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Preparation and Study the Structural and Optical Properties of CuS nano film

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Abstract: Thin films of CuS were prepared by Successive Ionic Layer And Reaction (SILAR) method from solution of CuCl2 and Na2S at two different molarities (0.03 M and 0.06 M) on glass substrates at room temperature. The structural and optical properties of CuS films were determined using X-ray diffraction (XRD) and UV-VIS spectrophotometer respectively. The films are polycrystalline, very adherent to the substrate and well crystallized according to the centered cubic structure with preferential orientation along (103) . It was found that the energy gap of CuS varies from 2.4eV to 2.8eV for thickness of 0.55μm and 0.82μm respectively (i.e depending on the deposition conditions).

Keywords: Copper sulphide, Thin films, SILAR method, Preparation and characterization

1. Introduction

In recent years, thin films of CuS have attracted much attention for the photovoltaic applications due to the high absorption coefficient [1, 2] and high conductivity. In search of new semiconducting materials for solar energy conversion through photoelectron chemical cells, metal chalcogenide thin films are increasingly studied. Thin films have been prepared by various techniques such as spray pyrolysis [3], pulsed laser deposition [4], vacuum evaporation[4] , electro-deposition method[5], electron beam evaporation[6], and chemical bath deposition[7]**.** The constituent elements are inexpensive, easy to prepare and its necessary vessels can be found in an ordinary chemistry laboratory. Therefore, the SILAR method has many advantages over others used to grow semiconductor thin films. Nontoxic and abundant in nature leading to the development of devices that are environmentally safe and have public acceptability. The optical properties of CuS vary depending on the synthesizing or fabrication method**.** The successive ionic layer adsorption and reaction (SILAR) method is a step-wise process of chemical deposition of thin films from aqueous precursor solutions. One cycle of the SILAR process is as follows: (i) the substrate is immersed in the cation precursor solution — an aqueous solution of a soluble salt of the cation of the compound to be grown. During this step the cations were adsorbed on the surface of the substrate. The hydrolysis of metal ions enhances adsorption. To promote hydrolysis and to increase the negative charge of the oxide surfaces, the pH is increased right beneath the precipitation pH. (ii) The substrate is then rinsed in high-purity deionized water. Because of the presence of adsorbed cations on the surface a double layer is formed — the adsorbed cations are in the inner layer and their counter ions in the outer layer. During the rinsing process, the excess cations, which are not adsorbed, are washed away together with the other ions in the diffusion layer. (iii) The substrate is now immersed in the anion precursor solution — an aqueous solution of salt of the anion of the compound to be grown. The anions react with the adsorbed cations and form the desired solid compound. (iv) The substrate is finally rinsed again in high-purity deionized water and the excess ions in the diffusion layer are washed away. By repeating these steps thin films can be grown in a controlled way[8-9]. The growth mechanism and the immersion time of the glass slides in cationic and anionic solution are very important because those include the reaction between the Cu^{2+} and S^{2-} on the active centers of the glass slide. Single SILAR deposition cycle involves the immersion of the substrate alternately in cationic and anionic precursor solutions and rinsing between every two consecutive immersions with deionized water to avoid homogeneous precipitation in the solution, so that only the tightly adsorbed layer stays on the substrate. The adsorption is a surface phenomenon occurring due to attractive force between ions and surface of substrate. This attractive force is of van der Waals type that basically originates due to the residual or unbalanced force present in the substrate. Thus, ad-atoms can be holding on the surface of the substrate by that residual force. The growth mechanism and the thickness of the films deposited depend on several factors, the temperature and concentration of the solution, nature of the substrate, immersion time in respective precursor solution and subsequent rinsing time in deionized water, etc. In this paper, we report the synthesize CuS films by SILAR method and study the structural, optical properties of these films.

