

ORIGINAL ARTICLES

Influence of Deposition Time on Structural and Optical Properties of Chemically Deposited CuSbS₂ Thin Films

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ABSTRACT

Copper antimony sulfide thin films were deposited on a pre-cleaned glass substrate by the chemical bath deposition technique at room temperature 300K. The chemical bath deposition contains antimony chloride [SbCl₃], sodium thiosulfate [Na₂S₂O₃] and copper nitrate [Cu(NO₃)₂] which provide Sb, S and Cu ions respectively. The CuSbS₂ thin films were deposited at different deposition time ranging from 1h to 9h. The effect of the deposition time on the structural and optical properties of CuSbS₂ thin films was studied. Structural properties of the films were measured using X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analysis (EDX) techniques. The as-deposited CuSbS₂ thin film is amorphous in nature. The amorphous-to-crystalline transition was obtained by annealing the as-deposited films in argon atmosphere at 523K for 1h. The optical transmission and reflection spectra of the as-deposited films were recorded within the wavelength range 400-2500 nm. The variation of the optical parameters of the prepared films, such as refractive index “n”, absorption coefficient “α”, and the optical band gap “E_g” as a function of the deposition time was determined. The refractive index decreased with increasing the wavelength, then became flat above 1400 nm. The CuSbS₂ thin films exhibited highest absorption coefficient “~ 10⁵ cm⁻¹”. The CuSbS₂ thin film has a direct optical band gap. The value of optical band gap “E_g” decreased from 1.74 to 1.52 eV by increasing deposition time from 1h to 9h.

Key words: thin films, chemical bath deposition, X-ray diffraction, scanning electron microscopy.

Introduction

The ternary semiconductors of the type I-III-VI₂ were intensively studied in recent years because of their potential applications in a variety of electro optic devices. In addition, they are promising materials for the fabrication of thin film solar cells because of their high absorption coefficient, suitable band gap, and good thermal, environmental and electrical stability and because of the potential low cost methods in their preparation (Ramanathan *et al.*, 2003; Rau *et al.*, 2001). For the past two decades, the explorative front in semiconductor materials centered on these compounds because of the early success of CuInSe₂ in the role of P-type absorber films in high efficiency solar cells (Ramanathan *et al.*, 2003). Among these, the CuSbS₂ thin films have a direct band-gap of about 1.52 eV and a large absorption coefficient, which are well suited for the photovoltaic conversion of solar energy (Lazcano *et al.*, 2001; Manolache *et al.*, 2007; Garza *et al.*, 2011; Colombrina *et al.*, 2011; Rabhi *et al.*, 2011; Jesse *et al.*, 2012). Several techniques are being used for elaborating this material, such as: thermal evaporation (Rabhi *et al.*, 2008), chemical vapor deposition CVD, close spaced vapor transport (CSVT), RF sputtering, co-evaporation, spray pyrolysis (Popovici and Duta, 2012), atomic layer deposition, electro-deposition (Lazcano, 2001) and chemical bath deposition. The last technique is one of the suitable techniques for the elaboration because of low cost (Mokrushin *et al.*, 1961; Kitaev *et al.*, 1965). The present study is an attempt to prepare crystalline stoichiometric CuSbS₂ thin films by a simple deposition technique. The chemical bath deposition was employed to directly deposit ternary thin films of CuSbS₂ at different deposition time ranging from 1h to 9h. Also, the structural and optical studies carried out on these films at different deposition times are presented here.

2. Experimental techniques:

The preparation of CuSbS₂ thin films on glass slides was carried out using chemical bath deposition technique. The glass substrates were previously degreased in acetone for 15 minutes, cleaned in cold water with

detergent, rinsed with distilled water and then dried in air. The reaction bath for the deposition of CuSbS_2 contained copper nitrate $[\text{Cu}(\text{NO}_3)_2]$, antimony chloride $[\text{SbCl}_3]$, and sodium thiosulfate $[\text{Na}_2\text{S}_2\text{O}_3]$. The bath was prepared by dissolving 1.3 g of SbCl_3 initially in 5 ml of acetone, then adding 25 ml of 1M $\text{Na}_2\text{S}_2\text{O}_3$ solution, then adding 15 ml of 0.2 M $\text{Cu}(\text{NO}_3)_2$, then adding sufficient double distilled water to make a total volume of 100 ml, and then stirring well. After 40 min, the solution began to turn into brown. At the end of different durations “from 1h to 9h”, the substrates were removed from the bath and washed well with distilled water and then dried in air. The coating on the substrate side facing the wall of the beaker was a specularly reflective, uniform, smooth and adherent thin film while that on the other side occasionally showed a mosaic appearance due to the setting of precipitate over the growing film. The film deposited onto the side facing the beaker wall was retained for the experimental measurements whereas; the film on the other side was cleaned off using cotton swabs moistened with diluted HCl.

