Structural, Optical and Electrical Properties of Cu₂S Thin Films Deposited by CBD Method

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Abstract: *Semiconducting Cu₂S thin films were deposited on glass substrate under two different conditions like as-deposited and preheated precursor solution by chemical bath deposition technique. Structural and optical properties of the films were characterized by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Energy and Dispersive X- ray (EDX) analysis. The XRD spectra showed the amorphous nature of thin films with hexagonal structure. The presence of more nucleation centres and fast reaction rate decreased the average crystallite size in films grown with pre heated precursor solution. The noticed blue shift in energy gap and the shift of XRD peak position towards the lower 2h side by heat treatment could be considered as a sign of the quantum confined effect due to the formation of the nano-sized Cu₂Scrystals on the surface. EDX spectra showed the chemical purity of the films. The observed broad absorption and blue shift in band gap of the heat-treated films were due to quantum confinement effect. Copper sulphide thin films can be used in many applications, such as solar control coatings, solar cells, photo thermal conversion of solar energy, electro conductive coatings and microwave shielding coatings.*

Keywords: *semiconducting, crystalline size, electrical properties, conductive coatings.*

1. INTRODUCTION

Copper sulphide thin films are considered as promising materials for solar energy conversion systems, especially as p-type semiconductors and/or absorbers of visible light, due to their structural, electrical and optical properties [1, 2]. It is reported [3] that the p-type conduction in Cu_xS is attributed to free holes from acceptor levels of copper vacancies. Cu_2S is one of the binary semiconducting material and its band gap varies between 1.2 to 2.5ev. $Cu_{2-x}S$ is a p-type semiconductor in which the copper vacancies act as acceptors [2], indicating the strong dependence of electrical properties upon the dencit amount of copper atom in $Cu_{2-x}S$. It has distinct composition because of the variation in x, 1<x>2, with different stoichiometry such as Cu_2S (chalcocite), $Cu_{1.9}S$ (djurlite), $Cu_{1.8}S$ (digenite), $Cu_{1.7}S$ (anilite). It is important to control their morphologies and compositions for application in opto - electrical devices. The density of copper vacancies increases with ''x'' value, from 1.8 to 2, with consequences on the electrical properties; it increases the sheet resistance [4, 5] and decreases the electrical conductivity.

Different techniques have been used for the Cu2S thin films deposition such as spray pyrolysis [6], metal organic chemical vapour deposition (MOCVD) [7], vacuum evap-oration [8] and chemical bath deposition (CBD) [9] to deposit cadmium cobalt sulphide. However, the popularization of the CBD technique in recent decades for thin film deposition is due to its relatively low cost and simple method for the deposition of high quality and large area films [10] and facilitates better orientation of crystallites with improved grain structure [10].

Copper sulphide thin films are used as cold cathodes, nanoscale switches, microwave shielding coating and dye -sensitized solar cells.

2. EXPERIMENTAL TECHNIQUE

2.1. Substrate Cleaning

The contaminated substrate surface provides nucleation sites facilitating the growth, which results in non-uniform film growth. Therefore, optically pure glass plates of dimensions 26* 76 * 2 mm were boiled in chromic acid for 2 h and kept in it for 12 h. Then, they were washed with detergent, and

again rinsed in acetone before the deposition of the films [16]. Finally, the substrates were heated in hot air oven for 1 h at the temperature of 100 0C.

2.2. Preparation of Cu₂S thin films

For the deposition of Cu_2S thin films, $CuSO_4\_5H_2O$, thio-urea (CS $(NH_2)_2$), and triethanolamine (TEA) purchased from Merc were used without further purification. The precursors copper (II) sulphate pentahydrate ($CuSO_4\_$ $5H_2O$) and ($CS(NH_2)_2$) were used as source materials of Cu^+ and S^{2-} ions respectively. In the present report, three different samples were prepared for comparison.

