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Structural and Optical Properties of Chemical bath Deposited Sb₂S₃ thin films

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ABSTRACT

Thin films of antimony tri- sulphide are prepared by chemical bath deposition technique. The effect of concentrations of Sb and annealing temperature is studied to determine the optimum conditions for deposition process. Films prepared with different molar ratios of Sb are annealed at a temperature of 423K. The structure, morphology and compositions of the deposited thin films are investigated by X-ray diffraction, scanning electron microscopy (SEM) and energy dispersive analysis spectrum (EDAX) respectively. Thin films deposited are found to be polycrystalline. X-ray diffraction shows the characteristic peaks with preferential orientation along (301) plane. Better crystalline quality of Sb_2S_3 films is obtained for pH values maintained at 2.3 and 2.53 respectively. The optical properties are measured to determine the transition type and band gap values. The band gap values are determined by optical absorption spectra and it is found to be direct band gap.

Keywords: Antimony tri Sulphide, Structural Properties, Thin films, Optical band gap.

INTRODUCTION

Antimony tri- sulphide is a semiconductor with high photosensitivity and high thermoelectric power [1]. The band gap (1.78-2.5 eV) covers the visible and near infrared range of the solar spectrum [2, 3] and in conjunction with its photoconductivity, stibinite has received some attention as a potential candidate in solar energy conversion. Annealing of the films after deposition in air, changes the optical properties of the deposited thin films because of the changes in their structure [4, 5]. Micro sphere of Sb_2S_3 have also been used as substrates for radio labeling in route clinical application [6]. Badachhape and Goswami [7] obtained Sb_2S_3 films by vacuum evaporation. George and Radhakrishnan [8] prepared Sb_2S_3 films by three temperatures method. Savadago and mandal [2] and lokhande [9] have deposited thin Sb_2S_3 films by chemical bath deposition. In the present work, we report the influence of Sb concentrations

and annealing temperature on structural, optical properties of Sb_2S_3 thin films deposited by chemical bath deposition.

MATERIALS AND METHODS

In a typical synthesis, films of three different concentrations of antimony tri-chloride (SbCl₃) (0.1M, 0.15M, 0.2 M) and 0.2M of thioacetamide are prepared by dissolving appropriate amount of salts in acetic acid (glacial) in separate beakers. Equal volume of (20ml) both the solutions are mixed in a beaker and stirred well for few minutes. The sulphur molar ratio is fixed to 0.2M. The pH of the resulting solution is found to be 2.13, 2.3, and 2.53 respectively. The microscopic glass slides are used as substrates. The ultrasonically cleaned glass substrates are immersed almost vertically into the chemical bath. The deposition is carried out to about 35hrs. Pink coloured thin homogeneous layers of Sb₂S₃ are obtained. All the films are heated at controlled temperature of 150°C for one hour in air. During deposition process the chemical bath is kept undisturbed. The deposited films are tested for adhesion by subjecting it to a steady stream of distilled water. Then the films are annealed to 423 K in air. X-ray diffraction (XRD) patterns of Sb₂S₃ thin films of different thickness are recorded by Shimadzu XRD-6000 X-ray diffractometer. Scanning electron microscopy techniques are employed to analyze the surface morphology of the films deposited. The elemental compositions of the obtained films are determined from EDAX. Absorption spectra are recorded using a JASCO-UV/VIS/NIR (JASCO V- 570) double beam spectrometer and studied in the span of wavelength range 190-1200nm.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

Depositing films of different concentrations of Sb³⁺ increases the thickness of the films [2]. Thickness of the films is found to vary from 293nm – 667 nm with Sb concentration (0.1 - 0.2 M) as depicted in Fig 1. The XRD patterns of annealed Sb₂S₃ films of different concentrations (0.1 M, 0.15 M and 0.2 M) are shown in Fig 2 (a, b, c). It can be seen that the films have polycrystalline structure and the intensity of the peaks increases for 0.15M Sb concentration and gradually decreases as we increase the Sb concentration along (301) plane with orthorhombic structure. The intensity of preferential orientation also increases along (301) plane for 0.15M concentrations of Sb and gradually decrease with further increase in Sb concentrations. The grain size, strain and dislocation density are estimated and presented in Table 1.The grain size (D) is calculated by using Scherrer's formula, from the full width at half maximum (FWHM) D= $k\lambda/\beta cos\theta$. From the table it is observed that as the grain size increases, the strain and dislocation density decreases as a function of the antimony concentration. This enhancement of grain size is due to increase in thickness and growth mechanism involved in thin films [10, 11].