The structural analysis of the deposited films were examined by means of an X-ray diffractometer (Type: Panalytical's empyrean PRO X-ray diffractometer) with monochromatic CuK_α radiation ($\lambda = 0.15408$ nm), operated at 30 mA and 45 kV. The surface morphology and the chemical composition of the films were investigated using scanning electron microscope (Type: JEOL, model: JSM-5410) interfaced with unit of an energy dispersive X-ray analysis (EDX). A double-beam spectrophotometer (Type: Jasco, V-570, Rer11-00), with automatic computer data acquisition, was employed at normal light incidence to record the optical transmission and reflection spectra of the deposited film in the wavelength range 400–2500 nm. The measurements were performed at room temperature on various parts of the deposited films, by scanning the entire sample.

Results and discussions

Structure characterization of CuSbS_2 thin films:

a- XRD studies:

The microstructures of CuSbS_2 thin films were studied by X-ray diffraction. XRD patterns of the as-deposited CuSbS_2 films with different deposition time 1h, 3h, 5h, 7h and 9h for 2θ values in the range $[0-90^\circ]$ shown in Fig.1. The patterns for the investigated films had the same feature and exhibited a broad band around 2θ range $20-35^\circ$. The Figure depicts that all the as-deposited CuSbS_2 thin film is amorphous in nature.

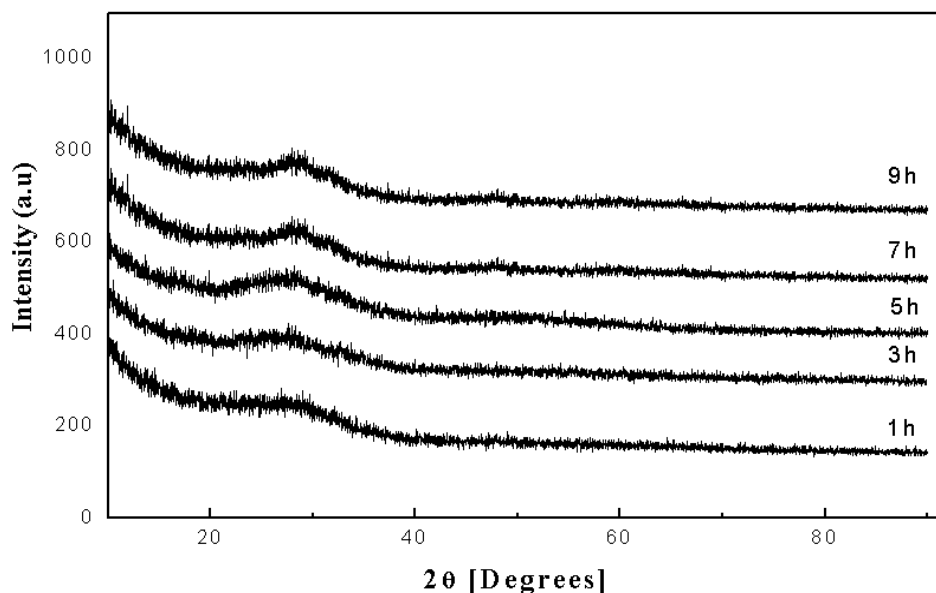


Fig. 1: X-ray diffraction patterns of as-deposited CuSbS_2 thin films with different deposition times 1h, 3h, 5h, 7h and 9h.

Fig.2 illustrates Polycrystalline CuSbS_2 thin films. They were obtained by annealing the as-deposited films in argon atmosphere at 523K for 1h. The annealed films were found to be polycrystalline in orthorhombic structure compared with the standard pattern. The comparison of the observed diffraction peaks with standard diffraction data file (JCPDF card No. 75-1018) confirmed that the peaks appeared at $2\theta = 28.62^\circ$, 47.71° , 56.77° and 77.59° in the 2θ patterns of the annealed samples, are respectively assigned to the (111), (020), (124) and (131) planes of CuSbS_2 orthorhombic structure.

