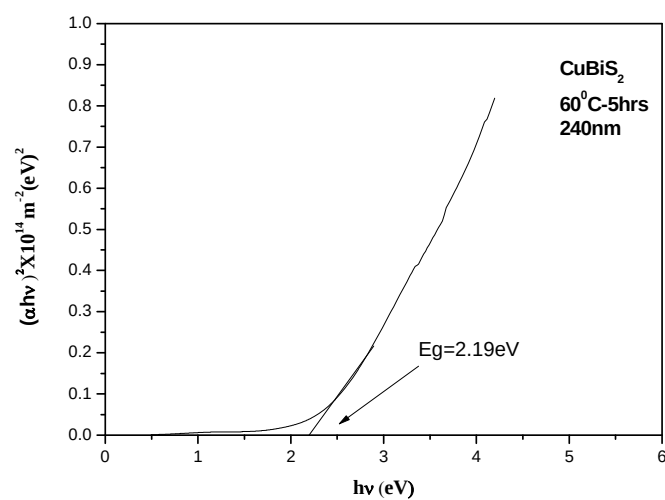


Fig. 11. Band gap plot of CuBiS₂ thin films of thickness 240 nm

Table 4 Optical band of CuBiS₂ thin films of different thicknesses at 60⁰C

Thickness (nm)	Deposition time period (hours)	Band gap (eV)
100	1	2.62
160	3	2.35
240	5	2.19

4. Conclusions

From the above study, it is concluded that CuBiS₂ thin films of three different thickness prepared by CBD are found to be polycrystalline with grain size within the range 237 Å to 752 Å. The grain size of CuBiS₂ thin films are found to increase with increase in thickness. The films are oriented in the (403) direction. Consequently, optical band gap energy was decreased with increase in thickness.

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