JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 10, October 2010, p. 2075 - 2081

Effect of annealing temperature and deposition time on Sb_2S_3 thin films

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In the present research paper, Sb_2S_3 thin films are deposited on glass substrates for various depositions time periods. Preparative parameters such as bath composition, complexing agent and deposition time are optimized. The effect of thermal annealing on the structural and optical properties of antimony tri sulfide (Sb_2S_3) thin films is studied. The structural investigations are performed by X-ray diffraction (XRD); Scanning electron microscopy (SEM) and the compositional analysis are carried out by Energy dispersive analysis (EDAX). As-deposited films are microcrystalline in nature. After thermal annealing at temperature 423K the Sb_2S_3 thin films are found to be polycrystalline. The absorption spectrum of as-deposited and annealed films indicates that the absorption depends on thickness and the band gap energy E_g is found to be direct.

(Received September 28, 2010; accepted October 14, 2010)

Keywords: Antimony tri Sulphide, Structural Properties, Thin films, Optical band gap, XRD, EDAX, SEM

1. Introduction

Antimony tri sulphide thin films (Sb_2S_3) have gained much attention during the past two decades due to their special properties such as high refractive index [1], well defined quantum size effects [2], photosensitive and thermo electric properties [3]. The technological importance of Sb_2S_3 is ascribed by many researchers earlier [4-7] to its applications in microwave devices. Depending on the preparative methods, the films may show either n- or p-type conductivity [4-6]. Amorphous and crystalline thin films of antimony tri sulphide were prepared by various thin film deposition techniques, which includes; chemical bath deposition [7-12], electrodeposition [13], spray pyrolysis [14, 15], vacuum thermal evaporation [16, 17] and tarnishing reactions [18]. Among these methods used for the preparation of Sb_2S_3 thin films, the chemical bath deposition method is often preferred because, it offers large possibilities to modify the deposition conditions so as to obtain films with required structure and physical properties for specific applications [7-12]. Improved optical properties of the deposited thin films are obtained after annealing the deposited films in air [19, 20]. The objective of this paper is to study the influence of annealing temperature and time of deposition on the structural and optical properties of Sb_2S_3 thin films.

2. Experimental details

Microscopic glass slides are used as substrates in this work. These slides are cleaned well with dilute solution of sodium hydroxide and subsequently with detergent solution. The substrates are rinsed with distilled water and subjected to ultrasonic agitation for about 30 minutes. The substrates are once again washed with some drops of detergent solution, by distilled water and then heated in an oven at about 100^0C for an hour. The dried Glass substrates are kept in an air tight box in order to avoid contact of moisture and impurities. The chemicals used for the preparation of Sb_2S_3 thin films are antimony chloride (99% purity- Merck) thioacetamide (99.1% purity-Merck) and acetic acid. The 0.1M solution of antimony trichloride and 0.2 M solution of thioacetamide are prepared by dissolving appropriate amount of salts in acetic acid (glacial). Equal volume (20ml) of both the solutions are mixed in a beaker and stirred for few minutes. The pH of the resulting solution is 2.26. The colorless solution becomes red after 30 hours, indicating the initiation of chemical reactions. In order to increase the rate of reaction, the solution is heated to 80°C bath temperature for 15 minutes. Cleaned glass micro slides (substrates) are suspended almost vertically closer to the inner wall of the beaker for better uniformity, good adherence and to avoid shaking of the substrate while deposition. The depositions are carried out at three different time intervals 25 hrs, 35 hrs and 45 hrs respectively. At 30°C pink colored thin homogeneous layers of Sb_2S_3 are obtained. Semiconducting thin films deposited at relatively low temperatures shows better orientation of grains due to slow releasing rate of ions which results in uniform and better adherent film on glass substrates. Films are taken out, washed with distilled water and dried in air. The thicknesses of the films are measured using sensitive microbalance by assuming the density (4.12g Cm^{-3}) of bulk Sb_2S_3. X-ray diffraction (XRD) patterns of Sb_2S_3 thin films of different thickness are recorded by Shimadzu *XRD-6000* X-ray diffractometer and all the films are analyzed in the 20°- 80° (2θ) scale range. 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.