2. Expermental

2.*1: CuS film fabrication*

Copper sulfide thin films were prepared using $CuCl_2$ solution on glass substrates in two different moralities of 0.03M and 0.06M using SILAR technique. A detailed procedure of this technique which used for thin film growth has been reported [10]. Different molarities (0.03 M and 0.06 M) of solutions of $CuCl_2$ (cation) have been used, while, the anionic solution was freshly prepared from sodium sulfide (Na_2S). The cationic and anionic precursor solutions characteristics: adsorption, reaction and rinsing times were detailed in literature for these thin films [11]. One SILAR cycle contained four steps:

(a) The substrate was immersed into first reaction containing the aqueous ($CuCl_2$) cation precursor.

(b) Rinsed with water at 80°C.

(c) Immersed into the Na_2S anion solution.

(d) Rinsed with water at 80°C

Fig. 1 shows the scheme of SILAR technique for the deposition of CuS at room temperature. After 80 SILAR cycles, we obtained CuS films of terminal thickness 0.55 µm for 0.03M and 0.82 µm for 0.06 M on glass substrate. We can use *thiuorya* solution instead of Na_2S in order to avoid the presence of highly mobile sodium ions in the film. The precursor solutions used for the CuS thin films were from 0.03 to 0.06M $CuCl_2$ (pH 4.3–6.7) as cation precursor and 0.022 to 0.035 M Na_2S (pH 11.0–12.0), as anion precursor. The concentration of the copper acetate solution was normally two times higher compared with the concentration of Na_2S. The adsorption and reaction immersion times ranged from 5 to 20 S and the rinsing times from (40-90) S depending on the concentration of the precursor solutions.

Using the concentrations 0.03M for $CuCl_2$ and 0.06 M for Na_2S, the immersion times were 15S and the rinsing times 20 S. Also the rinsing step between every immersion was avoided. The deposited films were subsequently annealed in air at 300°C for 45 minutes. Films thicknesses which determined

by (MINITEST – 3000) device were 0.55 µm and 0.82 µm for the solution molarities of 0.03 and 0.06M respectively. The overall reaction can be written as:

$$\mathbf{CuCl_2 + Na_2S \rightarrow CuS \downarrow + 2NaCl}$$

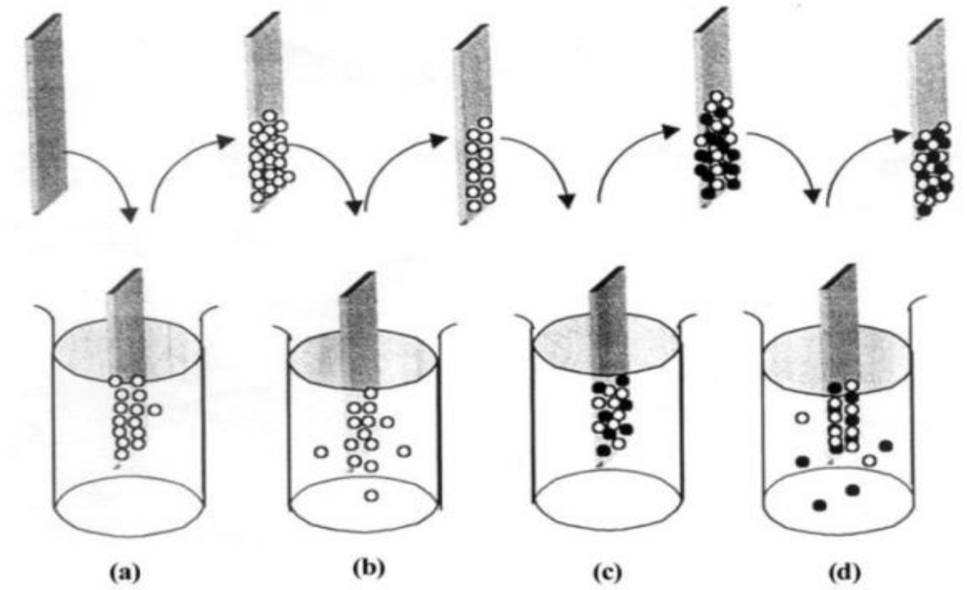


Figure 1: shows the SILAR technique of deposition CuS.

