

Properties of chemical bath deposited Cu_2S thin films

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Abstract: Thin films of Copper sulphide were deposited on glass substrates by chemical bath deposition using triethanolamine as complexing agent instead of commonly used ammonia. In order to investigate the film growth mechanism, samples were deposited at different room temperature. Film thickness was increased with increasing the time but the film peel-off was observed at the deposition time more than 60 min. The film structure analyzed by X-Ray diffraction, surface morphology was studied by SEM, elemental composition studied by EDS and optical absorption with UV-Vis spectrophotometer. The effect of film thickness on the optical & structural properties has been studied.

Keywords: Copper sulphide; CBD; XRD; SEM; EDS; Thin films.

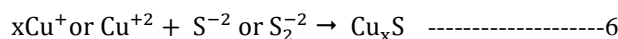
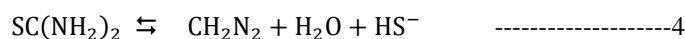
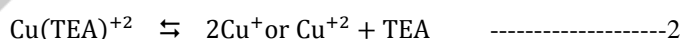
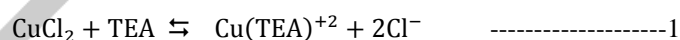
1. Introduction

Copper sulphide (Cu_xS , $1 \leq x \leq 2$) thin films driven considerable attention due to their potential in a photovoltaic cell, tubular solar cells, automobile glazing, solar control coatings, dye-sensitized solar cells, gas sensors, photo detector etc.[1-6]. The copper sulphide (Cu_xS) system is complex and exists in five stable phases which include CuS (covellite), $\text{Cu}_{1.75}\text{S}$ (anilite), $\text{Cu}_{1.8}\text{S}$ (digenite), $\text{Cu}_{1.96}\text{S}$ (djurleite) and Cu_2S (chalcocite) [7]. The variation in the crystalline phases depends on the temperature [8, 9], producing significant difference in the electrical conductivity [10] and optical band gap [11]. There are several techniques such as spray pyrolysis [12], reactive magnetron sputtering [13], successive ionic layer adsorption and reaction (SILAR) [14], chemical vapour deposition [15], chemical bath deposition [16-20] and microwave assisted chemical bath deposition [21] have been used for the deposition of copper sulphide thin films.

In this paper, we report the preparation of Copper sulfide thin films by CBD in an alkaline bath and studied the dependence of film thickness on the deposition time, the deposition temperature and pH of the solution. Further we studied the effect of film thickness on structural and optical properties of the deposited copper sulphide film.

2. Experimental

The recipe for the deposition of CuS thin film consists of an aqueous solution of cupric chloride (0.01 M), ammonia (1%), triethanolamine (0.002 M) and thiourea (0.01 M). The starting solution pH was in the range 10 – 11 based on the concentrations chosen. Chemically and ultrasonically cleaned soda-lime glass slides were used as substrates. For optical absorption studies, films were deposited on quartz substrates. Films were prepared at both room and elevated temperatures. In order to study the effect of time, substrates were removed from the bath at interval 10 min. The deposition of Cu_xS thin films mechanism follows the chemical reaction:



The film thickness was determined from the deposited mass measured using a METLER AE240 microbalance and the bulk density. The spectral transmittance of these films was recorded using a JASCO UV-VIS-NIR (Model V570) spectrophotometer. The X-ray diffraction (XRD) patterns of these films were recorded in glancing angle mode (glancing angle $\frac{1}{4}$ 0.3) using a PAN analytical Expert PRO X-ray diffractometer with Cu K α (0.15406 nm) radiation. The microstructure of the films was recorded by scanning electron microscope (SEM) using a model ZEISS, EVO MA50. Results and discussions.