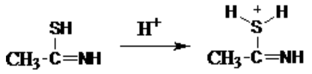
3. Results and discussion

3.1. Reaction mechanism

A reaction which was proposed by Savadogo and Mandal for Sb_2S_3 film formation from an alkaline medium for thioacetomide as an S^{2-} source. The reaction mechanism for acidic medium is given by

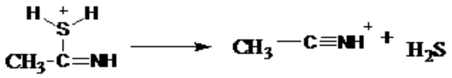
$$CH_3-\overset{\overset{S}{\|}}{C}-NH_2 \rightleftharpoons CH_3-\overset{\overset{SH}{|}}{C}=NH \qquad (1)$$

In an acidic medium, (pH = 1 and 2) protonation gives



$$CH_3-\overset{\overset{SH}{|}}{C}=NH \xrightarrow{H^+} CH_3-\overset{\overset{H\diagdown\overset{+}{S}\diagup H}{|}}{C}=NH \qquad (2)$$

The intermediate compound disassociates to gives H_2S.



$$CH_3-\overset{\overset{H\diagdown\overset{+}{S}\diagup H}{|}}{C}=NH \longrightarrow CH_3-C\equiv NH^+ + H_2S \qquad (3)$$

H_2S dissociates as

$$H_2S \longrightarrow H^+ + SH^-$$

Dissociation constant $K_1 = 5.7 \times 10^{-8}$

and

$$SH^- \longrightarrow H^+ + S^{2-}$$

Dissociation constant $K_2 = 1.2 \times 10^{-15}$

The S^{2-} ions react with Sb^{3+} ions to form

$$2\,Sb^{3+} + 3S^{2-} \longrightarrow Sb_2S_3$$

Thus, it is seen that the process of Sb_2S_3 formation is controlled by the S^{2-} release rate, which in turn is related to the dissociation constants of H_2S [3].

3.2 X-ray diffraction analysis

At lower temperature (300 K), the deposition rate is slow with large incubations and nucleation period. It takes about 25 hrs to obtain a film of about 233 nm thicknesses. This shows that the dissociation of metal complex as well as thioacetamide is temperature dependent, yielding very low condensation on the surfaces. Deposition time is varied (25hrs – 45hrs) to obtain films with different thickness (233 – 897 nm). Increase in film thickness with deposition time is due to the film formation and homogeneous precipitation with time [21, 22].

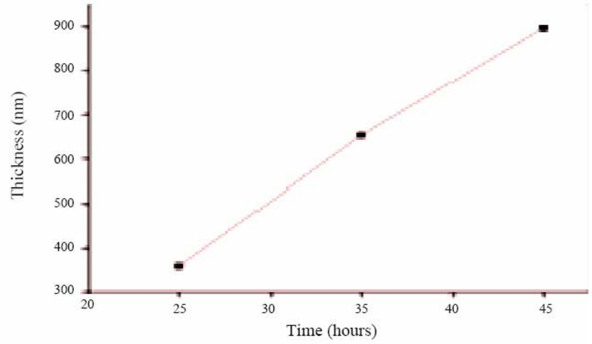


Fig. 1.Variation of Sb_2 S_3 thin films thickness as a function of duration of deposition (25hrs, 35hrs & 45hrs)

Fig 1. Gives the growth nature of Sb_2S_3 thin film with time period (h). X-ray diffraction patterns of the Sb_2S_3 thin films of different deposition time (25hrs, 35hrs & 45 hrs) are shown in Fig .2 (a, b, c). It reveals that the films are microcrystalline in nature without well defined peaks. These films which are annealed at 423 K give polycrystalline nature as shown in Fig .3. (a, b, c). The identified peaks for lower deposition time (25 hrs) at $2\theta = 15.5^o$, 17.75^o, 24.34^o, 29.48^o, 32.28^o, 47.5^o and 54.3^o associated with (002), (102), (301), (222), (121), (212), (020) and (603) planes respectively. But for higher deposition times (35 and 45 hrs) the peaks at $2\theta = 17.7^o$, 24.9^o and 29.4^o correspond to (102), (301) and (112) planes are appeared. In addition to these planes, (212) plane is obtained for the deposition time at 45 hrs and the intensity of other peaks decrease due to the formation of new smaller grains on the larger grains. The calculated lattice parameters corresponding to orthorhombic type with lattice constants a = 11.26 Å, b = 3.872 Å and c = 11.156 Å. The results are in good agreement with the previously reported values [23]. Table.1 shows a comparative study of the grain size, dislocation density and strain involved in the annealed Sb_2S_3 films of different thickness. It is observed that the grain size increases with thickness. Due to increase in grain size with film thickness, the defects in the lattices are decreased, which in turn reduce the internal micro strain and dislocation density or in other words the columnar grain growth is increased [24,25].