In the preparation of as-deposited sample, all steps were carried out at room temperature and all chemicals Used were AR grade. The distilled water was used as a solvent in the experiments. First, 50 ml of 0.1 M, 0.2M and $0.3MCuSO_4\_5H_2O$ was taken in a 100 ml beaker with constant stirring to get a homogeneous solution then appropriate amount of TEA was added. The resultant solution was stirred until it becomes homogeneous and clear navy -blue colour. The well cleaned glass substrates were slowly introduced into the bath vertically. 1 M thiourea was slowly added to the solution. During the whole reaction process, the reactants were vigorously stirred under air atmosphere at room temperature. The pH value of the final solution was maintained as 9.5. The chemical reaction was started at the mixture of solutions. The films deposited on glass substrates have been taken out after 5,8and 10 minutes when it became brown in colour. For the preparation of pre-heated sample, the same procedure is adopted as-deposited sample where as the temperature of the resultant solution was maintained at 80^0 C (353 K) throughout the reaction under continuous stirring.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

The crystal structure of Cu_2S thin films was determined by XRD. XRD patterns were recorded with (Make: RigaKu, Model C/max-2500) using $CuK\alpha$ radiation ($\lambda=1.54056$ A^0) operated at 40Kvand 30 ma in the wide Angle region from 10^0 to 80^0.The PH value of the cu $_2$s thin films was maintained as 9.5.Their crystalline structure exhibits peaks corresponding to (002), (100), (110), and (112) planes. The average size of crystallite is estimated by

Sherer formula: $D = k\lambda / \beta cos\theta$

Where λ is the wavelength of CuK_α radiation (0.154nm), k = 0.9 is the shape factor, θ is the Bragg angle and β is the experimental full-width at half maximum on the respective diffraction peak. The average grain size for the cu$_2$s orientation is about 1.45 nm. The typical XRD patterns of Cu_2S thin films with different Concentrations (0.1, 0.2and 0.3M) and different conditions such as deposited and pre-heated precursor at elevated temperature are shown in **Fig1**.The broad hump in the 2θ range of 23^0- 30^0 is mainly observed due to amorphous Glass substrate and similar result was observed in the literature [17]. **Fig 1a and 1b** show that the data are fitted with a long (002), (100), (101), (110) and (112) planes. The micro-strain was calculated using the formula (16).

ε = $\beta cos\theta \div 4$

3.2. Thickness of the Films

The gravimetric method was employed to find the thickness (t) of six different samples. Gravimetric method uses geometry and physics to determine the thickness of an applied coating. The simplest method is to weigh the part before and after coating. After the mass and area have been determined, the thickness is calculated using the following equation:

$$T = m \times 10 \tag{1}$$

$$m = A \times d \tag{2}$$

Where T is the thickness in micrometers, m is the mass of the coating in milligrams, A is the area tested in square centimeters and d is the density in grams per cubic centimeter. The accuracy of the thickness measurement is 27 nm. The fig 3(a) shows that as the thickness of the sample increases, crystalline size also increases respectively. The Fig 3(b) shows that as the concentrations of the deposited sample increases, crystalline size also increases. The fig 3(c) shows that as the concentrations of the preheated sample increases, the crystalline size also increases steadily. The Fig 3(d) shows that as deposition time increases, the thickness also increases steadily.

Table1. *The peak position (2θ), full width at half maximum (FWHM, β) value, d value, average crystallite size (D), and micro-strain (e) of as-deposited, pre heated and thickness of the Cu$_2$S thin films.*

Sample	Thickness (nm)	Peak position(2θ) (^{0})	FWHM (β)	d-value (A^0)	hkl planes	Average crystallite size (D nm)	Micro strain (10^{-3})
0.1m(deposited)	29	24.87	4.78	3.6445	002	1.78	**10.841**
0.1m(pre heated)	30	24.87	4.78	3.6445	002	1.78	**10.841**
0.2m (deposited)	14	25.09	4.32	3.3175	002	1.81	**9.78**
0.2m (preheated)	20	23.21	4.12	3.6329	002	1.97	9.46
0.3m (deposited)	31	23.21	4.12	3.2630	002	1.97	9.46
0.3m (preheated)	38	24.55	4.68	3.3720	002	2.06	10.64