3. Structural Properties

The microscopic examination of CuS thin film shows in Fig. (2:a and b) .It is clear from this figure the occurrence of crystallization for each of the concentrations (0.03 and 0.06)M.

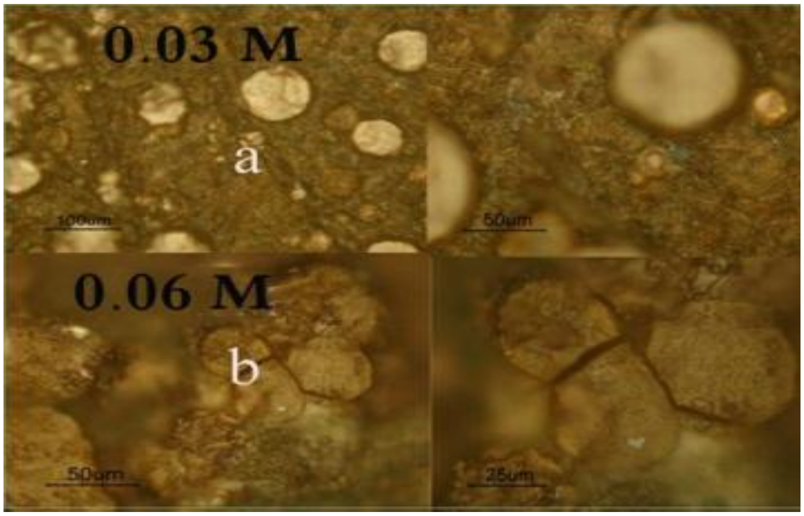
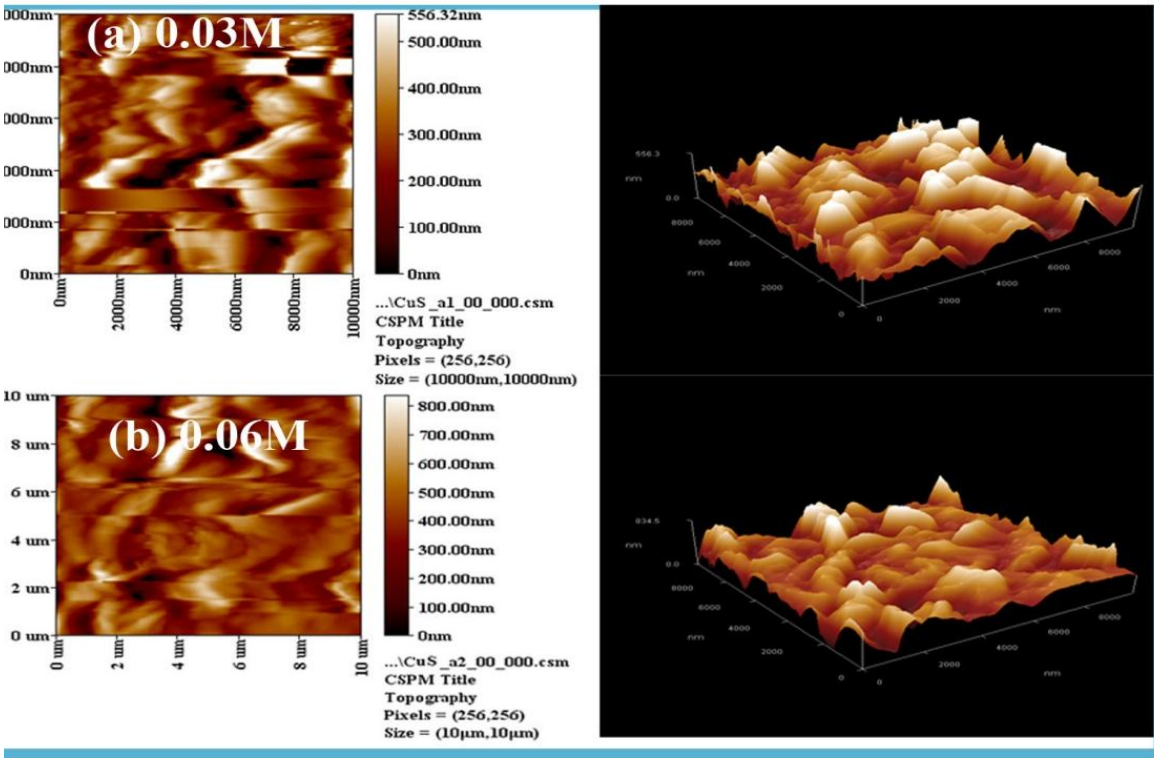