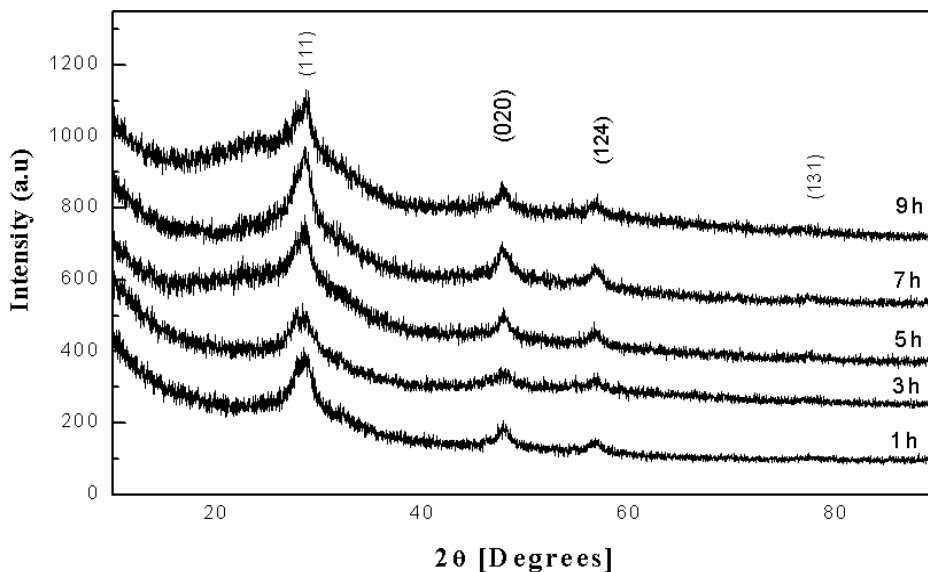


Fig. 2: X-ray diffraction patterns of CuSbS₂ thin films with different deposition times 1h, 3h, 5h, 7h and 9h, annealed at 523K for 1h in Argon atmosphere.

The crystallite average size “D” was calculated by using the Debye–Scherrer formula (Cullity and Stock, 2001):

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

Where K is a constant which is taken to be 0.94, λ is the wave length of X-ray used (1.54060), β is the full width at half maximum (FWHM) and θ is the angle of diffraction. The average crystallite size of CuSbS₂ nanoparticles was found to be nearly 12.25 nm.

b- Surface morphology:

In Surface morphology studies, the deposited films were coated with an ultra-thin gold film by low vacuum sputter coating unit. The scanning electron micrographs along with EDX results of as-deposited CuSbS₂ thin films deposited onto glass substrates with different deposition times 1h, 3h, 5h, and 7h are shown in figure 3[a-d]. The deposits appeared with a granular and compact morphology. The surface coverage is almost completed. The grains in the photograph represent aggregates of very small crystallites [fig.3a, b]. It was noticed that as the increase in the deposition time, the dimensions of the crystallites are uniform and higher grain size. An aggregate of islands with overgrowth scattered here as shown in fig.3[c, d] and some larger grains dispersed on the film surface.

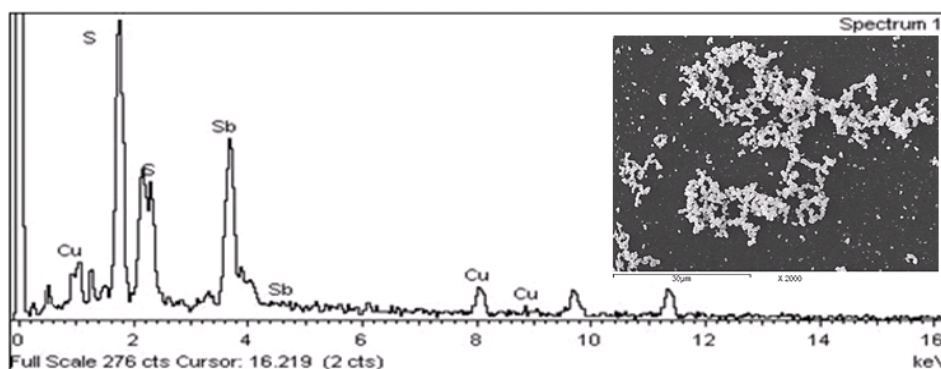


Fig. 3-a: SEM and EDX spectra of the as deposited CuSbS₂ films deposited at 1h.

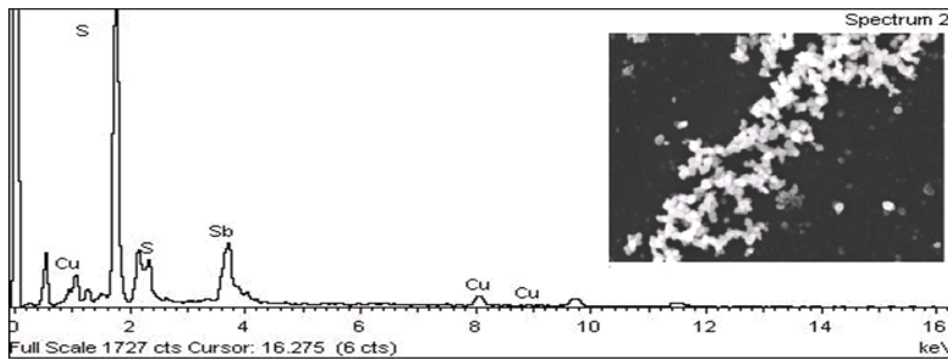


Fig. 3-b: SEM and EDX spectra of the as deposited CuSbS₂ films deposited at 3h.

