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Effects of deposition time on structural, optical and electrical properties of chemically deposited Cu_2S thin films

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Abstract: Binary Cu_2S (I-VI) thin films were prepared onto the glass substrates by chemical bath deposition technique at different deposition times (From 30 minutes to 105 minutes). Thicknesses of the thin films were determined using microbalance method. The structural, optical and electrical properties of the prepared thin films were studied using X-ray diffraction (XRD), scanning electron microscopic (SEM), UV-visible spectroscopic techniques and four-point probe method. X-ray diffraction pattern reveals that all the thin films prepared are polycrystalline in nature and crystallized in hexagonal structure with preferential orientation along (102) direction. The crystallite size increases from 11 nm to 27 nm with increase of deposition time. Morphology of the films as observed from the SEM indicates the presence of spherical particles. EDAX analysis shows that the films prepared were nearly stoichiometric without much deviation. From the optical spectra the nature of transition were found to be allowed and direct. Decrease of band gap energy with increase of deposition time was also observed. Resistivity measurement shows that the sheet resistances of the films are in the order of megaohms.
Keywords: Cu_2S thin film, Chemical bath deposition, Band gap, Activation energy.

Introduction

Copper sulfides (Cu_xS, $1 \leq x \leq 2$) are interesting materials due to their special physical and chemical properties. There are several stable phases of copper sulfides at room temperature with different stoichiometry (x = 2, 1.95, 1.8, 1.75, 1). Among them, cuprous sulfide (Cu_2S) is considered as an ideal absorber in photovoltaic conversions due to its high absorption coefficient (10^4 cm^{-1}) and narrow band gap (1.2 eV) [1-3]. Cu_xS thin films have been found to possess near ideal solar control characteristics and has transmittance in the infrared region, low reflectance (<10%) in the visible region and relatively high reflectance (>15%) in the near infrared region. The optical spectra of copper sulfide films exhibit high transmission in the visible region and absorption throughout the near-infrared region (800-1500 nm). The variation in electrical conductivity is from 0.07 Ω^{-1}cm to 2400 Ω^{-1}cm as 'x' varied from 2 to 1.8. Hence copper sulfide thin films are found to be very useful semiconducting material to harness solar energy from the sun [4-8].

There are several techniques such as Spray Pyrolysis [9], Solid State Reaction [10], Vacuum Evaporation [11, 12], Reactive Magnetron Sputtering, Atomic Layer Deposition (ALD), Co-Evaporation [13], Electrosynthesis [14], Chemical Vapour Deposition (CVD) [15], Chemical Bath Deposition (CBD) [16-20], Modified Chemical Bath Deposition [21], Electrochemical Methods [22], Successive Ionic Layer Adsorption And Reaction (SILAR) [23,24], Microwave Assisted Chemical Bath Deposition (MA-CBD) [25] used for the deposition of copper sulfide thin films. Among these methods, CBD has been selected for the present work as it is simple, economic and non-polluting. CBD is convenient for preparing homogeneous and smoother thin films with the required thickness. Chemical deposition of metal sulfide thin films can be carried out using different

sulfide ion sources such as sodium thiosulfate ($Na_2S_2O_3$) or organic sources such as thiourea ($CS(NH_2)_2$), thioacetamide (CH_3CSNH_2) and higher derivatives. The rate of release of sulfide ion changes from source to source and, accordingly thin film morphology and crystallinity are affected [26]. The applications of these materials depend on the chemical composition and crystalline structure of the film matrix. In the present study, Cu_2S thin films have been deposited using chemical bath deposition method in alkaline bath at different deposition time.