2.1 Effect of the bath temperature

To study the deposition bath temperature on film growth, deposition conditions are maintained at the optimized state and temperature varied from 30⁰ C to 70⁰ C. As increasing the temperature, film thickness is also increased. Table 1 shows the compositional analysis (atomic ratio) of the copper sulphide thin films prepared at various bath temperatures. The regular atomic ratio of Cu/S calculated from the quantification of the peaks, gives the value of 1.56, 1.88 and 2.02 for different bath temperatures of 50 °C, 60 °C and 70 °C respectively. Hence, results indicate that the average atomic ratio of Cu/S increases with increasing bath temperature.

Table 1: Atomic percentage composition of Cu₂S thin films deposited at different bath temperatures

S.NO	Bath temperature (°C)	Atomic percentage of copper (%)	Atomic percentage of sulphur (%)	Cu:S
1	40	60.87	39.13	1.56
2	50	65.32	34.68	1.88
3	60	66.89	33.11	2.02
4	70	68.20	31.80	2.15

2.2 Effect of pH

To study the effect of pH on the film growth, films are grown with optimum conditions by varying the solution pH from 9-11. Fig.1 shows that the films are found to be uniform and thickness at pH 10.2. A detailed study is necessary to explain this observation.

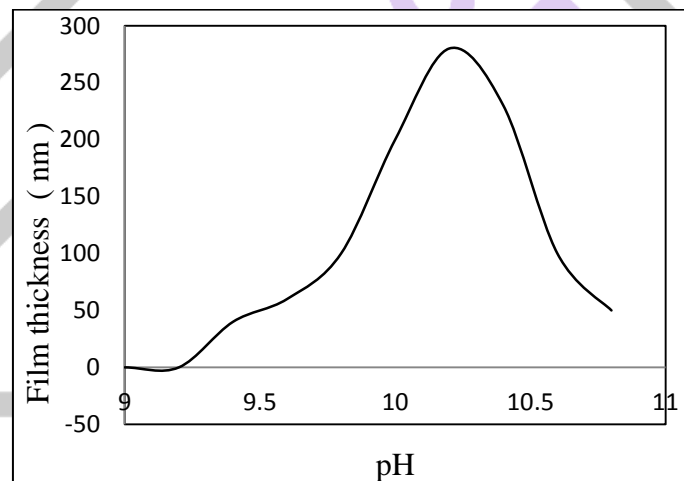


Fig.1: The effect of pH on the Cu₂S film thickness

2.3 Effect of deposition time

Fig.2 shows Cu₂S film thickness as a function of deposition time at room temperature. As the deposition time increases the films grow relatively faster and reach saturation earlier. The deposition found to vary mostly from 30 to 50 min. Films obtained at 10 and 20 min were found to be not uniform. Uniform and specular Cu₂S films were obtained at temp 50 to 60 min more than that time the formed films were peel off. The peel off of the films was observed above the 60 min deposition time.