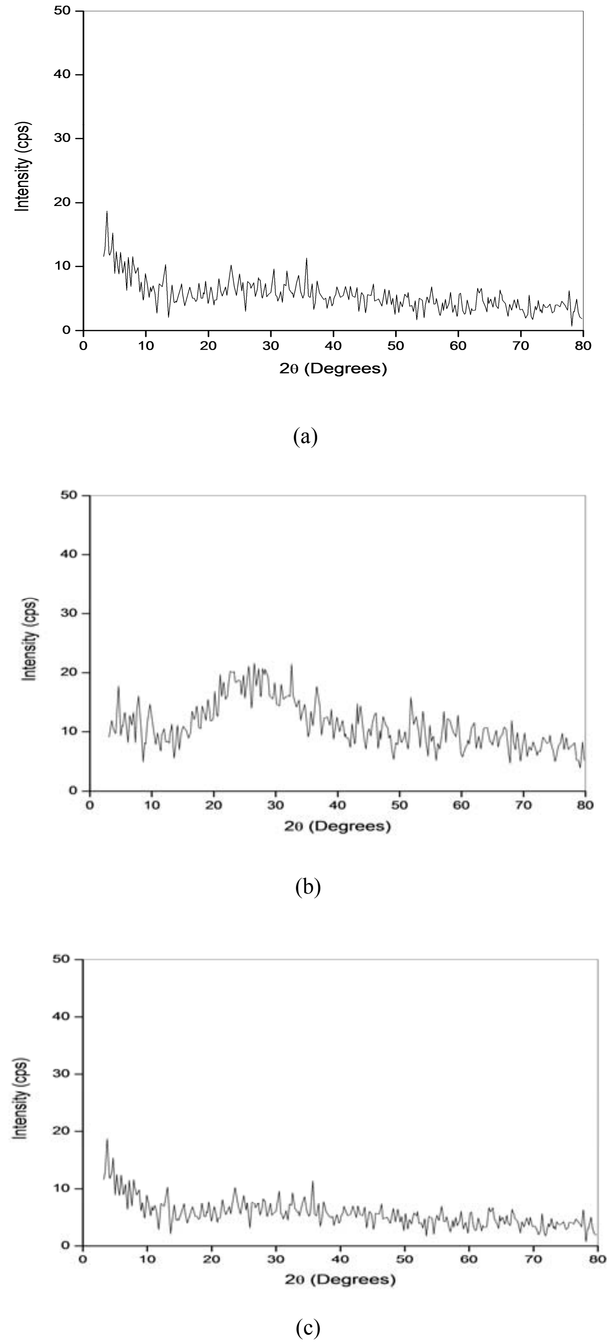


Fig. 2. As deposited Sb_2S_3 thin film for different deposition times a) 25hrs, b) 35 hrs, and c) 45 hrs

