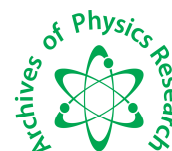




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XRD studies of Chemically Deposited Bi₂S₃ Thin Films

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ABSTRACT

Bi₂S₃ thin films have been prepared by chemical bath deposition method using Bismuth nitrate and Sodium thiosulphate. Films were deposited onto well cleaned glass substrates with different deposition time periods. The X-ray diffraction pattern revealed that bismuth sulphide thin films exhibit orthorhombic structure. The structural parameters (grain size 94-358Å, dislocation density 0.7789-11.22X10¹⁵ l/m² and strain (ε) 3.85-1.027X10⁻³) have been calculated.

Keywords: Bismuth sulphide; Chemical bath deposition; XRD studies; Thin films.

INTRODUCTION

Presently nanocrystalline materials have opened a new chapter in the field of electronic applications, since material properties could be changed by changing the grain size and thickness of the film [1]. Bismuth trisulphide in thin film form is a particularly challenging material because of its midway band gap ($E_g=1.7\text{eV}$), absorption coefficient of the order of 10^4 to 10^5 cm⁻¹, reasonable conversion efficiency and stability together with low cost [2, 3]. Several methods such as cathodic electrodeposition, anodic electrodeposition, vacuum evaporation, the hot wall method, solution gas interface, spray pyrolysis and chemical deposition have been used for Bi₂S₃ film preparation. As compared to other methods, chemical deposition is simple, economic and suited for a large area of any configuration [4].

The present work describes a chemical method for deposition of Bi₂S₃ thin film using thiosulfate as a sulphide ion source. The thickness of the films was varied by changing the deposition time period its effect on the structural parameters (grain size, dislocation density and strain) was studied and results are reported.

MATERIALS AND METHODS

2. Experimental details

Bismuth nitrate (Bi(NO₃)₃), sodium thiosulfate (Na₂S₂O₃) and ethylene di amine tetra acetic acid (EDTA) were used to prepare the Bi₂S₃ films. Glass was used as the substrate. Before the deposition of the films, the glass substrate was firstly ultrasonically cleaned by acetone and the ultrasonically cleaned by distilled water.

For the deposition of the Bi₂S₃ films, Bi(NO₃)₃ solution was added into EDTA solution, finally Na₂S₂O₃ solution was added to the mixed solution. The concentration of Bi(NO₃)₃, EDTA and Na₂S₂O₃ in the deposition solution was 0.2M, 0.1M and 0.2M respectively. After the preparation of the deposition solution, glass substrates were immersed into the solution. The temperature of the solution was increased slowly up to 333K, and then it was kept at room temperature for further deposition. After a deposition period of 4 hrs, 8 hrs and 12 hrs the substrates were taken out, rinsed in distilled water and dried.

RESULTS AND DISCUSSION

The deposition process of Bi_2S_3 is based on the slow release of Bi^{3+} and S^{2-} ions in the solution which then condenses ion by ion basis on the substrates. Deposition of Bi_2S_3 thin films occurs when the ionic product Bi^{3+} and S^{2-} ions exceeds the solubility product of Bi_2S_3 . The concentration of Bi^{3+} and S^{2-} ions in the solution controls the rate of Bi_2S_3 formation. The rate of Bi^{3+} ions is controlled by EDTA, which forms a complex $\text{Bi}[(\text{EDTA})\text{n}]^{3+}$ with Bi^{3+} . The chemical reaction responsible for Bi_2S_3 film from an acidic bath using $\text{Na}_2\text{S}_2\text{O}_3$ as the sulphide ion source [5] could be:



$\text{Na}_2\text{S}_2\text{O}_3$ is a reducing agent by a virtue of the half-cell reaction as:



In acidic medium, dissociation of $\text{S}_2\text{O}_3^{-2}$ takes place as:



The released electrons react with sulphur as:



Bi^{3+} from $\text{Bi}(\text{NO}_3)_3$ solution or a complex of Bi^{3+} formed by EDTA react to give



3.1 Structural Characterisation

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.I, II and III shows the XRD pattern of Bi_2S_3 thin films with thickness 210 nm, 437 nm and 860 nm is amorphous in nature. Films show polycrystalline nature with orthorhombic structure after annealed at 200°C in air.