Figure 2: The image of optical microscopic of CuS thin film with concentration (a) (0.03) and (b) (0.06) M.

It can be observed that the increase in the morality concentration a appreciably affected both the nanostructures and crystallite sizes of the films. This modifies the grain bounders of films and consequently increase the crystal size.

3.2: Atomic Force Microscope (AFM)

Typical AFM images for CuS films with two different molarities which were taken to support the XRD observations. Fig. (3a,b) shows the surface topography of the deposited films. The film 0.06 M of precursor solution have particle size about (120 nm) while the film of 0.03M have a particle size of (90 nm) . The size of the grains increased as the morality of the precursor solution increases In general, the grain size depends on the chemical composition of the starting solution and the post annealing process.



3.3: X-Ray diffraction (XRD)

The X-ray diffraction (XRD) of CuS thin film with different molarity 0.03M and 0.06 M is displayed in Fig. (4.a, b) The films showed only the CuS phase with a strong (103) preferred orientation.

The patterns appear the presence of traces of other phases along with predominant CuS phase**.** The intense and sharp peaks in the X-ray diffraction pattern reveal the crystalline of the films which also confirm the stoichiometric nature of the CuS films. The degree of crystallization in the film was improved by a sufficient thermal crystallization (300 C). The intensity of the peaks is found to decrease with less molarity (0.03 M) which means that the crystalline nature of the film is decreased**.**