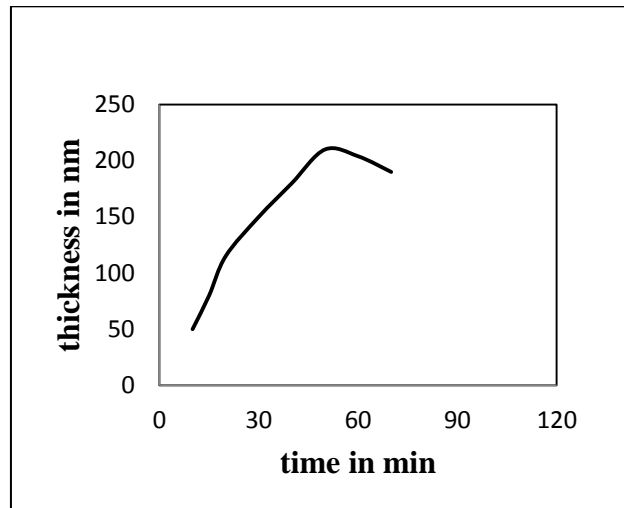


Fig.2: The Variation of Cu₂S film thickness as function of deposition time

2.4 Structural analysis

2.4.1 X-ray diffraction

The results of the XRD analysis for the Cu₂S films deposited by CBD at different temperatures and time are shown in Fig.3 and Fig.4 respectively. In both cases, high intensity peaks at 2θ values 37.2°, 42.5°, 44.8°, 48.3° and 51.5° show the presence of hexagonal crystal structure (Cu₂S) (JCPDS-26-1116) with lattice constant a= 3.9610Å, b=3.9610Å and c=6.7220Å. From the Fig.3, decrease in the intensity of the peaks with broadening of the peaks indicates decreased crystallinity and decrease in size of the particles. From the Fig.4, it is also observed that at longer deposition time (>70min) films are peeled off, hence no peaks are observed (i.e., amorphous in nature).

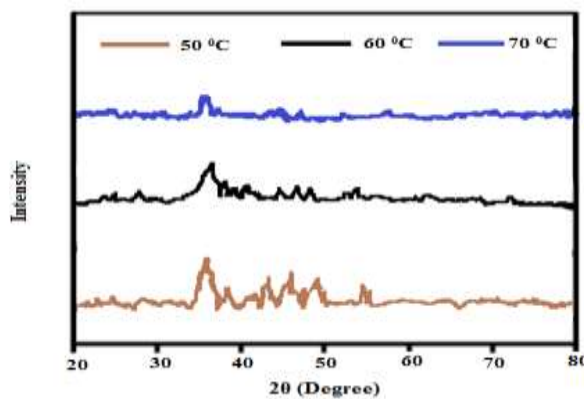


Fig.3: XRD patterns of Cu₂S films at different temperatures (60 min)

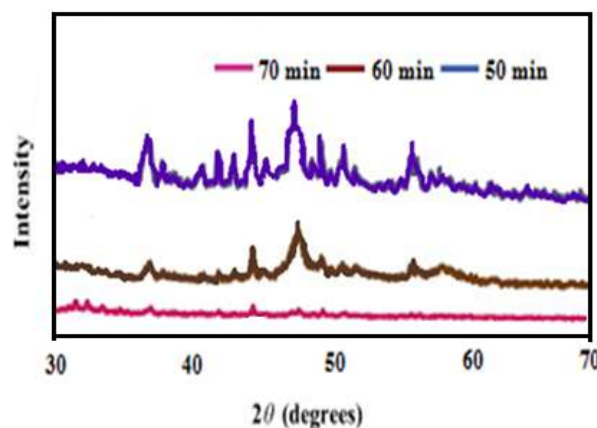


Fig.4: XRD patterns of Cu₂S films at different deposition time.

2.4.2 Micro structure

Fig.5 shows the SEM micrographs of Cu₂S films grown on glass substrates with different deposition time. The microstructure of the Cu₂S thin film shows uniform surface morphology. In addition, a number of large particles were seen on the film’s surface. Those were Cu₂S particles, not impurities because no impurity phase was observed in the XRD pattern. With increasing deposition time uniformity of morphology also increased (b) but at the time 70 min, films are peel off. These peeling off are observed in the SEM image (c).