Experimental

All the reagents obtained from Merck were of analytical grade and are used without any further purification. Chemical bath deposition method was used to deposit Cu_2S thin films onto amorphous glass substrates at room temperature. The stock solution of 0.5 M copper sulfate was added to the 20 ml of deionized water and stirred until the clear solution is obtained. Then the stock solution of 0.5 M Sodium thiosulfate was added to the 20 ml of deionized water and was added to the as prepared copper sulfate solution and their pH was adjusted to 10 under the control of a pH meter by adding excess ammonia. Finally the resulting solution was stirred for several minutes maintaining the pH value. Under continuous stirring pre-treated substrates were vertically immersed into the prepared bath at room temperature. After that the substrates were removed and rinsed with deionized water and were dried in air at room temperature for further characterization. Copper sulfide thin films of varying thicknesses were prepared by varying the deposition time to 30, 45, 60, 75, 90 and 105 min.

The structural studies of the chemical bath deposited Cu_2S thin film samples were done by using Schimadzu XRD-6000 X-ray diffractometer with a CuKα radiation (λ=1.5406A°) . The morphological and compositional analysis of the film were carried out using JEOL mode JSM 6390 SEM with EDAX and optical studies of the samples were done using spectrophotometer Jasco corp. V-570 which allows measurement in the spectral range 200-2500 nm with 1 nm resolution. Electrical resistivity was measured by the four-point probe method.

Result and discussion

X-ray diffraction pattern

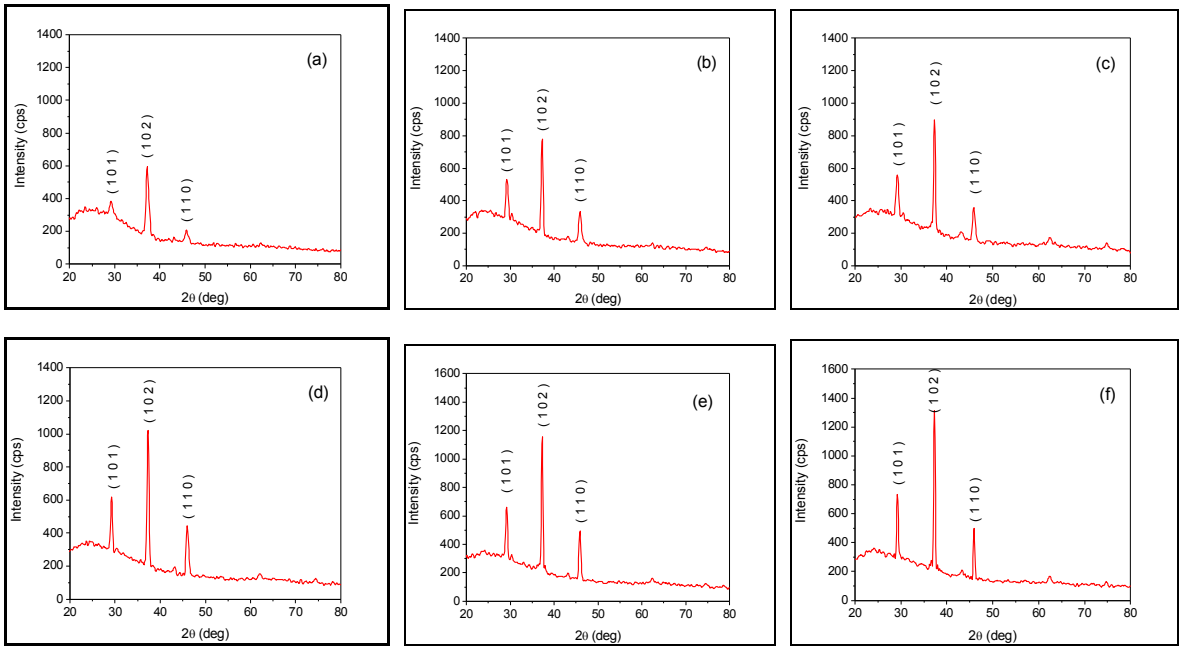

Fig . 1. XRD patterns of Cu_2S thin films prepared at deposition time for a) 30, b) 45, c) 60, d) 75, e) 90 and f) 105 minutes