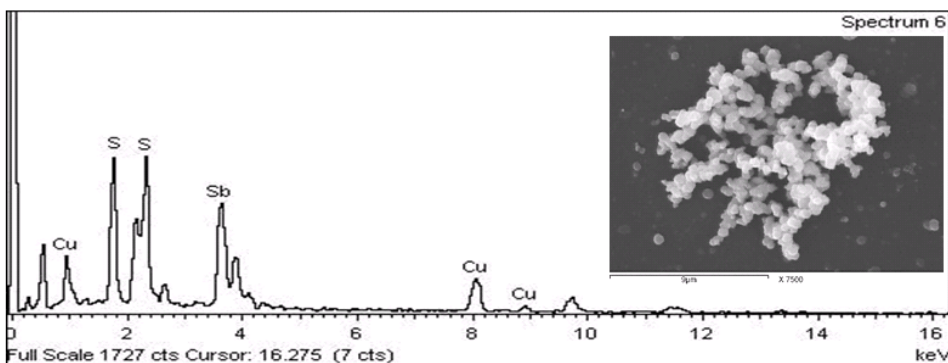


Fig. 3-c: SEM and EDX spectra of the as deposited CuSbS₂ films deposited at 5h.

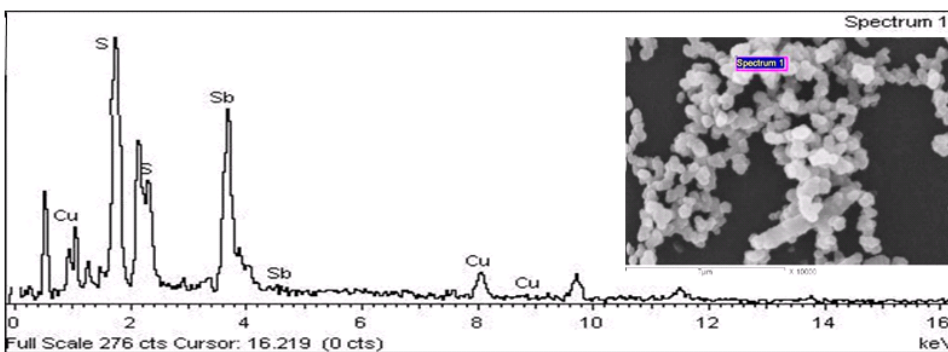


Fig. 3-d: SEM and EDX spectra of the as deposited CuSbS₂ films deposited at 7h.

The chemical composition of CuSbS₂ thin films investigated by energy dispersive X-ray spectrometry using energy dispersive unit attached to a scanning electron microscope. Data for quantitative analysis obtained in the form of an intensity ratio. It was equals to the peak count rate above the background for a selected characteristic line of an element from the sample, divided by that from a 100 per cent standard. The pattern confirms the presence of copper, antimony and sulphur.

The obtained results of the elemental chemical composition for thin films were summarized in Table 1.

Table 1: Chemical composition of the constituent elements of as deposited CuSbS₂ thin films deposited at 1h, 3h, 5h and 7h.

Deposition time	Elements composition (at %)		
	Cu%	Sb%	S%
1h	23.46	27.17	49.37
3h	25.17	23.21	51.62
5h	25.54	19.84	54.62
7h	24.94	24.57	50.49

3-2 Optical properties of as-deposited CuSbS₂ thin films:

The optical properties of as-deposited CuSbS₂ thin films were studied by recording optical transmittance and reflectance data using a double-beam spectrophotometer. An identical glass slide in the reference beam was

used to compensate for any loss in the transmission and scattering in the substrate. The transmittance and reflectance spectra of as-deposited CuSbS_2 thin films at normal incidence in the wavelength range of 400-2500 nm are shown in Fig. 4(a, b). This range covers the fundamental optical absorption edge and the inter-band transition region of the semiconductors materials. The transmittance and reflectance spectra of the CuSbS_2 films were measured to investigate the optical properties of the films. The films had maximum transmittance values (80%) for wavelengths around 1000 nm. The sharp increase of transmittance in the absorption edge (300-500 nm) showed that the films were of a good compound. Two peaks appeared for different (T) values in all CuSbS_2 thin films at different deposition times [at 550 nm and 1010 nm] respectively.

