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Influence of Molar Concentrations on Optical Properties of Copper Sulphide Thin Films by Silar Method

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Abstract: Copper sulphide (CuS) thin films are deposited on microscopic glass substrate by chemical technique called successive ionic layer adsorption and reaction (SILAR) method at room temperature. The technique involves multiple dipping of the substrate in an aqueous solution of copper nitrate, sodium sulphide and in deionised water. The aim of this study is to establish the optical properties (Absorbance, Transmittance and Band gap) of Copper sulphide thin films by UV-VIS spectrometer and the influence of molar concentration was studied to determine the optimum condition for deposition process. The band gap energy decreases from 2.26 V and 1.86 eV when molar concentration increases from 0.05M to0.25M. The high absorbance of the films made them good materials for conversion of solar energy.
Keywords: Copper sulphide, CuS, SILAR, Transmittance, Absorbance, Band gap, Molarity.

Introduction

Copper sulphide is wide energy gap semiconductor and an important material for photovoltaic cell[1]. In recent times, different chemical techniques such as chemical bath deposition (CBD)[1,2], spray pyrolysis[3,4], chemical precipitation[5], electrode position[6], atomic layer deposition (ALD)[7,8], Sol-Gel[9], solution growth[10] etc. have been used to obtain thin films. All these experimental techniques either demand stringent reaction conditions such as high temperature, pressure and hazardous chemicals or both. Among different methods the Successive Ionic Layer Adsorption and Reaction (SILAR)[11, 12, 13, 14] method is attracted for its large area deposition and easy control on film thickness by adjusting number of deposition cycles. Also, it is simple and inexpensive which comprises excellent material utilization efficiency, good control over deposition process along with film thickness and convenient for large area deposition on any type of substrate. Also this method can be used to deposit compound materials on a variety of substrates such as insulators, semiconductors, metals, glass etc. Thus, both thick and thin films can be prepared by this method. Hence, in the present work, SILAR method has been used for deposition of copper sulphide thin films. In this method, thin film was prepared by immersing substrates into separately placed cationic and anionic precursors and precipitate formation in the solution i.e. wastage of the material was avoided. The studies of Copper sulphide thin films have been reported by many researchers by various methods and different chemicals. Copper sulphide films were deposited onto glass substrates using precursor such as Copper Nitrate and Sodium sulphide solutions. This method has great advantage for deposition of thin films at low temperature[11]. Hence, effort has been made and succeeded to synthesis the copper sulphide thin films onto microscopic glass substrates at room temperature for solar control coatings, solar cells, photo-thermal conversion of solar energy, electro-conductive coatings, and microwave shielding coatings. The developed thin film was subjected to analyze its optical properties with different molar concentrations and the optical band gap also determined and reported.

Experimental work

Glass microscope slides were cleaned by immersing them in concentrated nitric acid (con.HNO_3) for 2 days, washed in detergent solution, rinsed in distilled water and dried in air.

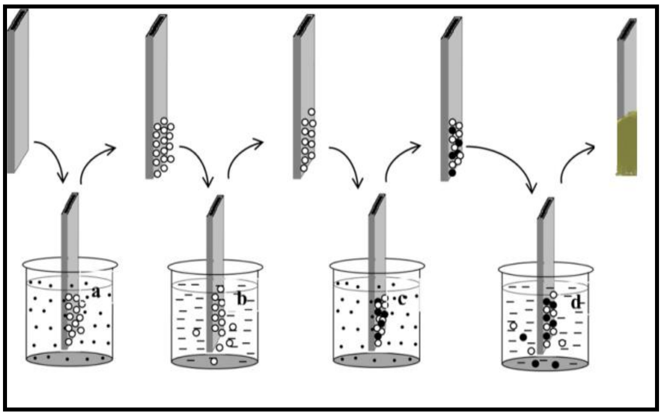

Fig 1 SILAR Experimental set up for the deposition of CuS

(a) cationic precursor copper Nitrate[$Cu(NO_3)_2 \cdot H_2O$],
(b) deionised water
(c) anionic precursor Sodium Sulphide [Na_2S] and
(d) deionised water