Table 1. Structural parameters of Cu_2S thin films

Deposition time (min)	Film thickness (nm)	2θ (Deg)	Crystallite size D (nm)	Dislocation density δ (10^{15} lines/m^2)	Strain ε (10^{-3} m)	Lattice parameter (Å)	
						JCPDS	Observed
30	290	37.17	11	9.7966	3.4327	a = 3.95 c = 6.75	a = 3.93 c = 6.86
45	379	37.31	13	7.9925	3.1005		a = 3.96 c = 6.77
60	548	37.35	15	6.3768	2.7695		a = 3.95 c = 6.77
75	696	37.34	17	3.6950	2.1081		a = 3.95 c = 6.76
90	844	37.29	21	2.0520	1.5710		a = 3.95 c = 6.78
105	928	37.33	27	1.2786	1.2401		a = 3.95 c = 6.76

Fig. 1 (a-f) shows the XRD spectra of Cu_2S thin films deposited at room temperature on glass substrates with deposition time varying from 30 to 105 min. It is inferred from the figure that all the spectra exhibit peak at 2θ equal to 37.39° corresponding to the orientation along (102) direction. In addition to that, weak diffraction peaks also appear along (101) and (110) plane. The observed results are in good agreement with the standard JCPDS data (Card No 24-0057) thus confirming the presence of hexagonal structure. It is also observed that the intensity of the peaks increase with increase of deposition time/thickness. This change may be attributed to the fact that during the atomic condensation of film formation, the deposited atoms are at random orientation and when the deposition time increases, the polycrystalline grains may begin to orient along their direction which is evident from the diffractograms. The lattice parameters are calculated for the most preferred orientation and are found to be in excellent agreement with the standard values.

The microstructural parameters such as grain size, microstrain and dislocation density are calculated from XRD data and their values as a function of thickness are presented in table. 1. The grain size is found to increase with increase of film thickness. Increase of grain size with increase of film thickness is in conformity with increase of peak height and decrease in FWHM (β) along the preferred orientation. This may be due to enhancement of horizontal velocity of ad-atoms and condensation of energetic copper and sulfur atoms. The decrease of strain and dislocation density with increasing deposition time/thickness may be due to the movement of interstial copper atoms from its grain boundary to the crystallites which may be leading to the reduction in the concentration of lattice imperfections. The decrease in strain with increasing thickness may be obviously due to the increase in grain size and also due to the piling up of energetic atoms one over the other which is in good agreement with reported literature [27, 28].

Morphological analysis

The scanning electron micrographs of the Cu_2S thin films of different thicknesses on glass substrate at various deposition times are shown in fig. 2 (a-f). It is observed that all the films are homogeneous and have dense microstructures. The film surface looks smooth and uniform. It is well clear from the micrographs that the particles are spherical and adherent. It can be seen that these spherical grains are uniformly distributed to cover the surface of the substrate completely. The size of the grain slightly increased with increase in film thickness and deposition time.