The peak position is shifted towards lower 2θ side by the angles Δ2θ approximately 0.3^0 to 1.6^0 for preheated and deposited thin films respectively. From 25.2^0(deposited), the d value and micro strain get slightly increased, whereas the average crystallite size is increased from 1.7 to 1.8 and 2.0 nm respectively. Thickness of the cu$_2$s films (deposited) decreases compared to Pre-heated films. Calculated d spacing values are compared with standard JCPDS values of various thicknesses of Cu2s thin films. Creation of more nucleation centers and fast reaction rate are the general properties of heating on chemical reaction. Increase of nucleation centers in the initial reaction mixture and fast reaction rate reduce the average crystallite size of the Cu$_2$S thin films. The decreased average crystallite size creates more defects inside the crystallites such as vacancies and interstitials. The created crystal imperfections increase the strain inside the Cu–S lattice and also the d value [18, 19]. Table 1.2 shows dislocation density of Cu$_2$S films deposited and pre-heated samples decreased from 3.15 to 2.35.

Table2. *Comparison of thickness and dislocation density of Cu2s films*

	Sample	Thickness (nm)	Dislocation density (10^{14}) lines m^{-2}
0.1m	(deposited)	29	3.15
0.1m	(pre heated)	30	3.15
0.2m	(deposited)	14	3.05
0.2m	(preheated)	20	2.57
0.3m	(deposited)	31	2.57
0.3m	(preheated)	38	2.35

3.3. Morphology and Compositional Analysis

Scanning electron microscope (SEM) is one of the promising techniques for the topography study of the samples and it gives important information regarding the surface morphology, shape and size of the particles in the film. The surface morphology of the as-deposited, post and pre heated precursor Cu2S films are shown in Fig. 2a–c, respectively. Figure 2a shows the uniform distribution of particles with the size less than 60 nm. Some well agglomerated grains spread out over the surface with non-uniform size more than several ten nano meters. These grains are loosely bounded and thus most of the larger size grain are absent in post heat-treated thin film as shown in Fig. 2b. Figure 2b also shows the uniform distribution of particles with few nano meter dimension throughout the surface. Figure 2c shows the uniform distribution over the surface with smaller particle size compare to other films for pre heated precursor thin film. Figure 2d shows the surface morphology of pre heated precursors Cu2S thin film with high resolution. All the films have almost compact globular structures composed of hierarchical spherical particles. The noticed morphologies are well agreed with our previous theoretical results from XRD.

The presence of nominal compounds and chemical purity of the Cu2S thin films are confirmed by EDX spectra. The typical EDX spectra of as -deposited, and pre heated precursor Cu2S thin films the atomic % of Cu and S is very nearly equal to their nominal stoichiometry within the experimental error of ±2 %. The additional Si peaks noticed in EDX spectra (all the films) was due to the Si glass substrate. The atomic ratio of Cu/S is derived to be 2.08, which confirms the formation of stoichiometry Cu2S film. The constant peak intensity in all films reveals that there is no compositional change with deposited and pre heated of precursor in Cu2S thin films.

3.4. Electrical Characterizations

The electrical conductivity can be measured by using dc two- probe method (20). In this method, copper wires were attached to both ends of the film sample. Silver paste was applied to the surfaces of

the sample to serve as electrodes. The current I, which flowed through the film samples was measured by Keithley System consisting of voltage source and current detector. The electrical conductivity (ρ), was calculated from equation (3).

$$\rho= RA \div L \tag{3}$$

Where R is the resistance of the sample A is the surface area and L is the thickness of the sample

3.4.1. Conductivity Analyses

From the figures 4(a),4(b),4(c) and 4(d) shows a marginal values of electrical conductivities were observed at regions where the concentration Copper(II) Sulfate Pentahydrate is low, and that, this could probably be due to the fact that at lower Copper(II) Sulfate Pentahydrate concentration, the Cu_2S samples showed a remarkably marginal electrical conductivity as compared to the samples with $CuSO_4\_5H_2O$ concentration(21).