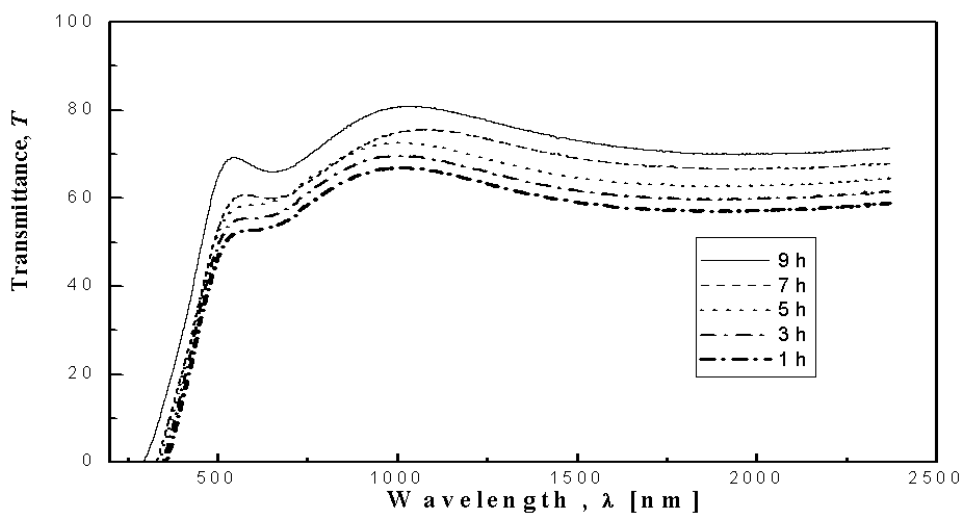


Fig. 4a: Transmittance (T) against wavelength(λ) in as-deposited CuSbS_2 thin films at different deposition times 1h, 3h, 5h, 7h and 9h.

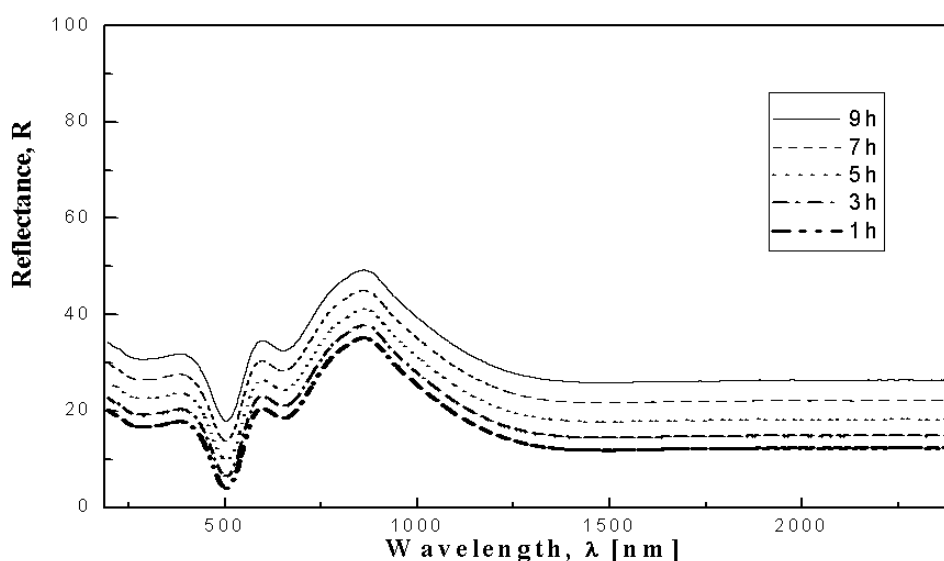


Fig. 4b: Reflectance (R) against wavelength(λ) in as-deposited CuSbS_2 thin films at different deposition times 1h, 3h, 5h, 7h and 9h.time.

The following relation (Boudaoud *et al.*, 2006) calculated the refractive index “n” of the films:

$$n = [(1 + R)/(1 - R)] - \{[4R/(1 - R)^2] - k^2\}^{1/2} \quad (2)$$

Where R is the reflectance and k ($k = \alpha\lambda/4\pi$) is the extinction coefficient (Rabhi and Kanzari, 2011).

Figure (5, 6) shows the refractive index “n”, and extinction coefficient “k”, of CuSbS_2 films as a function of wavelength. The dispersion curve of refractive index is flat in the long wavelength region and rises rapidly towards shorter wavelengths, showing the typical shape of dispersion curve near an electronic inter-band

transition. This suggests that the films show normal dispersion. The extinction coefficient decreases gradually with the increase in wavelength of the incident photon (Kastner, 1972).