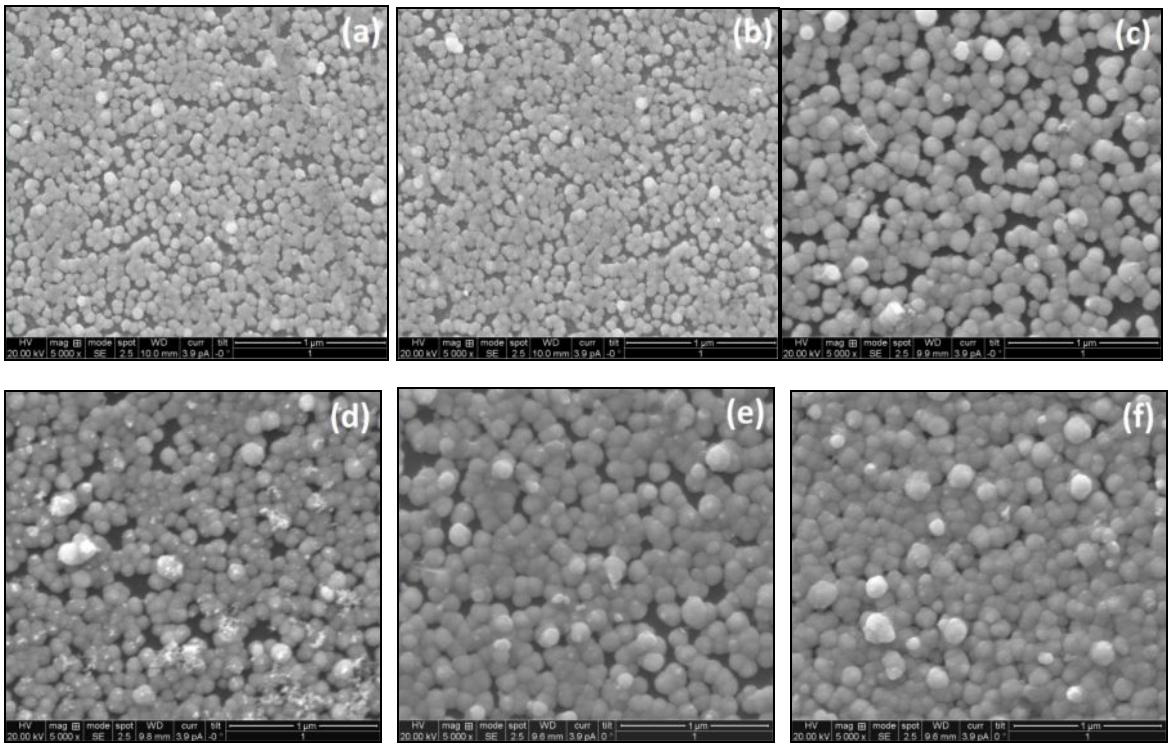

Fig. 2. SEM Micrographs of Cu_2S thin films prepared at deposition time for a) 30, b) 45, c) 60, d) 75, e) 90 and f) 105 minutes

Based on the SEM micrographs, it is clearly observed that the grains of the sample deposited at the highest duration time are relatively larger in size than that of the films prepared at lower deposition time. The SEM micrographs of higher deposition time shows that the substrate is covered completely indicating that more nucleation sites have been formed and the number of grains has increased. It can be seen that the morphologies of films show a clear dependence on the deposition time. It was evident that with the increase in deposition time, the grains become larger in diameter and is in confirmation with the XRD results of the samples.