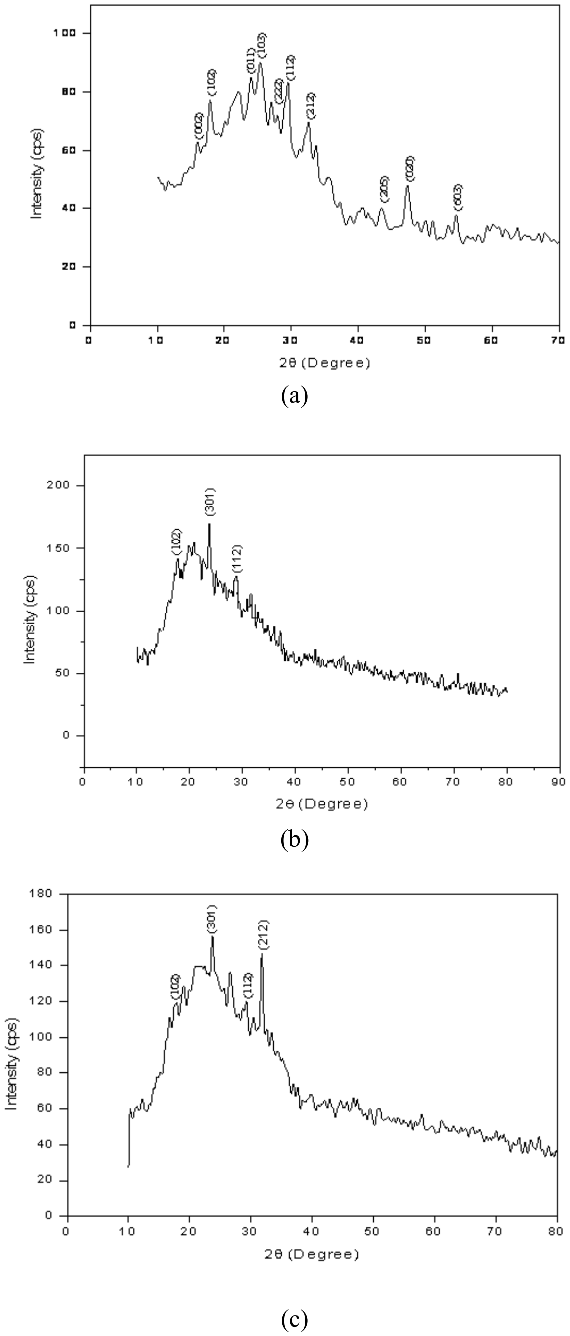


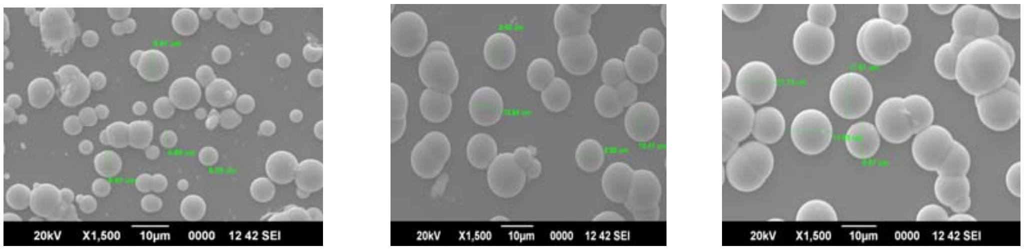
Fig. 3.Annealed Sb_2S_3 thin films at 423K for different deposition times a) 25hrs, b) 35 hrs, c) 45 hr

Table 1. Structural parameters of 423K annealed Sb_2S_3 thin film at different deposition time. (25hrs, 35 hrs& 45hr).

Hours	2θ (degrees)		d(Å)		Grain Size (nm)	hkl plane	Strain $\varepsilon x10^{-4}$	Dislocation density $\delta x10^{15}$ (lines/m^2)
	Standard value	Observed value	Standard value	Observed value				
25	17.558	17.501	5.063	5.063	35.742	102	10.129	0.782
	24.912	24.340	3.571	3.653	36.138	301	10.018	0.765
	29.275	29.480	3.048	3.027	39.018	112	9.278	0.656
35	17.558	17.720	5.063	5.001	39.631	102	9.135	0.636
	24.912	24.540	3.571	3.624	40.074	301	9.034	0.622
	29.275	29.570	3.048	3.018	45.669	112	7.227	0.479
45	17.558	17.912	5.063	4.992	44.692	102	8.100	0.500
	24.912	24.920	3.571	3.426	45.317	301	7.988	0.488
	29.275	29.601	3.048	3.015	48.238	112	7.105	0.429

3.2 Scanning electron microscopic studies

The SEM micrographs of the annealed Sb_2S_3 thin films are shown in the Fig. 4 (a, b, c) for different deposition times (25hrs, 35hrs&45hrs) respectively. Sb_2S_3 particles in the form of well defined spheres are distributed irregularly over the surface of the film. At low deposition time (25hrs), the 8µm diameter spheres are the dominant products and when the time is increased to 35 and 45hrs, large spheres of diameter about 10µm and 11µm are more abundant. The overgrowth of particles is clearly seen from the SEM micrographs with increase in thickness of Sb_2S_3 thin films [26]. From the SEM studies the nature of the spherical grains are confirmed.