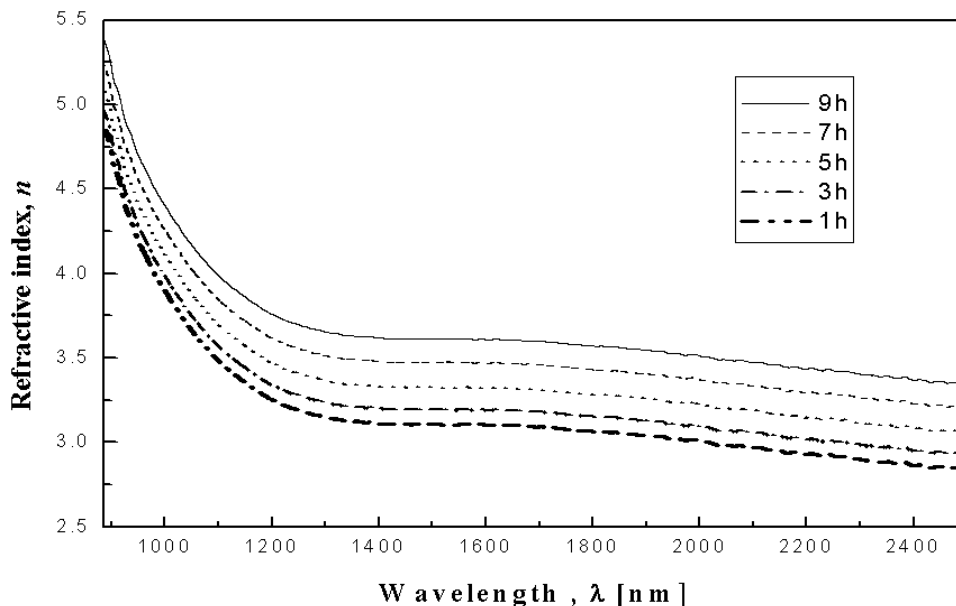


Fig. 5: The refractive index(*n*) vs. wavelength (λ) of CuSbS₂ thin films at different deposition times 1h, 3h, 5h, 7h and 9h.

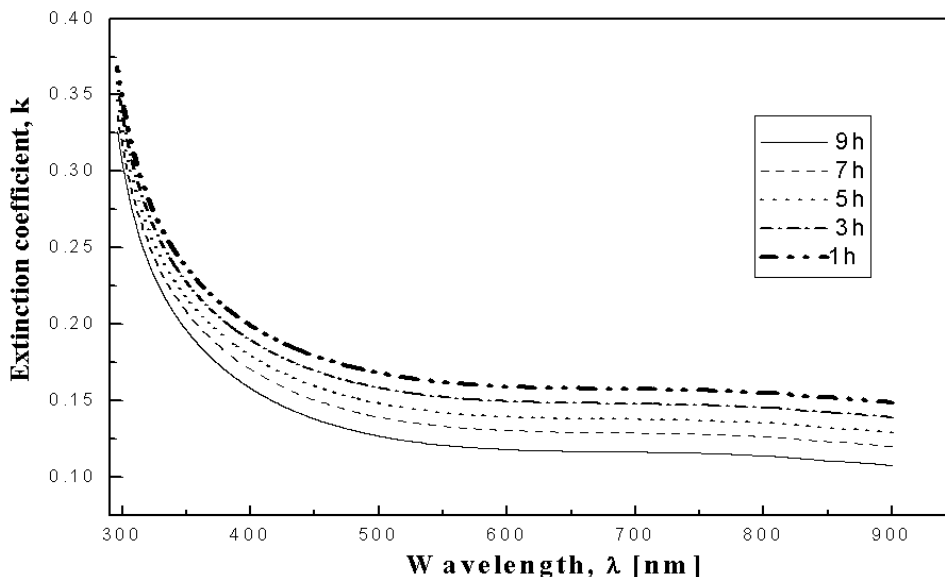


Fig. 6: The extinction coefficient, (*k*) vs. wavelength (λ) of CuSbS₂ thin films at different deposition times 1h, 3h, 5h, 7h and 9h.

The optical absorption coefficient in the present work will be calculated from the recorded transmission and reflection data according to the following relation (Shaaban *et al.*, 2009; Moss *et al.*, 1965).

$$\alpha = \frac{1}{t} \ln \left[\frac{(1-R)^2 + [(1-R)^4 + 4R^2T^2]^{1/2}}{2T} \right] \tag{3}$$

Where: *t* is the film thickness; *R* and *T* are the reflection and the transmission coefficients respectively.

Fig.7 shows the spectral variation of the logarithmic plots of absorption coefficient as a function of the photon energy, ($\hbar\omega$). It is apparent from this figure that, the absorption coefficient increases as photon energy

increases in the range 2 to 3.4 eV. The CuSbS₂ thin films exhibit the highest absorption coefficient, which is more than 10⁵ cm⁻¹ in the photon energy near 3.4 eV.