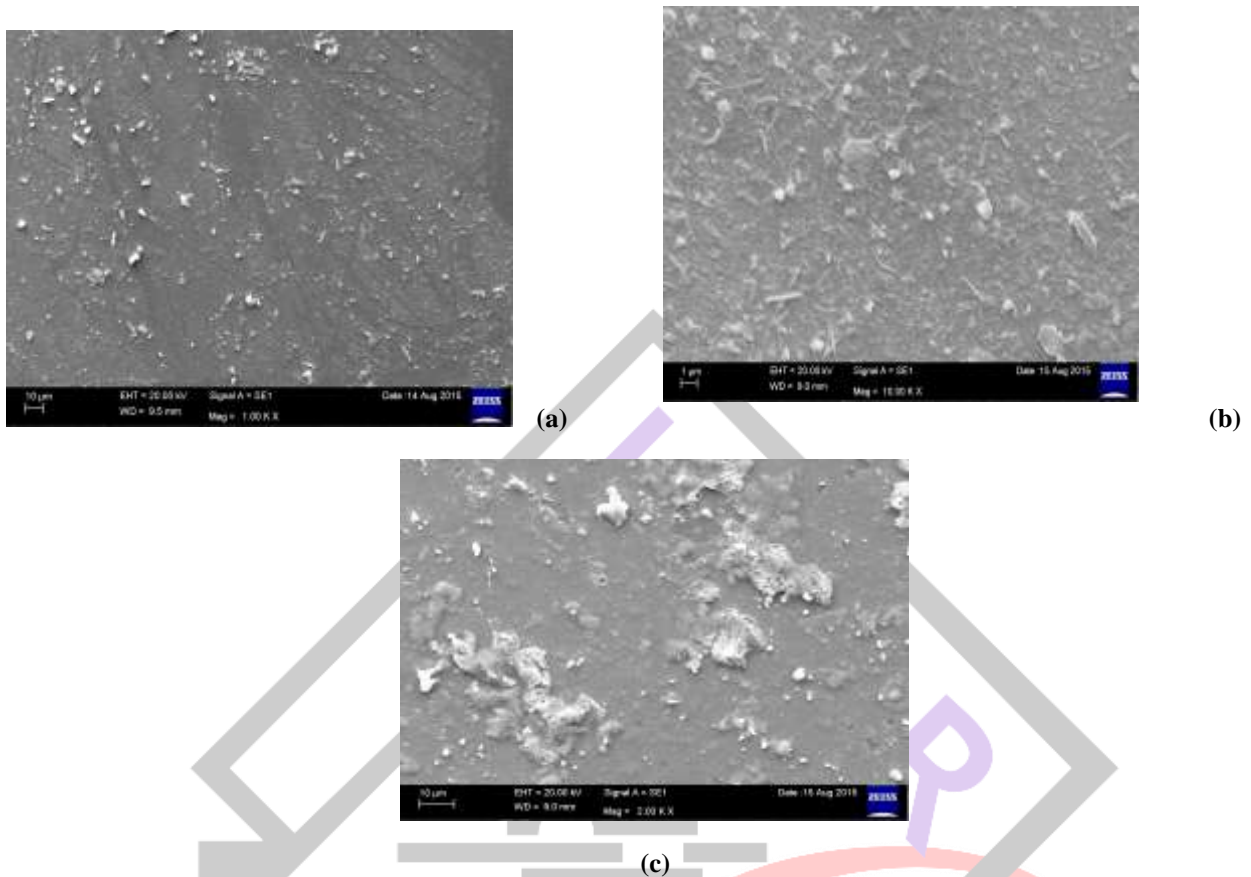


Fig. 5: SEM image of Cu₂S thin film at different deposition time
 (a) 40 min (b) 50 min (c) 60 min

2.5 Optical properties

The optical properties of the films synthesized on glass substrates under different sonication times at room temperature are determined from the absorbance (A), reflectance (R) and transmittance (T) measurements in the range 350–1000 nm. Fig.6 reveals that the maximum percentage transmission is 62% at λ = 630 nm. A sharp increase in the transmission in the wavelength range 500 nm matches with the earlier reports and it is close to the effective band gap of Cu₂S. The band gap of the synthesized films was calculated using the Tauc relation

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

-----5.7

Where *n* is a factor which depends on the nature of the optical transition and E_g is the band gap. The values of *n* are 1/2, 2, 3/2 for direct-allowed, indirect-allowed and direct-forbidden transitions respectively. The values of (αhν)² plotted with photon energy (hν) is drawn for determination of optical band gap. The extrapolation of the linear region of the plot onto X- axis gives the direct optical band gap of the Cu₂S films. The plots shown in Fig.5.9 reveals that the optical band gap of the films slightly decreases from 1.85 eV to 1.81eV with increase in deposition time at room temperature(30⁰C). It is due to the increase in particle size with increasing the film thickness.