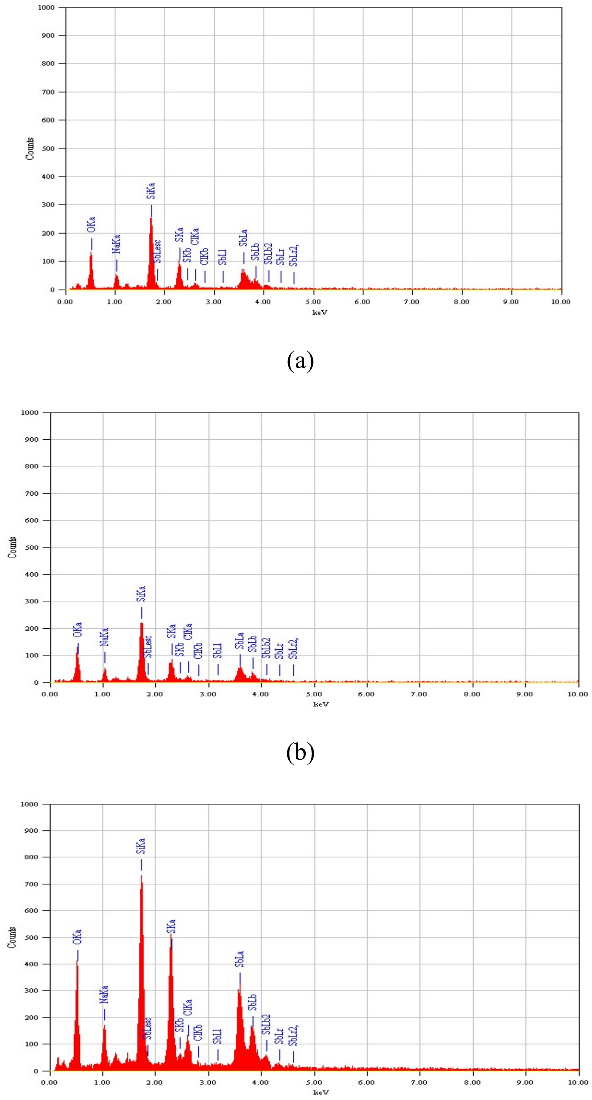


(a) (b) (C)

Fig 4.Annealed Sb_2S_3 films at 423K for different deposition times a) 25 hrs, b) 35 hrs, c) 45 hr

3.3 Energy dispersive analysis spectrum

The EDAX spectrum of annealed Sb_2S_3 thin films at 423K are shown in the Fig 5 (a, b, c) for different deposition times (25hrs,35hrs&45hrs) respectively . The atomic percentages of Sb, S and Cl elements are depicted in table 2. As observed in the table the atomic percentage of Sb and Cl increases with increase in deposition time, whereas atomic percentage of S gets decreased. Besides the peaks of Sb and S, there are peaks of Si, Na and Cl. The peaks corresponding to sodium, silicon and chlorine show a transition from 'L' to 'K' shell which can be confirmed from (Kα) peaks. The Si peaks are formed from the glass substrate (a silicon wafer). The Oxygen peaks are detected from the EDAX pattern which is unavoidable in chemically deposited films reported by C.D. Lokhande [27] and the presence of 'Cl' peaks are due to the precursor $SbCl_3$ [26]. This reagent could not be removed even when the samples are washed several times in acetic acid. Since, $SbCl_3$ hydrolyzes easily in an aqueous solution; a non aqueous solvent (acetic acid) is to be used as the reaction medium. When the Sb^{3+} ions encounter S^{2-} ions released from thioacetamide, aggregates of Sb_2S_3 polycrystalline thin films are formed. This is a convenient method which provides an effective route to synthesize antimony tri sulphide micro spheres.



(a)

(b)

(c)

Fig 5. Annealed Sb_2S_3 films at 423K for different deposition times a) 25 hrs,b) 35 hrs,c) 45 hrs.

Table 2. Atomic percentages of Sb, S and Cl for the films prepared by different deposition time (25 hrs, 35 hrs& 45 hrs)

Elements	Atomic percentage		
	Different deposition time(hours)		
	25	35	45
Sb	39.31	39.39	39.65
S	64.08	58.98	57.83
Cl	1.45	1.63	2.52