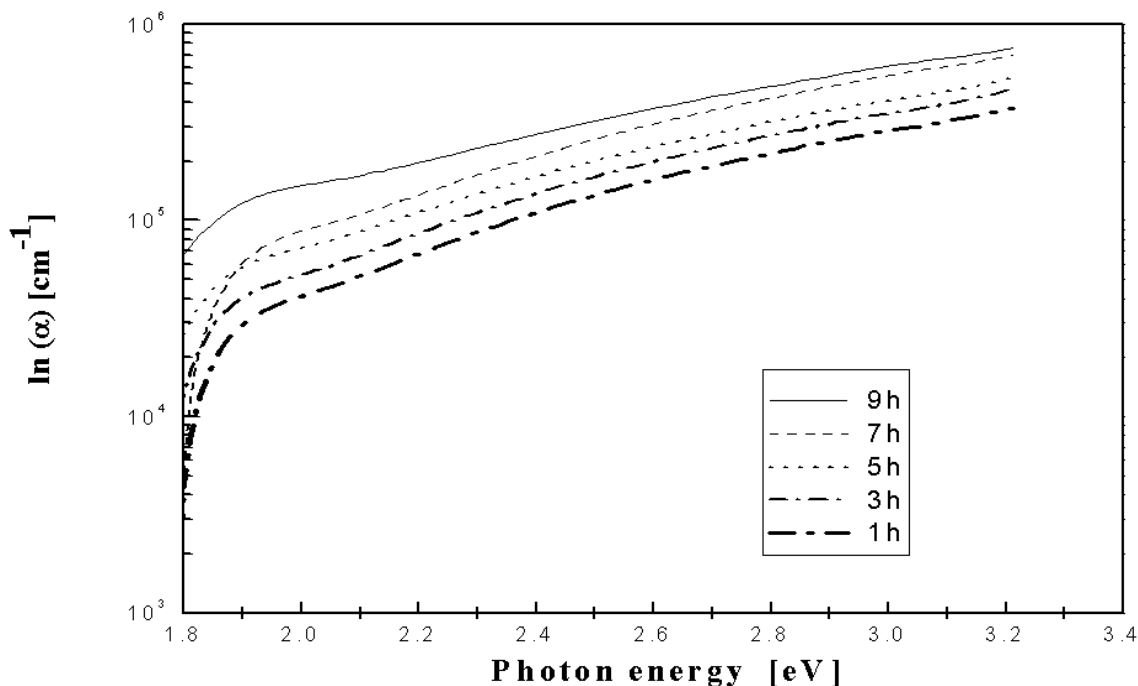


Fig. 7: The absorption coefficient (α) vs. photon energy of CuSbS₂ thin films at different deposition times 1h, 3h, 5h, 7h and 9h.

Optical band gap of the as-deposited CuSbS₂ thin films will be determined using the relation between the absorption coefficient (α) and the incident photon energy ($\hbar\omega$) by the following equation (Pankove, 1971):

$$\alpha(\hbar\omega) = A(\hbar\omega - E_g)^\gamma \quad (5)$$

where, A is a constant, E_g is the optical band gap of the material and the exponent and γ is an index parameter, that characterize the type of the optical transition and is theoretically equal to 2, 1/2, 3 or 3/2 for allowed indirect, allowed direct, forbidden indirect, and forbidden direct transitions, respectively. The variation curve of $(\alpha\hbar\omega)^2$ with photon energy $\hbar\omega$ for CuSbS₂ thin films at different deposition time from (1h to 9h) is shown in Fig. 8.

The CuSbS₂ thin film has a direct band gap (Rabhi and Kanzari, 2009) and the value of direct optical band gap (E_g) calculated by taking the intercept with x-axis and the value of " E_g " for CuSbS₂ thin films at different deposition time is given in Table 2. It is evident from the table that the value of optical band gap (E_g) decreases from 1.74 to 1.52 eV by the increasing in deposition time from 1h to 9h. Fig.9. shows the direct band gap (E_g) decrease from 1.74 to 1.52 eV by increasing the thickness of CuSbS₂ thin film.

Table 2: Shows the determined values of optical band gap (E_g) of CuSbS₂ thin films.

deposition times	Thickness (nm)	Direct energy gap $E_g^{dir.}$ eV
1h	76	1.74
3h	212	1.70
5h	305	1.63
7h	377	1.56
9h	423	1.52