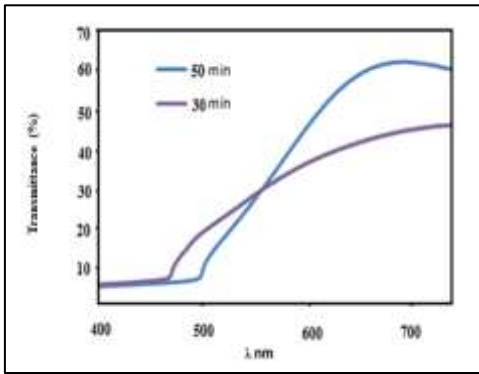


Fig.6: Optical transmission spectra of

Cu₂S thin films at different deposition time

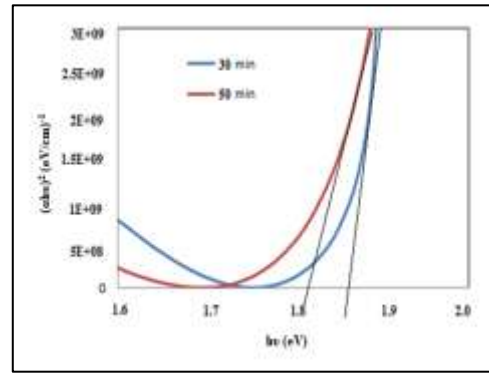


Fig. 7: A plots of $(\alpha h\nu)^2$ versus $(h\nu)$ of

Cu₂S films at different deposition time

5.3.2 EDS Analysis

The presence of nominal compounds and chemical purity of the Cu₂S thin films are confirmed by EDS spectra. Fig.5.11 (a) and (b) shows the typical EDS spectra of as -deposited, and air dried Cu₂S thin films. The atomic percentage of Cu and S is very nearly equal to their nominal stoichiometry within the experimental error of $\pm 2\%$. The tall Si peaks noticed in EDS spectra (all the films) was due to the Si glass substrate. The atomic ratio of Cu/S is varied with increasing the bath temperature which is shown in 5.2.1(e) section. In the case of room temperature the atomic ratio of Cu/S is derived to be 2.001 and 2.052 at deposition time 30 min and 50 min respectively, which confirms the formation of stoichiometry Cu₂S film.

Table 5.6 EDS analysis of Cu₂S films deposited at room temperature for 30 min

S.NO	Deposition time (min)	Cu (%)	S (%)	Cu:S
1	30	66.68	33.32	2.001
2	50	67.24	32.76	2.052

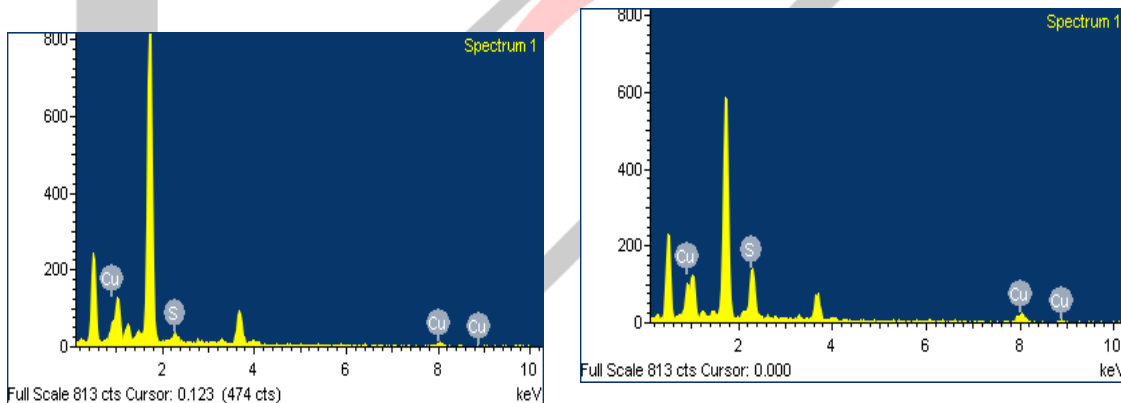


Fig.8: EDS spectrum of Cu₂S thin film at different deposition time.