The fig 4(a) and fig 4(b) shows variation of electrical conductivity of Cu_2s thin films with concentrations of the deposited and pre-heated samples increases and then conductivity also increases respectively. The Fig 4(c) shows whenever thickness increases conductivity firstly increases and then steadily increases. The graph shows a broad hump in between 20nm -32nm (thickness) pre-heated precursor solution respectively. The Fig 4(d) shows when ever deposition time increases conductivity firstly steadily increases and then a broad hump in between 8min -10min again conductivity also increases.

From the figures 4(a) and 4(b) shows whenever the concentration of the $CuSO_4\_5H_2O$ increases and then conductivity also increases steadily. From the figures 4(a) and 4(b) states that conductivity depends on concentration of the Copper (II) Sulfate Pentahydrate deposited and pre heated conditions. Electrical conductivity depends on concentration of the cu_2s samples. Conductivity states that there is a uniformity thickness of the cu_2s samples.

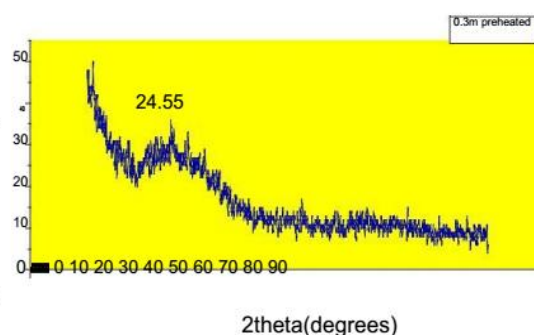**Table3.** *The variation in the electrical conductivity of as deposited and pre-heated samples.*

Concentration (M)	Deposition time (minutes)	Thickness (nm)	Conductivity σ (mho-cm)$^{-1}$
0.1	5	14	11
0.1 pre heated	8	20	11.2
0.2	10	29	12.4
0.2pre heated	12	30	12.6
0.3	14	31	12.8
0.3 preheated	16	38	13.3

3.5. Structural and Electrical Properties of Cu_2s Thin Films
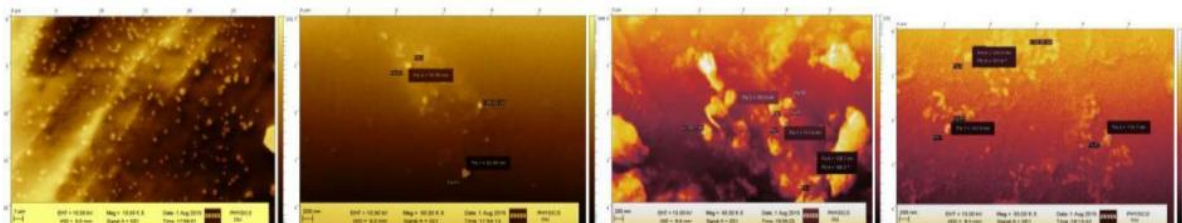
3.5.1. XRD Patterns
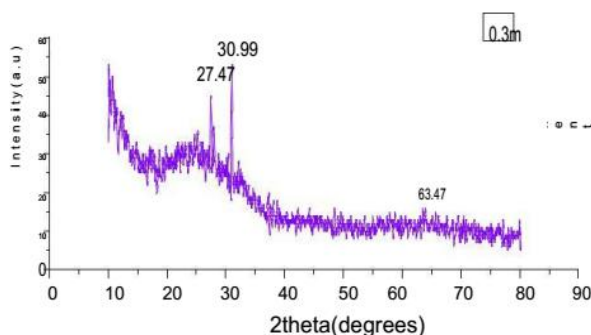
Fig1(a). *0.3M XRD GRAPH*   **Fig1(b).** *0.3 M Pre-heated Graphs*