Compositional analysis

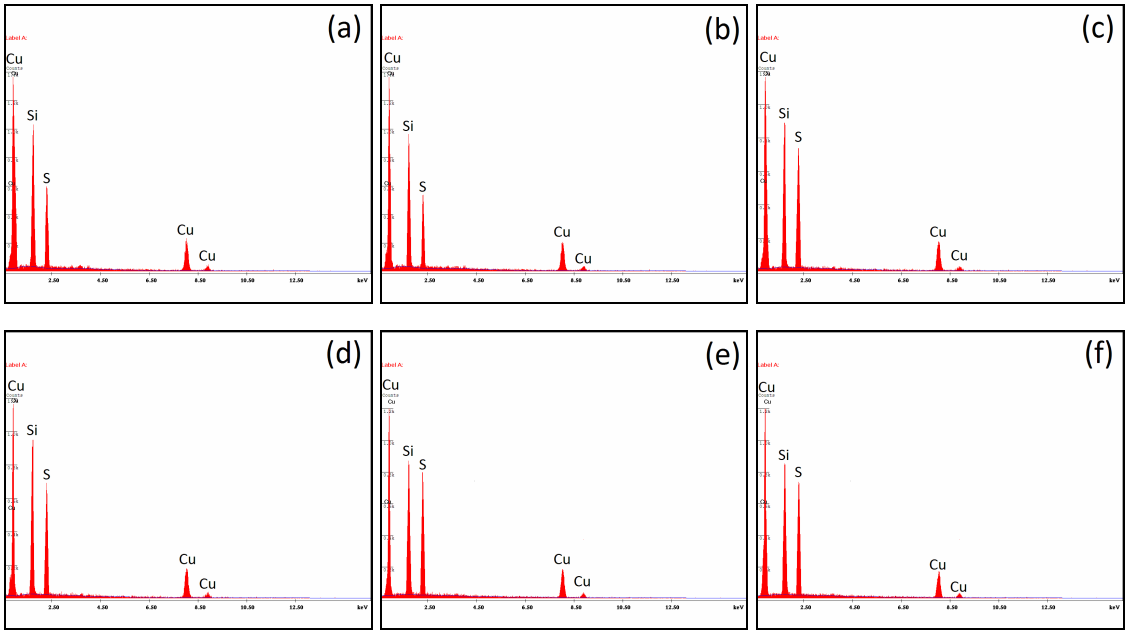

Fig. 3. EDAX Spectra of Cu_2S thin films prepared at deposition time for a) 30, b) 45, c) 60, d) 75, e) 90 and f) 105 minutes

The elemental analysis of the Cu_2S thin films deposited at different deposition time on glass substrate were investigated by energy dispersive X-ray analysis (EDAX) technique. A typical EDAX patterns are shown in fig. 3 (a-f). EDAX analysis indicates the presence of copper and sulfur for all the deposited films. The average atomic ratio of Cu/S was calculated from the quantification of peaks. Theoretically expected stoichiometry composition of Cu_2S (in terms of At %) was Cu:S equal to 66.67 : 33.33. Table.2 lists the atomic and weight % of Cu and S in Cu_2S thin films prepared at different deposition time. It is inferred from the table that with increase in deposition time from 30 to 105 min, the atomic percentage of copper decreases from 71.23 to 67.44 and sulfur increases from 28.77 to 32.56 as against the actual value of Cu_2S. This shows that the atomic percentage of both copper and sulfur are nearly the same as actual values at higher deposition time (90 and 105 min) and slight deviation in stoichiometry for films prepared at lower deposition time. From this it may be confirmed that the atomic percentage of the thin films is altered as the films are prepared at different duration time. Therefore, the deposition time and film thickness has significant influence on the composition of the deposited films. Film prepared at 105 min is nearly stoichiometric and this is in confirmation with the improvement in grain size as evinced from the structural studies in XRD section. This might be due to the better orientation of grains in the films.

Table. 2. Atomic and Weight % of Cu and S in Cu_2S thin films

Deposition time (min)	Standard				Calculated			
	(Atomic %)		(Weight %)		(Atomic %)		(Weight %)	
	Copper	Sulfur	Copper	Sulfur	Copper	Sulfur	Copper	Sulfur
30	66.67	33.33	79.85	20.15	71.23	28.77	83.07	16.93
45					70.27	29.73	82.41	17.59
60					69.17	30.23	81.93	18.07
75					68.52	31.48	81.18	18.82
90					68.02	31.98	80.83	19.17
105					67.44	32.56	80.41	19.59

Optical studies

The optical properties of the films deposited on glass substrates for different deposition time are determined from the absorbance (A) measurements in the range 450-800 nm. Fig. 4 shows the absorbance spectra for Cu_2S thin films of varying film thicknesses deposited at different deposition time. All the films exhibit the same patterns with higher absorption on the shorter wavelength side. These spectra reveal that Cu_2S film has high absorbance at higher thicknesses [29] and the films synthesized with high absorbance, relatively low transmittance could be useful for the construction of poultry houses.