3.4 Optical absorption studies

Study of materials by means of optical absorption provides a simple method for explaining some features concerning the band structure. Optical absorption for Sb_2S_3 thin films deposited for different deposition time periods (a) 25 hrs (b) 35 hrs and (c) 45 hrs are studied in the span of wavelength range 190-2500 nm is shown in the Fig 6. From the figure it is clear that the absorption increases with deposition time due to the increase in grain size which is confirmed from the XRD analysis. Garcia *et al* have suggested that overgrowth of particulates on the film surface increases the absorbance due to scattering losses [28, 29]. Optical band gaps of Sb_2S_3 thin films are obtained from the plots of photon energy (hυ) against $(\alpha h\upsilon)^2$ for different deposition times (25hrs, 35hrs &45hrs). The energy band gap of the films are obtained by the extrapolating the linear portion of the curve to the energy axis as shown in Fig. 7 (a, b, c). All the plots have shown a straight line portion supporting the interpretation of direct band gap for the films. The band gap values of as deposited Sb_2S_3 films for different deposition time are shown in Table 3 and from the table it is clear that with increase in deposition time the band gap of Sb_2S_3 decreases due to increase in thickness of the film. The band gap E_g is found to decrease from 2.24 to 1.09 eV as the deposition time increases from 25hrs – 45hrs. This can be attributed to the quantum size effect in Sb_2S_3 thin films. Similar 'blue shift' in Eg values for the films with smaller thickness and / or grain size has been reported for many chemically deposited chalcogenide films [30, 31].

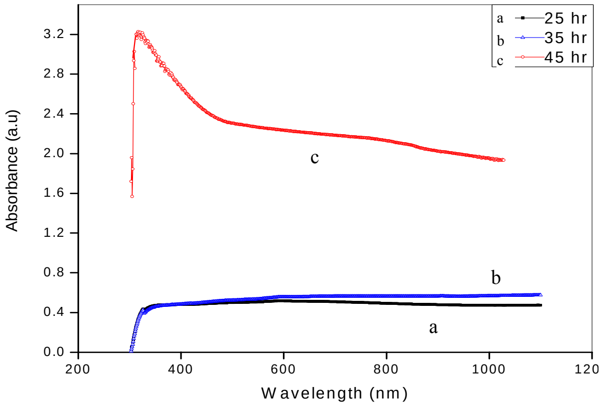
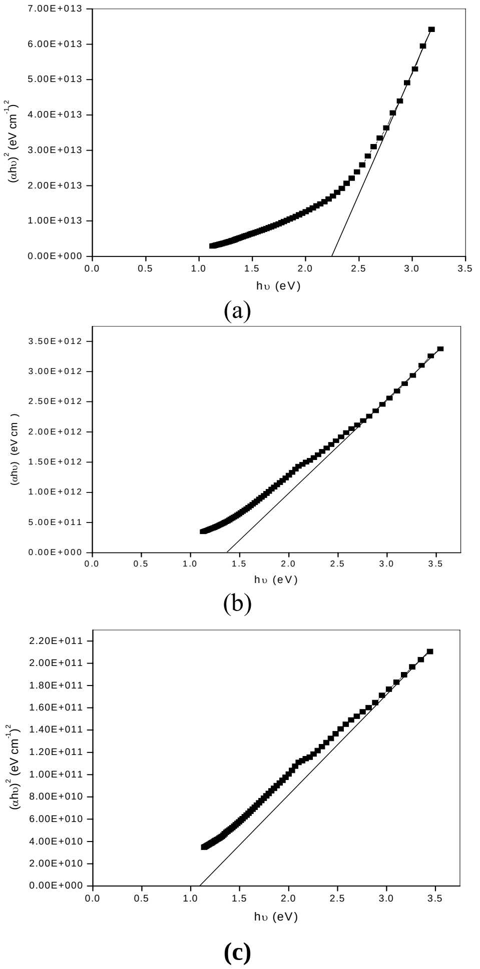


Fig. 6.Wavelength Vs absorbance of as- deposited Sb_2S_3 thin films for different deposition time (25hrs, 35hrs & 45hrs)



(a)

(b)

(c)

Fig7. h v Vs $(\alpha h\nu)^2$ of as- deposited Sb_2S_3 thin film of different deposition time a) 25hrs, b) 35hrs, and c) 45hrs

Table 3.Band gap of as deposited Sb_2S_3 thin films for different deposition time (25hrs, 35hrs & 45hrs)