The copper Sulphide thin films were prepared by dipping substrate in a beaker containing aqueous solutions of copper Nitrate [$Cu(NO_3)_2 \cdot H_2O$], Sodium Sulphide [Na_2S] and distilled water. Molar ratio between copper and Sulphide was kept as 1:1 for all the solutions. Deposition process time is given in Table 1. Pre-cleaned glass substrates immersed in cationic precursor for 30 seconds for the absorption of Cu ions and then immersed in distilled water for 30 seconds, in order to remove the de-adsorbed ions. Then, substrates were again immersed in anionic precursor for 30 seconds for adsorption and reaction of sulphide ions. Unreacted sulphide ions were removed by rinsing them in distilled water for 30 seconds. Thus, a SILAR cycle is completed after these four operations. Deposition continues by repeating above procedure for 20 cycles. The resulted Copper Sulphide thin films were annealed in vacuum at 100 $^{\circ}$C for two hour in hot air oven.

Table 1 Deposition parameters

Start position	0
Dip length	75 mm
Dip speed	5 mm/sec
Retrieval speed	4 mm/sec
Dip duration	30 sec
Ex dip duration	4 sec
No of cycles	20
No of dips No of Dips	4

Results and discussion

Absorbance

Figures 2 and 3 shows the absorbance spectrum of wavelength from 200 nm to 900 nm. Shoulder peak obtained at 297 nm which is the peak of glass substrate SiO_2. Minimum peak of absorbance is observed at 379 nm which is the peak of CuS. The same value of miminum peak is observerved for both the case of Copper and Sulphur in 1:1 rario and 1:2 ratio. The absorbance increases for the decreasing wavelength from 600 nm to 300 nm. For the increasing molar concentration, absorbance is higher in the UV-Vis regions, but is lower at the NIR region.

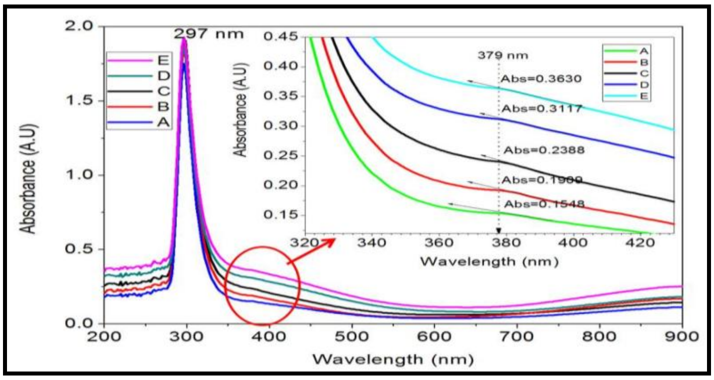

Fig 2 The absorbance spectrum of CuS thin films at 1:1 ratio

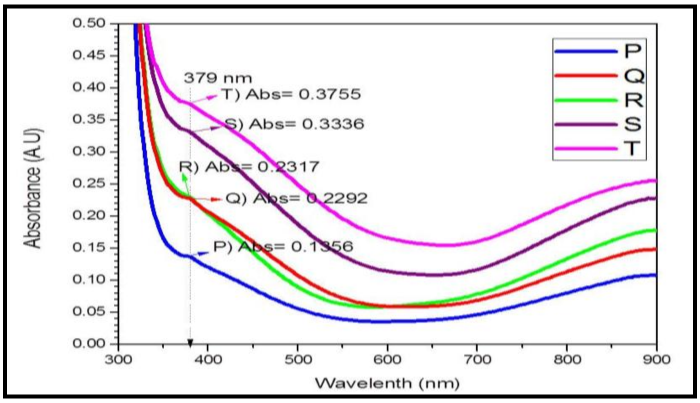

Fig 3 The absorbance spectrum of CuS thin films at 1:2 ratio

Transmittance

Transmittance spectra of the title compound is shown in Figures 4 and 5. For all the concentrations of CuS film, transmittance is increases from 3 % to 91 % in the UV-Vis to NIR regions. The transmittance of the films increases with increase in wavelength from UV- VIS regions (300nm to 600nm), but decreases in the NIR region (above 600nm). Transmittance increases rapidly in the UV region, but increased slowly and constantly towards NIR regions. For all the concentrations of CuS film, the average transmittance is greater than 70% throughout UV- VIS-NIR regions.