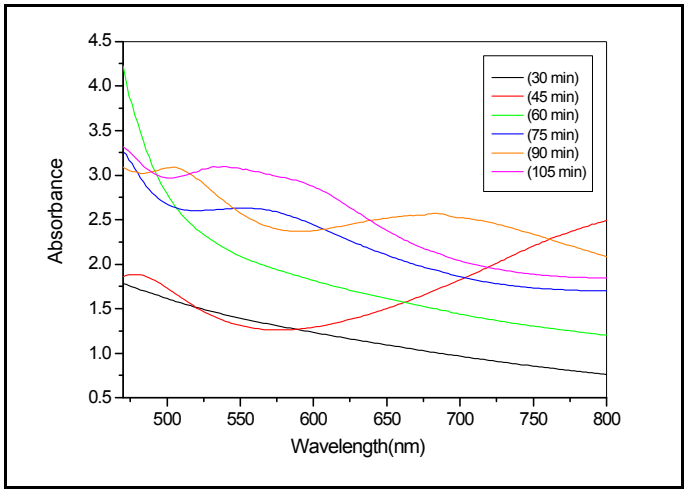

Fig. 4. Wavelength Vs Absorbance of Cu_2S thin films with different deposition times

The thickness does not affect the phase and crystalline structure of the Cu_2S thin film, the fundamental absorption which corresponds to electron excitation from the valence band to conduction band and can be used to determine the nature and value of the optical band gap. The band gaps have been determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ graph is shown in fig. 5 for different film thickness of Cu_2S thin films. Extraplotting the straight line portion of the plot of $(\alpha h\upsilon)^2$ against $(h\upsilon)$ to energy axis for zero absorption coefficient ($\alpha = 0$) gives optical band gap energy. The linear nature of the plots indicates the existence of the direct transitions. The band gap energy decreases with increasing deposition time and thickness.