(a) 30 min (b) 50 min

3. Conclusion

The thickness of the Cu₂S films was greatly increased by increasing the deposition time, and the crystallinity of the films was improved. However, the thickness was decreased as deposition time increased due to peeling off. With increasing the deposition time the film band gap is also reduced from 1.85 eV to 1.81 eV. XRD analyses showed that the deposited films have hexagonal crystalline structure. The deposition time and temperature played a significant role in the structural and optical properties of the Cu₂S films.

References

- [1] Ghosh, C., Verma, B. P., *Thin Solid Films.*, 60, 619(1979).
- [2] Nayak, B. B., Acharya, H. N., Chaudhari, T. K., Mitra, G. B., *Thin Solid Films.*, , 92, 309(1982).
- [3] Pavaskar, N. R., Menzes, C. A., Sinha, A. P. B., *J. Electrochem. Soc.*, Vol.124, 743(1977).
- [4] Pawar, S. H., Tamhankar, S., Bhosle, P. N., and Uplane, M. D., *Thin Solid Films.* Vol. 110, 165(1983).
- [5] Pawar, S. H., Bhosale, P. N., *Mater. Chem. Phys.*, Vol. 11, 461(1984).
- [6] R. S. Patil, T.P. Gujar, C.D. Lokhande, R.S.Mane, Sung-Hwan Han, *Journal of non-crystalline Solids*, 353(2007).
- [7] A. E. Pop, V. Popescu, M. Danila, M. N. Batin, "Chalcogenide Letters", Vol. 8, 363(2011).
- [8] J.J. Loferski, J. Shewchun, S.D. Mittleman, A.E. De Meo, R. Arnott, H.L. Hwang, R. Beaulieu, G. Chapman, *Sol. Energy Mater.* 157(1979).
- [9] M. Savelli, J. Bougnot, H. Luquet, M. Perotin, O. Maris, C. Gril, *Solar Cells*, Vol. 5, 213(1982).
- [10] K. Okamoto, S. Kawai, *J. Appl. Phys.*, Vol. 12, 1130(1973).
- [11] S. Couve, L. Gousskov, L. Szepessy, J. Vedel, E. Castel, *Thin Solid Films*, Vol. 15, 223(1973).
- [12] L. Isac, A. Duta, A. Kriza, S. Manolache, M. Nanu, *Thin Solid Films*, Vol. 515, 5755(2007).
- [13] X. B. He, A. Polity, D. I. Osterreicher, D. Pfisterer, R. Gregor, B. K. Meyer and M. Hard, *Physica B: Condensed Matter*, Vol.308, 1069(2001).
- [14] Y.-J. Wang, A.-T. Tsai, C.-S. Yang, *Mater. Lett.*, Vol. 63, 847(2009).
- [15] S. Schneider, J.R. Ireland, M.C. Hersam, T.J. Marks, *Chem. Mater.*, Vol. 19, 2780(2007).
- [16] S.V. Bagul, S.D. Chavhan, R. Sharma, *J. Phys. Chem. Solids*, Vol. 68, 1623(2007).
- [17] S.G. Chen, Y.F. Huang, Y.Q. Liu, Q. Xia, H.W. Liao, C.G. Long, *Mater Lett.*, Vol. 62, 2503(2008).
- [18] S. Bini, K. Bindu, M. Lakshmi, C. SudhaKantha, K.P. Vijayakumar, Y. Kashiwaba, T. Abe, *Renewable Energy* , Vol. 20, 405(2000).
- [19] C.G. Munce, G.K. Parker, S.A. Holt, G.A. Hope, *A. Colloids Surf.*, Vol. 295, 152(2007).
- [20] E. Fatas, T. Garcia, C. Montemayor, A. Medina, E. Garcia Camarero, F. Arjona, *Mater. Chem. Phys.*, Vol. 12, 121(1985).
- [21] MudiXin, KunWei Li, Hao Wang, *Applied Surface Science*, Vol. 15, 1436(2009).