3.5.2. Sem Images

Fig 2(a). *0.1M*   **Fig2(b).** *0.2M*   **Fig2(c).** *0.3M*   **Fig2(d).** *0.3m pre-heated*
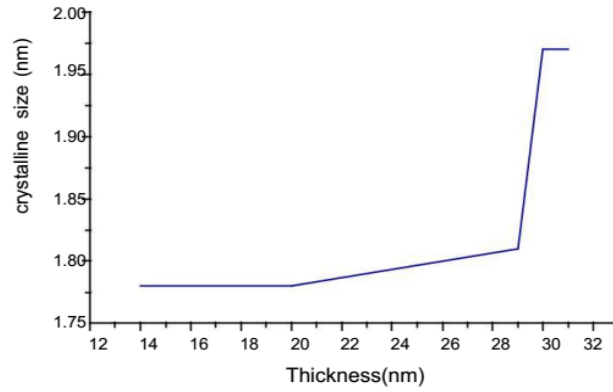
3.5.3. Thickness Dependent Properties

Fig3(a). *Thickness of different crystalline size samples*
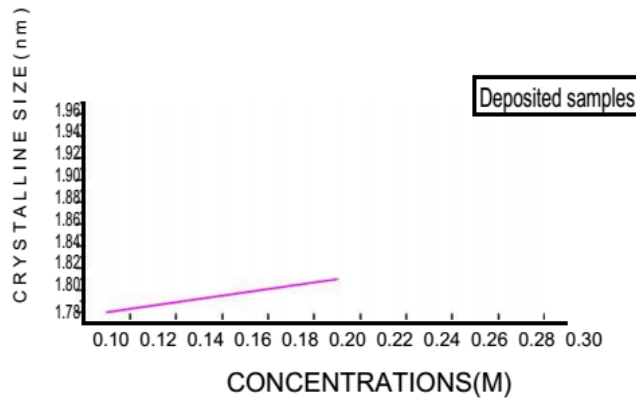

Fig3(b). *Concentrations of different crystalline size samples (Deposited)*

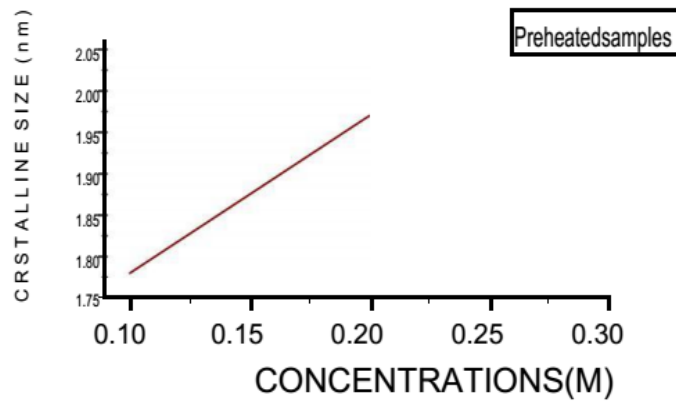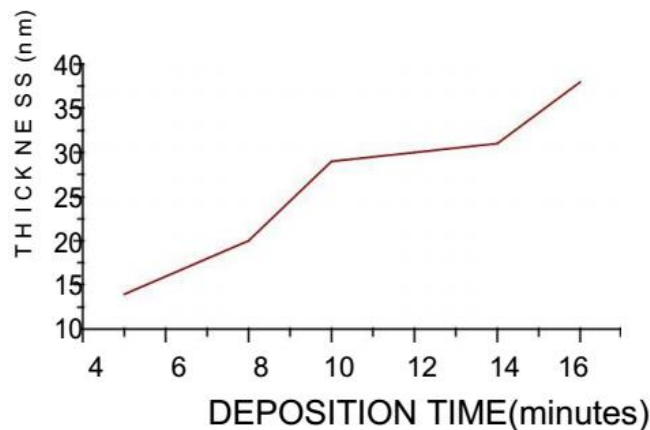**Fig3(c).** *Concentrations of different crystalline size samples (Preheated)*

Fig3(d). *Deposition time with different thickness of the samples*

4. CONCLUSIONS

Deposited and Pre -heated samples of Cu2s thin films deposited on glass substrates by Cbd method. The structural and electrical properties were studied. The depositions are carried out the value of PH= 9.5.The thickness of the films is carried out 27nm.The crystallized films exhibit a hexagonal structure. The above most of the properties are thickness dependent and concentration dependent properties. It states that thickness depends on the conductivity. The above figures conclude that all cu2s samples have uniform thickness.

ACKNOWLEDGMENTS

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