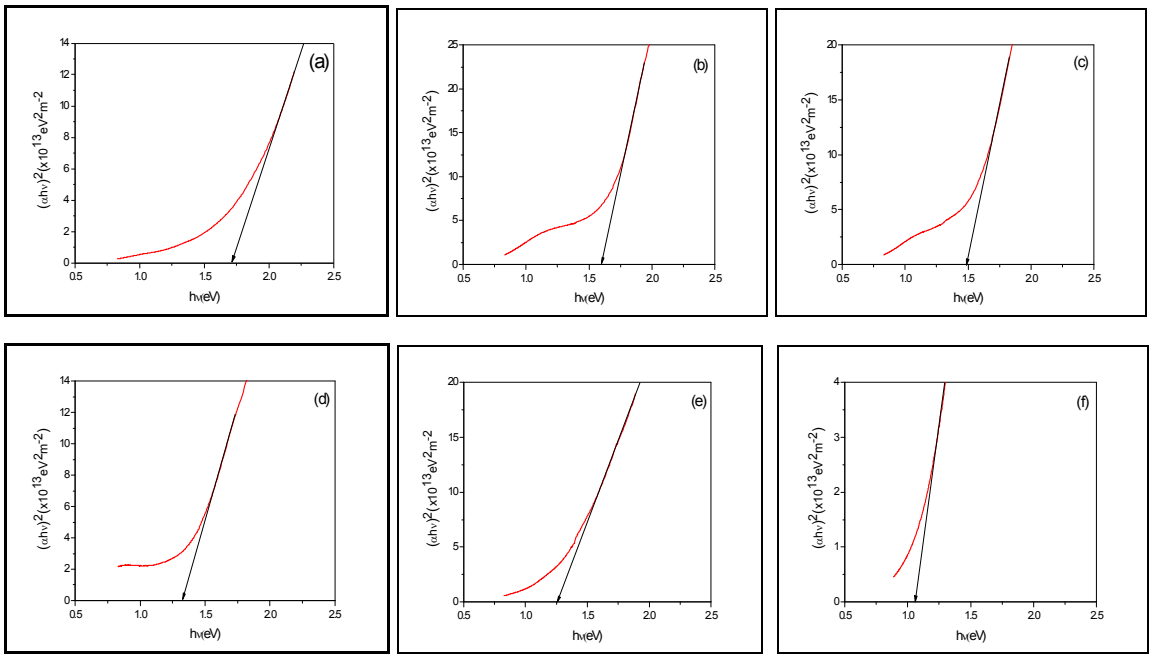

Fig. 5. Plot of $(\alpha h\upsilon)^2$ Vs $(h\upsilon)$ for Cu_2S Cu_2S thin films prepared at deposition time for a) 30, b) 45, c) 60, d) 75, e) 90 and f) 105 minutes

The optical band gap of the film estimated from the graph is reported in table. 3. It is seen that band gap (Eg) increases from 1.05 to 1.71 eV as film thickness was reduced from 928 to 290 nm. The change in band gap was attributed to the increase in crystallinity of the films [30,31]. The band gap values are also close to those presented in literature [22]. Optical band gap values distinct from that of the bulk crystalline material are known to exist in polycrystalline thin films. In general thickness dependence of band gap can arise due to the following causes (i) large density of dislocations (ii) height of the crystalline films. In the present case, the decrease in band gap may be due to the increase in height of the crystalline films. Film thickness together with the energy band gap shows that these films can be used as potential absorbers in solid state solar cells.

Resistivity studies

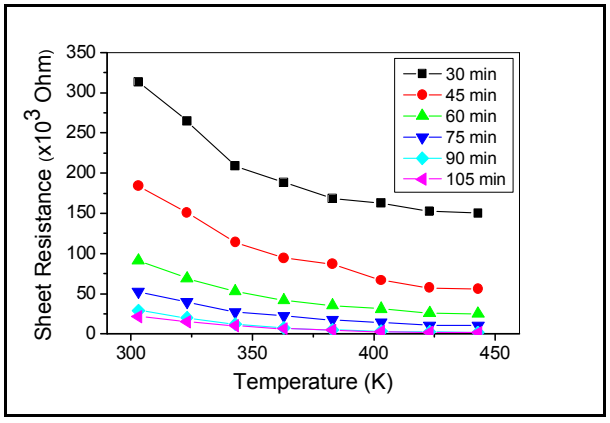

Fig . 6. Sheet Resistance Vs Temperature

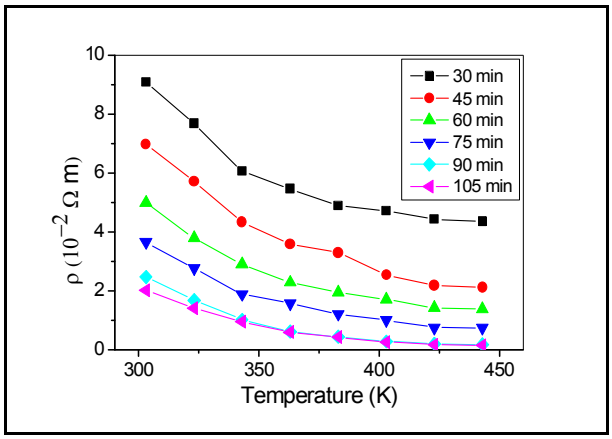

Fig . 7. Resistivity Vs Temperature

The electrical measurements on Cu_2S thin films for different thicknesses are made using four point probe technique and the resistance-temperature measurements show that the films behave as a typical semiconductor. Variation of sheet resistance and resistivity with film thicknesses at room temperature are shown in fig. 6 & 7. The decrees of sheet resistance and resistivity with increase of film thickness (table. 3) are found to be in agreement with that of the previously reported values [21, 32-34] and the reason may be that the electrical resistivity of nanocrystalline thin film decreases with increase in film thickness because for very thin films, there are islands of aggregated particles with lot of insulating gaps. As thickness increases the islands of aggregated particles transform into continuous bands. So the insulating gaps are minimized with increase in film thickness. The decrease in sheet resistance and resistivity linearly with increase in temperature indicates the semiconducting behaviour of the material. The high resistivity for the thinner films could also be attributed to the lattice defects and dislocations in the thin films and can be explained on the basis of sondheimer's theory [35] that the scattering of carriers at the surface of the film effectively reduces the mean free path of the carriers, so that the resistivity decreases with increase in film thickness. It is well known that the thermal activation energy can promote an electron into the conduction band of a semiconductor and thereby both the electron and accompanying hole are mobile leading to electrical conductivity.