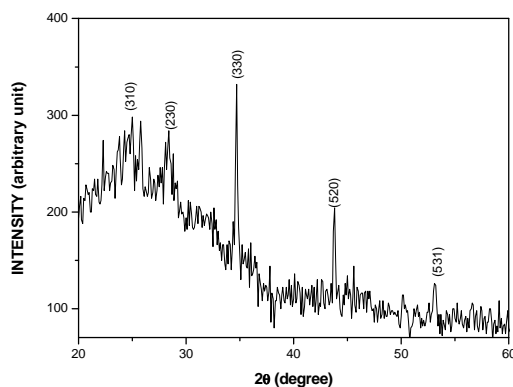


Fig.I. X-ray diffraction pattern of Bi_2S_3 thin films of thickness 210 nm

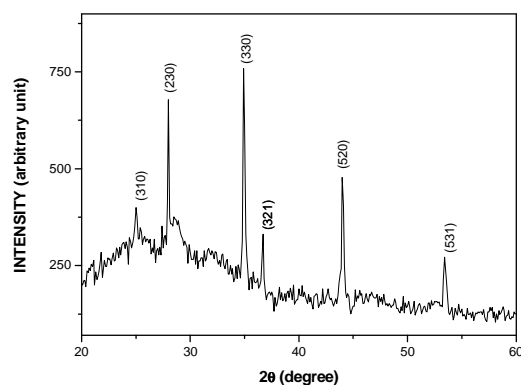


Fig.II. X-ray diffraction pattern of Bi_2S_3 thin films of thickness 437 nm

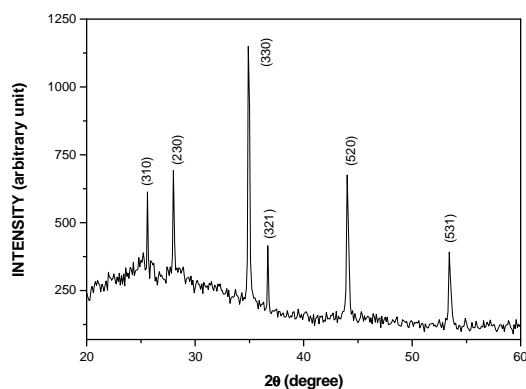


Fig.III. X-ray diffraction pattern of Bi_2S_3 thin films of thickness 860 nm

Table I Summaries the crystallographic data of these films compared with JCPDS data file (JCPDS 65-2435). The Structural parameters of the deposited Bi_2S_3 films like grain size, dislocation density and strain have been evaluated in Table II. It was observed that grain size increases but the strain and dislocation density decreases with increase of deposition time period. Table III Summaries the preferential orientation factor of Bi_2S_3 thin films. The films are oriented in the (330) direction.

Table I Comparison of XRD data for Bi_2S_3 thin films with the JCPDS card (65-2435)

Deposition time period (hours)	Thickness (nm)	Planes (hkl)	2θ values (degree)		FWHM (β) (degree)
			JCPDS	Experiment	
4	210	310	25.288	25.26	0.7649
		230	28.729	28.79	0.7926
		330	34.017	34.06	0.7019
		520	43.751	43.79	0.8469
		531	53.118	53.16	0.9676
8	437	310	25.288	25.26	0.6916
		230	28.729	28.74	0.4414
		330	34.017	34.06	0.3646
		321	36.799	36.79	0.7046
		520	43.751	43.74	0.6024
12	860	310	25.288	25.26	0.4864
		230	28.729	28.79	0.4334
		330	34.017	34.06	0.2448
		321	36.799	36.70	0.6864
		520	43.751	43.76	0.4416
		531	53.118	53.12	0.6811

Table II The Structural parameters of the deposited Bi₂S₃ films

Deposition time period (hrs)	Thickness (nm)	Planes (hkl)	Grain size d (Å)	Dislocation Density X10 ¹⁵ lines/m ²	Strain ε X10 ⁻³
4	210	310	112.36	7.9209	3.255
		230	109.24	8.3798	3.348
		330	123.92	6.5120	2.771
		520	101.93	9.6248	3.588
		531	94.82	11.1222	3.857
8	437	310	124.27	6.4754	2.9430
		230	196.14	2.5993	1.8647
		330	240.57	1.7278	1.5203
		321	125.43	6.3561	2.9157
		520	150.02	4.4432	2.4379
12	860	531	122.01	6.7175	2.4975
		310	176.70	3.2027	2.0698
		230	199.77	2.5057	1.8308
		330	358.30	0.7789	1.0207
		321	128.73	6.0344	2.8410
		520	204.66	2.3874	1.7871
		531	137.66	5.2769	2.6567

Table III Preferential orientation factor of Bi₂S₃ thin films

Deposition time period (hours)	Thickness (nm)	Plane (hkl)	Orientation factor (f)
4	210	310	0.3152
		230	0.2946
		330	0.3657
		520	0.1928
		531	0.1131
8	437	310	0.1588
		230	0.3026
		330	0.3509
		321	0.1283
		520	0.1959
12	860	531	0.1027
		310	0.1847
		230	0.2131
		330	0.4122
		321	0.1177
		520	0.2071
		531	0.1105

The crystal size of the film was determined by using Scherrer formula

$$d = \lambda / \beta \cos \theta \quad (6)$$

where λ is the wavelength used (1.54Å); β is FWHM in radians; θ is the Bragg's angle.

It was found that grain size increases from 94.82 to 358.30Å as film thickness increases from 210 to 860 nm. This significant improvement in crystallite size is due to controlled slow release of bismuth ions from its complex [Bi(EDTA)]⁺ in the solutions which give probability of growth of larger particles [6].

CONCLUSION

The films are found to be poly crystalline in nature with orthorhombic structure. The films are oriented in (330) direction. The grain size of Bi₂S₃ thin films are found to increase with increase of deposition time period.

REFERENCES

- [1] A.Tanaka, S.Onari and T.Arai, *Physics Review*, B47 (1993).
- [2] R.N. Bhattacharya, P.P.Pramanik, *Journal of Electrochemical Society*, 128 (1983) 332.
- [3] C.D.Lokhande, *Materials Chemistry and Physics*, 29 (1991) 1.
- [4] C.D.Lokhande, A.U.Ubale, P.S.Patil, *Thin Solid Films* 302 (1997) 1-4.

[5] V.Balasubramanian, N.Suriyanarayanan, S.Prabahar, S.Srikanth, *Chalcogenide Letters*, Vol.8, No.11, November 2011, 671-681.

[6] A.U.Ubale, *Materials Chemistry and Physics*, 121 (2010) 555-560.