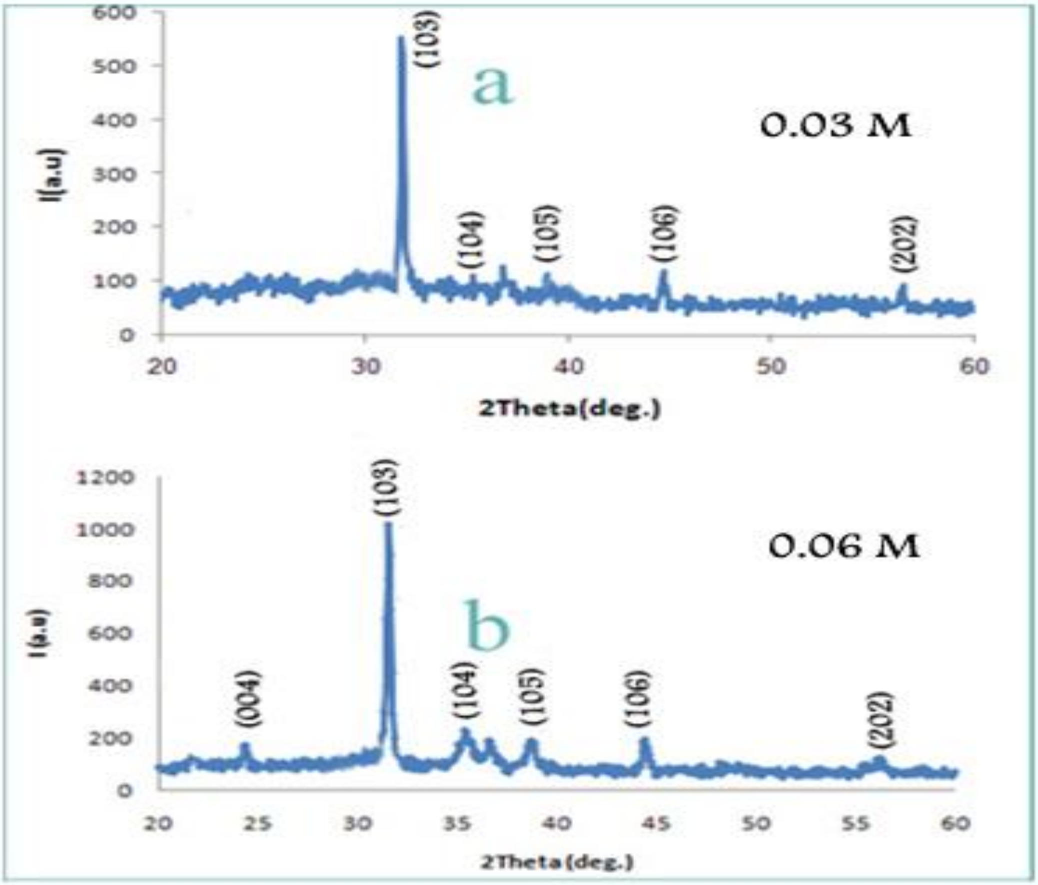


Figure (4: a and b) XRD patterns of CuS thin films.

Grain size was calculated by compensation values that were obtained from the X-ray diffraction results of the previous figures in the equation of Scherrer (1)**:**

$$D = 0.94\lambda /(\beta \cos\theta) \quad (1)$$

where β is the FWHM intensity in radians. The mean size of crystallization calculated using Scherrer formula for 0.03M and 0.06M of CuS is found to be 93.5nm and 121.5 nm as shown in tables 1 and 2.

To find the correct size of the crystal, we must add a correction factor of the basic equation (1) to take into account the broadening of the XRD patterns output from the device, several methods has assumed for this purpose. Including:-

1-Warren – Scherer Method

$$(\beta_{cs} = \beta_m - \beta_i) \tag{2}$$

By compensation (2) in (1) we get

$$D = K\lambda / [(\beta_m - \beta_i)\cos(\theta) \tag{2-1}$$

Which is called Warren's Correction $(\beta_{cs}^2 = \beta_m^2 - \beta_i^2)$ …(3) by compensation (3) in (1) we get

$$D = K\lambda / [(\beta_m^2 - \beta_i^2)^{½}\cos(\theta)] \tag{3-1}$$

Geometric meaning [16,17].

$$(\beta_{cs} = [(\beta_m - \beta_i)(\beta_m^2 - \beta_i^2)^{1/2}]^{1/2}) \tag{4}$$

By compensation (4) in (1) we get

$$D = K\lambda / [[(\beta_m - \beta_i)(\beta_m^2 - \beta_i^2)^{1/2}]^{1/2}\cos\theta] \tag{4-1}$$

βm: Show X-ray diffraction curve in the middle of the great intensity measured in practice.

βi: Show X-ray diffraction curve in the middle of the great distress caused by the device used.

Table 1: Size of Crystallization by using Scherrer's &Warren's correction and their comparison with Scherrer's equation before the correction for concentration (0.03)M.

300 °C	D(nm) Scherrer's eq.(1)	D(nm) eq.(1-2) Scherrer's correction	D(nm) eq.(1-3) Warren's correction	D(nm) eq.(1-4)Warren's geometrical correction
CuS **0.03 M**	93.5	165	103.88	123.37

Table 2: Size of Crystallization by using Scherrer's &Warren's correction and their comparison with Scherrer's equation before the correction for concentration (0.06) M.