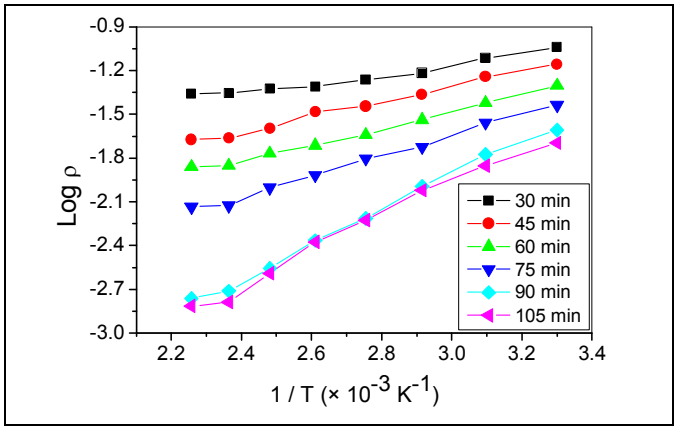

Fig. 8. Variation of log of resistivity with Inverse of Temperature

Table. 3. Optical and electrical parameters of Cu_2S thin films

Deposition time (min)	Film thickness (nm)	Band gap (eV)	Sheet resistance R_S ($10^3\Omega$)	Electrical resistivity ρ (10^{-2} Ωm)	Activation energy (eV)
30	290	1.71	313.614	9.094	0.253
45	379	1.60	184.301	6.985	0.248
60	548	1.49	91.002	4.986	0.238
75	696	1.33	52.497	3.653	0.226
90	844	1.26	29.252	2.468	0.198
105	928	1.05	21.700	2.013	0.173

From the plot of ln ( ) against 1000/T (fig. 8), the activation energy of the film could be determined. The activation energies are calculated and the summary of the activation energy obtained for different thicknesses are presented in table. 3. Activation energy decreases with increase of film thickness and this variation may be due to the following reasons. (i) Change in the barrier height due to size of the grains in a polycrystalline film, (ii) Large density of dislocations, (iii) Quantum size effect and (iv) Change in stoichiometry. The decrease of activation energy with increase of film thickness may be due to the increase in grain size of Cu_2S thin films and may also be due to the change in barrier height caused by the grain size variation with increase of film thickness as suggested by slater's model [30]. An alternate explanation for higher value of activation energy for thinner films may be given qualitatively on the basis of island structure theory suggested by Neugebaur [36].

Conclusion

Polycrystalline Cu_2S thin films were prepared by simple chemical bath deposition technique onto glass substrates. XRD measurement shows that the prepared films are polycrystalline hexagonal in nature. A morphological study shows that the films are smooth, dense and homogeneous without discontinuity. Nearly stoichiometric films were obtained at higher deposition time as observed from the EDAX spectra. From the absorbance-wavelength measurement, it is found that the films are highly absorbing with very less percentage of transmission. The band gap values were also found to decrease with increase of film thickness. Resistivity studies show the semiconducting nature of the Cu_2S material as the sheet resistance and resistivity decreases with increase of temperature and thickness. The activation energy of the film also decreases with increase of film thickness. From all these measurements, it may be concluded that the lower thickness copper sulfide film could be useful in solar thermal devices and eyeglass coatings, those with higher thickness could be useful in anti dazzling coatings.

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