It is considered that, architectural use of these films as spectrally selective window coatings. It is observed that, the transmittance decreases with increase in molarity of precursor solution. The film deposited for 0.05 M shows higher transmittance compare to 0.25 M. This property of high transmittance makes it as a good material for optical coatings. From the spectra, it is revealed that, the CuS films have low absorbance in the visible region, which is the characteristic of the transmittance edge. It is shifted slightly towards higher wavelength as the molarity concentration was increased. This shift indicates decrease in bandgap, which can be attributed to increase in the molarity concentration. In Figures 4 and 5, peaks are attributed to the formation of excitons of CuS thin films, which increases with increase in molarity concentration . The band gap energies were calculated from maximum transmittance of wavelength. For CuS thin films band gap is decreases from 2.26 eV to 1.86 eV for the molarity concentrations from 0.05 M and 0.25 M concentration respectively at room temperature.

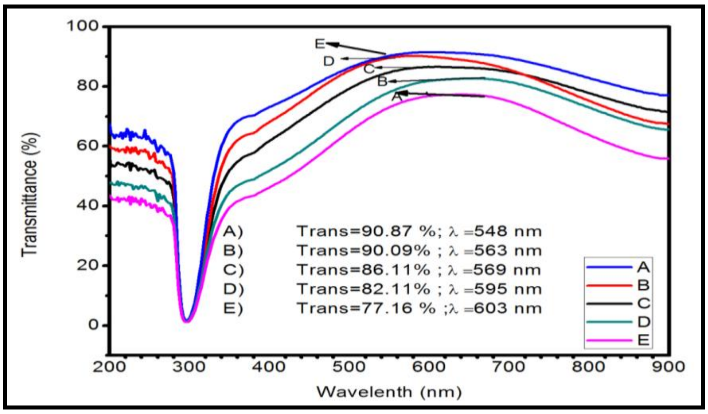

Fig 4 The Transmittance spectrum of CuS thin films at 1:1 ratio

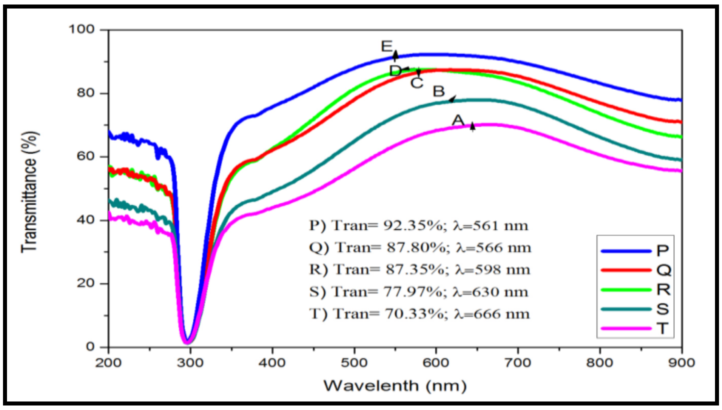

Fig 5 The Transmittance spectrum of CuS thin films at 1:2 ratio

Band gap measurement

Band gap energy and transition type can be derived from mathematical data. Fig 6 shows the energy versus $(Ah\nu)^2$ of CuS films with different molar concentration.