Deposition time (hours)	**Band gap Energy (eV)**
25	2.24
35	1.36
45	1.09

Optical absorption spectra of annealed Sb_2S_3 thin films at 423 K deposited for different deposition periods (a) 25 hrs (b) 35 hrs (c) 45 hrs are shown in the Fig. 8. The figure shows that the absorption increases with deposition time and well defined peaks are obtained when compared with absorption spectra of as- deposited films this may be due to increase in Grain size of the film [28]. The photon energy (hυ) is plotted against $(\alpha h\upsilon)^2$ for annealed films of different deposition times which are shown in the Fig. 9 (a, b, c). The plots have shown a straight line portion supporting the interpretation of direct band gap for all the films. The band gap values of annealed Sb_2S_3 films for different deposition time are shown in Table 4. The table shows that there is decrease in band gap after annealing. The band gap E_g is found to decrease from 1.79 to 0.47 eV as the deposition time increases from 25hrs – 45hrs. The decrease in band gap is attributed to the improvement in grain size of the material after annealing. Similar type of observation in the semiconductor has also been reported [32, 33].

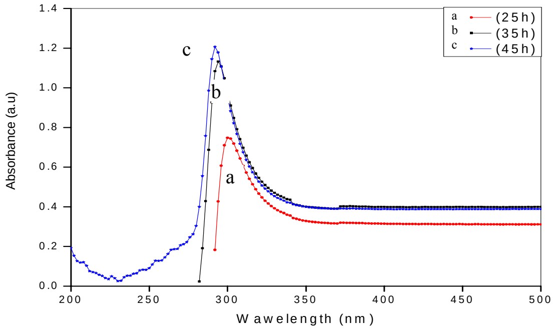
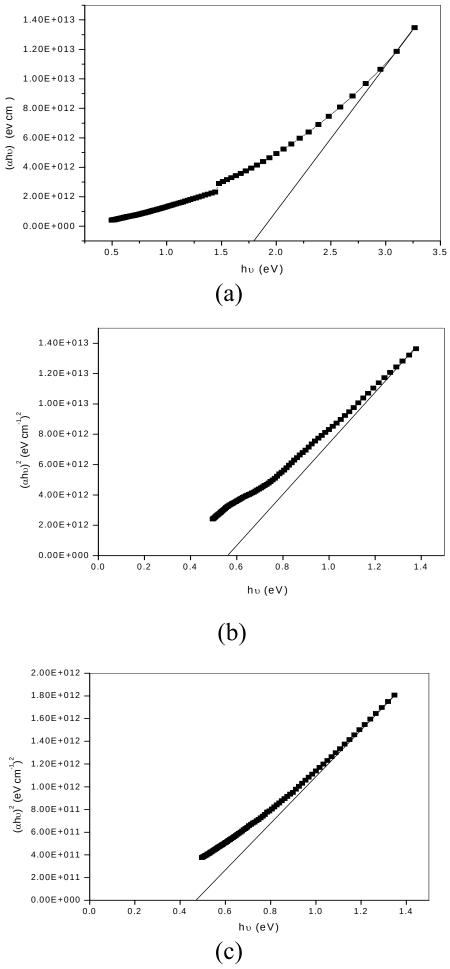


Fig 8.Wavelength Vs absorbance of annealed Sb_2S_3 thin films of different deposition time (25hrs, 35hrs &45hrs).



(a)

(b)

(c)

Fig. 9. $(\alpha h\nu)^2$ Vs hν of 423K annealed Sb_2S_3 thin film of different deposition time a) 25hrs, b) 35hrs, c) 45hrs.

Table 4. Band gap of 423K annealed Sb_2S_3 thin films for different deposition time (25hrs, 35hrs & 45hrs).

Deposition time (hours)	**Band gap energy (eV)**
25	1.79
35	0.56
45	0.47

4. Conclusions

The structural and optical properties of Sb_2S_3 thin films prepared by chemical bath deposition technique are studied. The X-ray diffraction patterns reveal that the as-deposited films are micro crystalline, whereas the films annealed at 423K are polycrystalline in nature. The structural parameters such as strain and dislocation density are found to be decreased as the grain size and deposition time is increased. The SEM micrographs of annealed films indicate that the grains are micro spherical and distributed irregularly over the surface of the film. It is evident that the diameter of the spheres increases with deposition time. EDAX spectrum shows the composition of the elements present in the film. It is confirmed that Sb^{3+} ions increases with deposition time. The optical absorption spectrum indicates that the absorption increases with deposition time. The band gap E_g decreases as the deposition time is increased. The variation of band gap with deposition time and grain size reveals quantum size effect.

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