Fig 1.Variation of $\mathrm{Sb}_2\mathrm{S}_3$ thin film thickness as a function of concentration of Sb





(c)

Fig 2. XRD of Annealed Sb₂S₃ thin films at 423K for different concentration a) 0.1M, b) 0.15M c) 0.2M of Antimony

Molar ratio of	2θ (de Standard	egrees) Observed	d(Standard	Å) Observed	Grain Size	hkl plane	Strain ɛx10 ⁻⁴	Dislocation density $\delta x 10^{15} (lines/m^2)$
30.5	value	value	value	value	(IIII)			0x10 (Intes/III)
0.1:0.2	15.669 25.056 32.391	15.500 25.120 32.280	5.651 3.551 2.761	5.712 3.542 2.771	35.651 36.191 36.775	002 301 212	0.1015 0.1000 0.0984	0.786 0.763 0.739
0.15:0.2	15.669 25.056 32.391	15.660 25.180 31.900	5.651 3.551 2.761	5.6542 3.5339 2.8031	38.664 39.526 40.726	002 301 212	0.0936 0.0915 0.0888	0.668 0.640 0.603
	15.669	15.100	5.651	5.862	40.154	200	0.0901	0.620
0.2:0.2	25.056 32.391	25.580 31.740	3.551 2.761	3.479 2.816	44.544 45.907	301 212	0.0812 0.0788	0.503 0.474

Table 1 Structural parameters of 423K annealed Sb₂S₃ thin film for different molar ratios of Sb: S

Scanning Electron Microscopic Studies

The SEM micrographs of the chemically deposited and annealed Sb_2S_3 thin films at 423K are shown in Fig. 3 (a, b, c) for different concentrations of Sb. The particles formed on the film surface are found to be spherical and are slightly elongated; 3μ m diameter spheres are formed on the surface for 0.1M Sb. The number of particle formation and their growth increases for 0.2M Sb concentration which can be evidenced by XRD pattern obtained for 0.15M concentration of Sb (Fig.2b) along (301) plane. The particle size is found to be 2- 4 μ m. While increasing the concentrations of Sb further to 0.2 M, large sized spherical grains of 8-10 μ m diameter are observed indicating the growth of the particles. The results are in good agreement with XRD results [12].

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Fig 3 Annealed Sb₂S₃ at 423K for different concentrations of antimony a) 0.1M b) 0.15M c) 0.2M

Energy Dispersive Analysis Spectrum

The EDAX spectrums of annealed Sb_2S_3 thin films at 423K are shown in Fig. 4 (a, b, c) for different concentrations of Sb 0.1, 0.15, 0.2 respectively. The atomic percentage of Sb, S and Cl is shown in Table.2. It is concluded that the films are not highly stoichometric. The peaks corresponding to Na, Si and Cl shows transition from L to K shell which can be confirmed from (k α) peaks. The peaks of 'Na' and 'Si' are due to the use of glass substrate and the 'Cl' peaks from the starting material SbCl₃. Inclusion of oxygen is also observed for all the films. This oxygen inclusion is unavoidable for chemically deposited film. It is also reported by C.D. Lokhande [13].