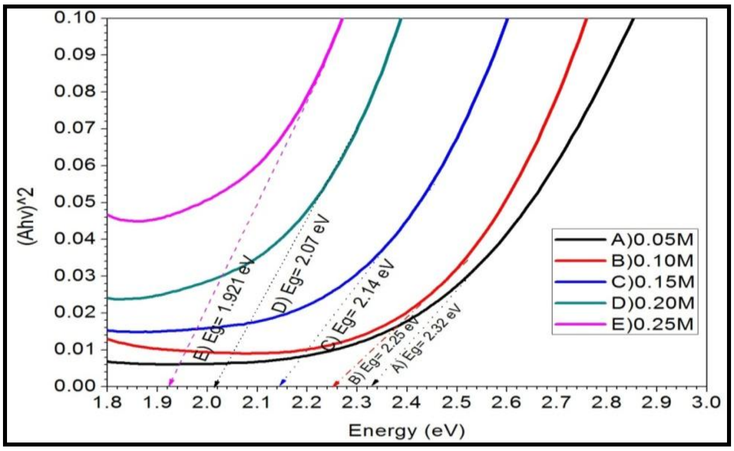

Fig 6 Optical $(Ah\nu)^2$ vs Energy(hν) plots of CuS thin films

$$A = \frac{[k(h\nu - E_g)n/2]}{h\nu} \quad \text{------------------------(1)}$$

where ν is the frequency, *h* is the Planck's constant, *k* is a constant and *n* carries the value of either 1 or 4.The *n* value is 1 for a direct gap material and 4 for indirect gap material. The plot of $(Ah\nu)^2$ against *h*ν for the films deposited at various deposition molar concentration is presented in Fig 6. For a direct band gap semiconductor (n=1), the $(Ah\nu)^2$ against *h*ν is predicted to be a straight line with a photon energy (*h*ν) axis intercept gives the band gap value. The band gap energies of the thin film of CuS deposited for the concentrations 0.05M, 0.10 M, 0.15 M, 0.20 M and 0.25 M are 2.32 eV, 2.25 eV, 2.14 eV, 2.07 eV and 1.92 eV respectively.

Table 2 Absorbance Results

S.No	Molarity	From (Fig 2&3) Absorbance Spectrum			
			Eg = 1240/λ_{max} eV	Absorbance (A.U) 1:1 ratio	Absorbance (A.U) 1:1 ratio
1	0.05M	379	3.27	0.1548	0.1356
2	0.10M	379	3.27	0.1909	0.2292
3	0.15M	379	3.27	0.2388	0.2317
4	0.20M	379	3.27	0.3117	0.3332
5	0.25M	379	3.27	0.3630	0.3755

Table 3 Transmittance and band gap result at 1:1 ratio

S.No	Molarity	From (Fig 4) Transmittance Spectrum		
		Transmittance (%)	λ_{cutoff} (nm)	Band gap E_g=1240/ λ_{cutoff} ; (eV)
1	0.05M	90.87	548	2.26
2	0.10M	90.09	563	2.20
3	0.15M	86.11	569	2.17
4	0.20M	82.17	595	2.08
5	0.25M	77.16	603	2.05

Table 4 Transmittance and band gap result at 1:2 ratio

S.No	Molarity	From (Fig 5) Transmittance Spectrum		
		Transmittance (%)	λ_{cutoff} (nm)	Band gap E_g=1240/ λ_{cutoff} ; (eV)
1	0.05M	92.35	561	2.21
2	0.10M	87.80	566	2.19
3	0.15M	87.35	598	2.07
4	0.20M	77.97	630	1.96
5	0.25M	70.33	666	1.86

Conclusion

Copper sulphide thin film was deposited on glass substrates using the SILAR method at room temperature and the results of optical absorbance, transmittance and band gap studies were discussed. In the deposited Copper sulphide thin film, optical band gap energy decreases from 2.32 eV to 1.92 eV with increasing Molar concentration and the band gap value decreases. For the increasing concentration of copper Nitrate and Sodium Sulphide, 1:1 and 1:2 maximum transmittance of wavelength is shifted from shorter wavelength region 548 nm to longer wavelength region 666 nm.

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