Temperature 300 ˚C	D(nm) Scherrer's eq.(1)	D(nm) eq.(1-2) Scherrer's correction	D(nm) eq.(1-3) Warren's correction	D(nm) eq.(1-4)Warren's geometrical correction
CuS 0.06 M	121.5	279.5	147	202.88

It was found that the lattice spacing (d) for concentration of (0.06)M is less than that of 0.03M for the same of lattice planes (hkl) as shown in tables 3 and 4 .

Table 3: Size of Crystallization by using Scherrer's &Warren's correction and their comparison with Scherrer's equation before the correction for concentration (0.06) M.

Sample	**(*hkl*)**	***d* [Å]**
CuS 0.03 M	(103)	2.8
	(104)	2.5
	(105)	2.26
	(106)	2.19
	(202)	1.8

Table 4: The concentration of (0.06)M values of (hkl) and d [Å].

Sample	**(*hkl*)**	***d* [Å]**
CuS 0.06 M	(004)	2.6
	(103)	2.3
	(104)	2.12
	(105)	2
	(106)	1.6
	(202)	1.5

4. Optical Properties

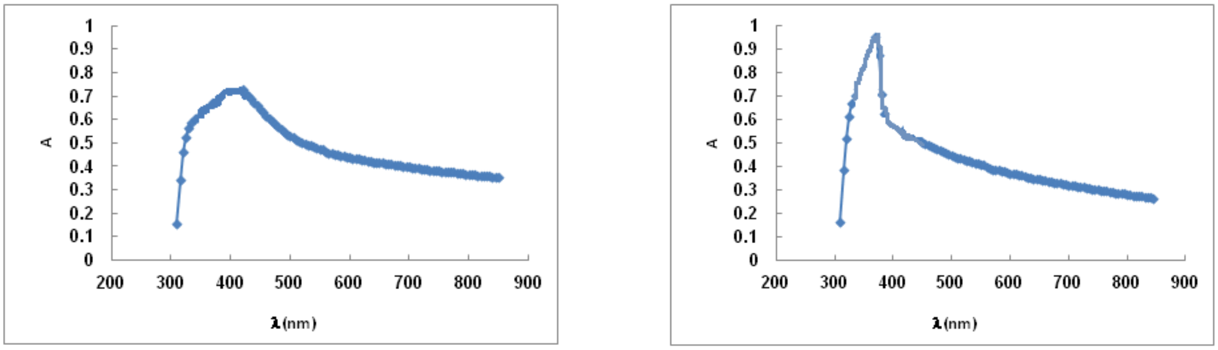
It is observed that the absorption increase with increasing the molarity of precursor solution as show in fig. 5(: a and b).The absorption coefficient (α) and the incident photon energy (hν) is related by the following equation (5) as show in fig (6: a and b)· It is clear from this figure that in the visible region there is no significant change in absorption edge by increasing the morality of the solution from 0.03M - 0.06M. This implies that the basic crystal structure is not changed. The energy gap of CuS film can be estimated from the absorption spectrum using Taucs equation described as follows[12]:

$$\alpha h\nu = A(h\nu - E_g)^m \tag{5}$$

The typical plots of $(\alpha h\nu)^2$ versus hν for CuS thin films with 0.03M and 0.06M deposited on glass substrate is shown in Figure (7: a and b). It is observed that increment in molarities of CuS precursor solution causes a slight increment in optical band gap from 2.4 eV to 2.8 eV.

$$\alpha = (2.303 * A)/t \tag{6}$$

where, t is the Thickness and A is the Absorbance.



(a) **(b)**

Figure (5:a and b): absorbance spectra of CuS thin film (a):0.03M,(b):0.06M.