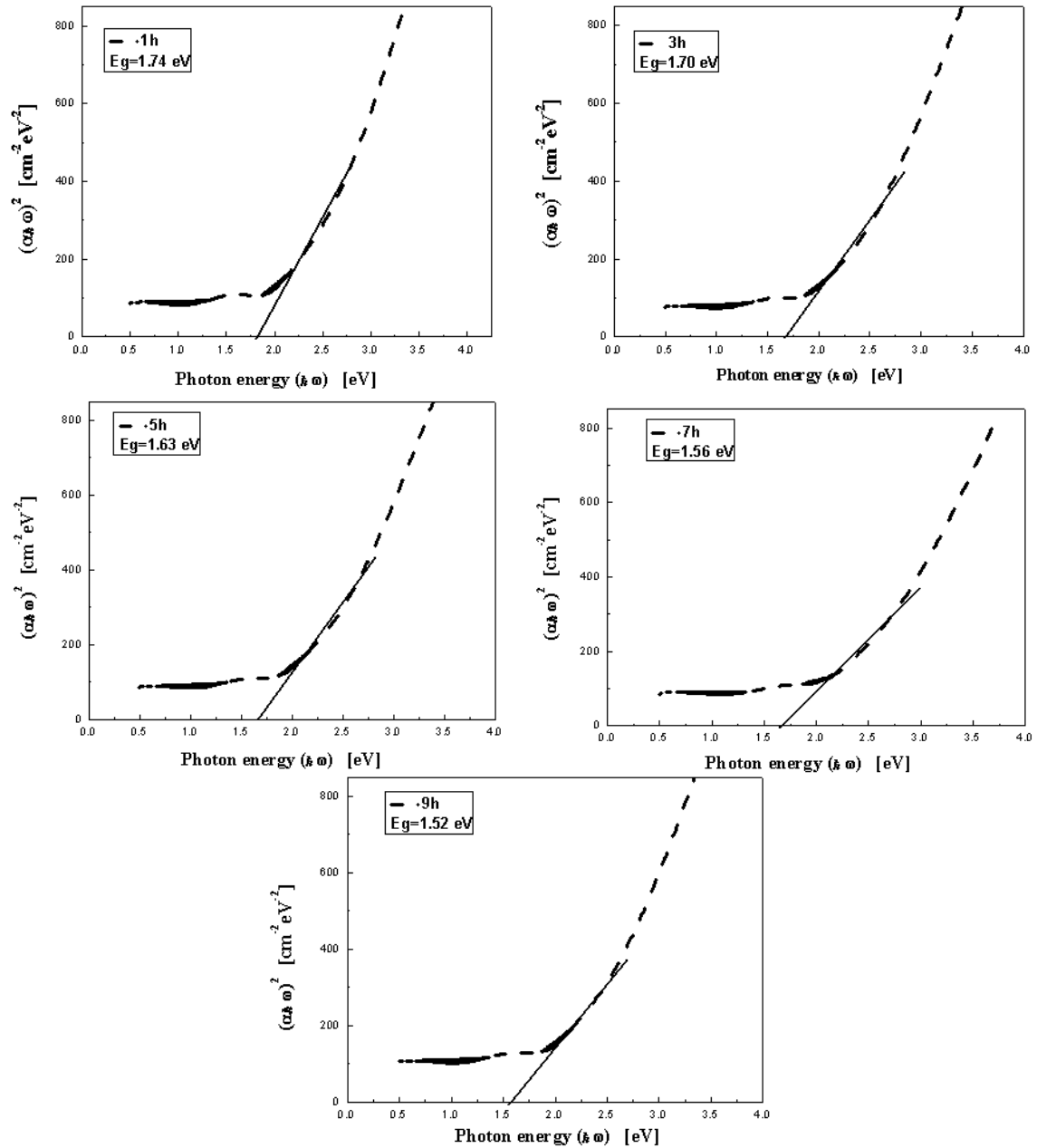


Fig. 8: Plot of $(\alpha h\omega)^2$ vs. $h\omega$ for the as deposited CuSbS_2 thin films.

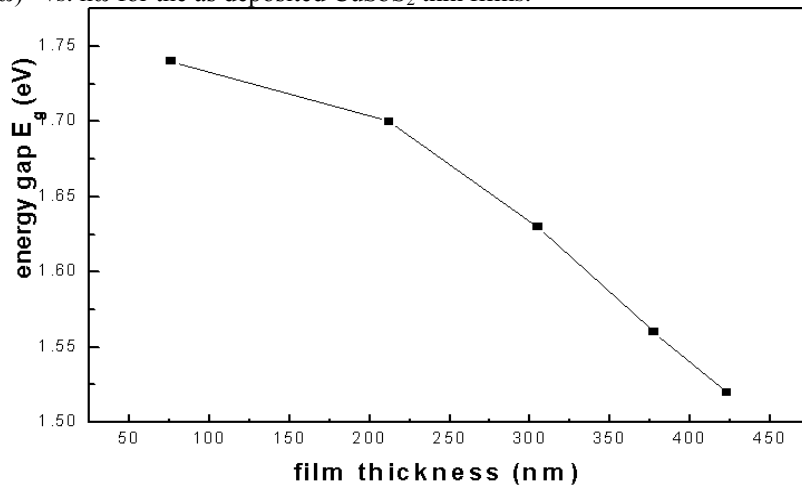


Fig. 9: Direct energy gap E_g versus the film thickness.

4-Conclusions:

The CuSbS₂ thin films were prepared from a chemical bath containing antimony chloride [SbCl₃], sodium thiosulfate [Na₂S₂O₃] and copper nitrate [Cu(NO₃)₂] at room temperature. The structural characterizations were done through XRD, SEM and EDX. The as-deposited CuSbS₂ thin film is amorphous in nature. The amorphous-to-crystalline transition was obtained by annealing the as-deposited films in argon atmosphere at 523K for 1h. The average crystallite size of CuSbS₂ nano-particles found to be about 12.25 nm. The EDX analysis indicates that the deposited films are almost stoichiometric in composition. The CuSbS₂ thin films exhibit highest absorption coefficient, which is more than 10⁵ cm⁻¹ in the photon energy near 3.4eV. The optical studies reveal that the CuSbS₂ thin film has a direct band gap. The value of optical band gap (E_g) decreases from 1.74 to 1.52 eV by the increasing in deposition time from 1h to 9h.

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