Fig 4. EDAX spectra of Annealed Sb_2S_3 films at 423K for different concentrations of Antimony a) 0.1M, b) 0.15M, c) 0.2M

	Atomic percentage					
	Different molar ratio		Sb:S			
Elements	0.1:0.2	0.15:0.2	0.2:0.2			
Sb	38.99	39.39	41.19			
S	58.49	57.9	56.82			
Cl	2.52	2.71	1.99			

Table 2.Elemental compositions of annealed Sb₂S₃ films (423K) prepared by different molar ratios

Optical Absorption Studies

The study of materials by means of optical absorption provides a simple method for explaining some features concerning the band structure. Optical absorption spectra for Sb₂S₃ thin films deposited for different concentrations of Sb are studied in the span of wavelength range 190-1200nm. The absorption spectra of as deposited films for different antimony concentrations (a) 0.1 M, (b) 0.15 M (c) 0.2 M are shown in Fig 5. From the figure it is clear that the absorption increases with increasing Sb concentrations. It is due to the increase in particle size of the film and it is evidenced by XRD, SEM results. The $(\alpha h v)^2$ is plotted against the photon energy (hv) for films of different Sb concentrations are shown in Fig. 6(a, b, c). The band gap values are shown in table 3. It is observed that the band gap decreases with increase in Sb concentrations. The decrease in the optical band gap can be attributed to improved growth of grain size and/ or decrease in defect level [14].Fig 7 shows the absorption spectra of 423K annealed films for different Sb concentrations. Figures show that the absorption increases with increase in antimony concentrations. This is due to improvement in grain size of the film as it is well established from the XRD and SEM results. The $(\alpha h v)^2$ is plotted against the photon energy (hv) for films of different Sb concentrations are shown in Fig. 8 (a, b, c). The table 4 shows the band gap energy of annealed films. The band gap decreases with increase in concentrations of Sb. The decrease in band gap values are due to increase in effective grain size on annealing [16]. The decrease in band gap after heat treatment of Sb₂S₃ thin film is in good agreement with the previous results obtained for CdS and CdSe thin films [15, 2].



Fig 5. Wavelength vs absorption of as deposited sb₂s₃ thin films of different sb concentrations

(a)

(b)

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Fig 6. hv Vs (ahv) 2 of as deposited Sb₂S₃ thin film of different molar ratios. a) 0.1:0.2, b) 0.15:0.2M, c) 0.2:0.2M

Fig 7 Wavelength Vs absorption of annealed $\mathrm{Sb}_2\mathrm{S}_3$ thin films of different Sb concentrations

Fig 8 .hv Vs (αhv) ² of 423K annealed Sb₂S₃ thin film of different molar ratios. a) 0.1:0.2, b) 0.15:0.2M, c) 0.2:0.2

Molar ratio of Sb:S (M)	Band gap Energy (eV)		
0.1:0.2	1.36		
0.15:0.2	1.23		
0.2:0.2	1.12		

Table 3. Band gap of as deposited Sb_2S_3 thin films for different molar ratios

Molar ratio of Sb:S (M)	Band gap Energy (eV)
0.1:0.2	1.07
0.15:0.2	1.01
0.2:0.2	0.56

Table .4. Band gap of 423K annealed Sb₂S₃ thin films for different molar ratios

CONCLUSION

 Sb_2S_3 thin films have been prepared after optimizing the deposition parameters such as deposition time and molar ratio of Sb using a non-aqueous (acetic acid) bath and subsequent annealing at 423 K. The X-ray diffraction reveals that the as deposited films are amorphous and the structural properties of annealed Sb_2S_3 thin films strongly depend upon the deposition time and molar ratios of Sb: S and it shows the polycrystalline nature. The intensity of preferentially oriented direction of (301) plane increases with increase in molar ratio of 0.15M of Sb. The various structural aspects such as grain size, strain and dislocation density are thickness dependent. SEM images show Sb_2S_3 particles are in the form of spheres and distributed irregularly over the surface of the film. Overgrowth of the particle is clearly seen from the SEM micrographs with increase in concentration of Sb of annealed Sb_2S_3 thin films. EDAX analysis determines the atomic percentage of the elements present in the film. The absorption spectra of as deposited and annealed films indicate that the absorption is found to be thickness dependent. The optical band gap decreases with increase in film thickness. The possible transition in these films is identified as direct transitions.

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