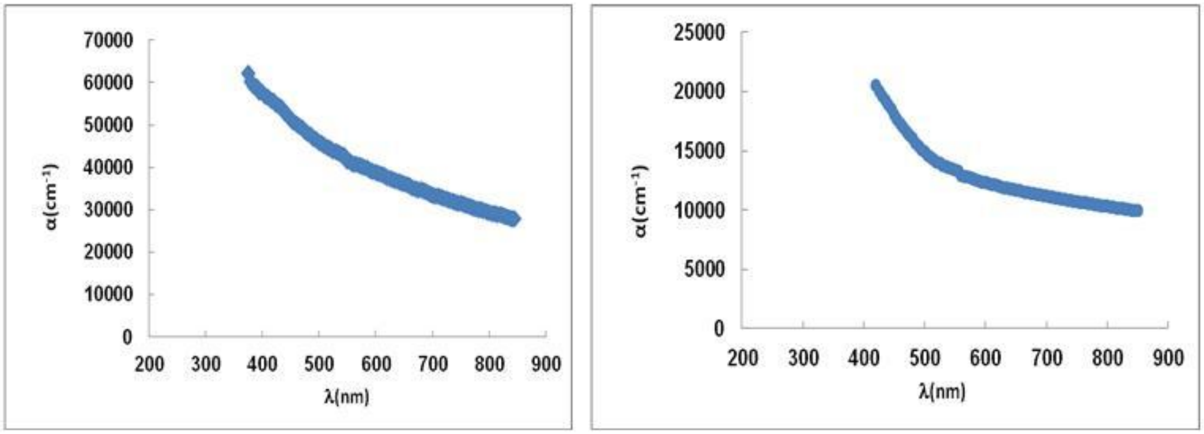


Fig. (6:a and b): Variation of absorption coefficient as a function of photon energy for CuS films for different films molarities (0.03M and 0.06M).

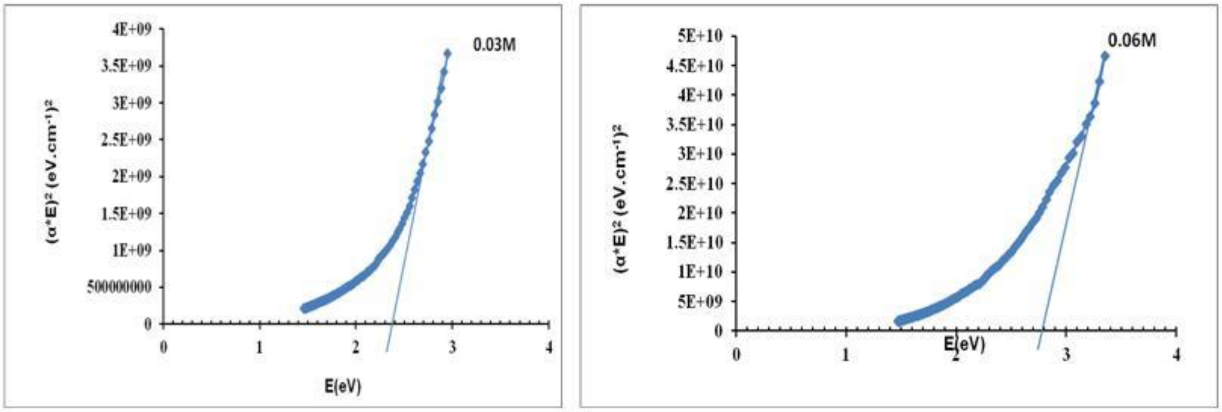


Fig. (7:a and b): Variation of (αhυ)^{2}as a function of photon energy for CuS films for different films molarities.

5. Conclusions

CuS thin film was successfully deposited on to glass substrates by SILAR at room temperature. The X-ray diffraction spectrum shows that CuS film is polycrystalline with an orthorhombic structure. The direct energy gaps of the film were determined as 2.4 eV and 2.8 eV for concentrations (0.03 and 0.06 M) respectively .Due to the suitable direct energy gap value for an absorber layer for efficient light absorption, CuS thin films can be used as absorber layer in solar cells.

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