



Preparation of thin films of copper sulfide by chemical bath deposition

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Abstract

CuS thin films were deposited onto microscope glass slide by chemical bath deposition method. Recently, chemical bath deposition method became very popular method due to some advantages such as simple, low cost, ability to cover large substrate areas and can operate at low processing temperature. In this study, aqueous solutions of copper sulphate, thiourea and tartaric acid have been used as precursors during deposition process. In this experiment, the solution concentration was varied from 0.05 to 0.2 M in order to investigate the optimum conditions for the preparation of CuS thin films. The structural, morphological, compositional and optical characterization of the films were carried out by X-ray diffraction, scanning electron microscopy, energy dispersive analysis X-ray and UV-Visible spectrophotometer, respectively. The X-ray diffraction analysis showed the polycrystalline in nature with hexagonal crystal. The dense morphology of CuS films with homogeneous grains could be observed for the films deposited using 0.2 M of solution concentration. These films also exhibited higher absorption value as compared with other solution concentrations.

Key-Words: Chemical bath deposition, Copper sulphide, Thin films, Solution concentrations

Introduction

In search of new semiconducting materials for solar energy conversion through photoelectrochemical cells, metal chalcogenide thin films are increasingly studied. Thin films have been prepared by various techniques such as spray pyrolysis¹, pulsed laser deposition², vacuum evaporation³, electrodeposition method⁴, electron beam evaporation⁵, chemical bath deposition⁶ and SILAR method⁷. Here, chemical bath deposition method was used for the deposition of copper sulphide thin films due to some advantages such as low material cost, low temperature and convenient for larger area deposition of thin films. So far, a number of thin films such as CdSe⁸, ZnS⁹, PbS¹⁰, NiS¹¹, Bi₂S₃¹², ZnIn₂Se₄¹³, Pb_{1-x}Fe_xS¹⁴, CdS_{1-x}Se_x¹⁵ and Zn_xCd_{1-x}S¹⁶ prepared using chemical bath deposition method have been reported by many researchers.

In the present work, we report the chemical bath deposition of CuS films from acidic solutions. The influence of solution concentration (0.05, 0.1 and 0.2 M) on the films is investigated for the first time for the deposition of CuS thin films in the presence of tartaric acid as complexing agent. The results of the investigation on structural, morphological, compositional and optical properties of CuS thin films have been carried out by using XRD, SEM, EDAX and UV-Vis techniques, respectively.

Material and methods

All the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionised water (Alpha-Q Millipore). The copper sulphide thin films were prepared from an acidic bath using aqueous solutions of copper sulphate (CuSO₄) and thiourea (CS(NH₂)₂) acted as a source of Cu²⁺ and S²⁻ ions, respectively. The tartaric acid was used as complexing agent during the deposition process. The microscope glass slides were used as the substrate for the chemical bath deposition of CuS thin film. Before deposition, the glass substrates were degreased with ethanol for 10 min. Then, ultrasonically cleaned with

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distilled water for another 10 min and dried in desiccators. Deposition of CuS thin films was carried out at 80 °C by using following procedure: 25 mL of copper sulphate was complexed with 25 mL of tartaric acid in beaker. Then, 25 mL of thiourea was mixed in it with constant stirring. The pH was adjusted to 3 by addition of hydrochloric acid with constant stirring using pH meter. The cleaned glass substrate was immersed vertically into beaker. The deposition process was carried out at different solution concentrations (0.05, 0.1 and 0.2 M) in order to determine the optimum conditions for the deposition of CuS thin films. After the completion of deposition (100 minutes), the films were washed with distilled water and kept for analysis.

The X-ray diffraction data were obtained by means of Philips PM 11730 diffractometer using $\text{CuK}\alpha$ ($\lambda=1.5418 \text{ \AA}$) radiation source. Data were collected by step scanning from 25° to 50° with a step size of 0.05° (2 θ). Surface morphology was studied by JEOL (JSM-6400) scanning electron microscopy operating at an accelerating voltage of 20 kV under 1000 X magnification. The elemental composition of the films was studied by scanning electron microscope attached with energy dispersive analysis of X-ray (EDAX) analyzer. The optical properties of the film were measured with a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The data were recorded from 300 to 800 nm with an uncoated glass as a reference.

Results and Conclusion

The aim of this study to prepare copper sulfide thin films using chemical bath deposition method. The deposition process was carried out at different solution concentrations (0.05, 0.1 and 0.2 M) in order to determine the optimum conditions for the deposition of CuS thin films. Structural characterization of the thin films was carried out using X-ray diffraction (XRD) technique. Figure 1 shows the X-ray diffraction patterns of copper sulfide thin films deposited under different solution concentrations. The films prepared using 0.05 M and 0.1 M of copper sulphate, thiourea and tartaric acid show two peaks at $2\theta=27.7^\circ$ and 35.3° correspond to (101) and (104) planes, respectively. Meanwhile, for the films deposited using 0.2 M of copper sulphate, thiourea and tartaric acid, all the intensities are increased accompanying with an increase in (105) and (107) peaks. The observed d-spacing values which coincide well with the JCPDS17 (Reference code: 00-065-3928) data. Therefore, it has been concluded that the deposited CuS thin films are polycrystalline in nature with hexagonal structure ($a=3.768 \text{ \AA}$, $b=3.768 \text{ \AA}$, $c=16.27 \text{ \AA}$). The presence of the hexagonal structure has been already reported for

the CuS thin films prepared using spray pyrolysis technique¹⁸ and SILAR method¹⁹.

The scanning electron micrographs (SEM) of the CuS films prepared at different solution concentrations are shown in Figure 2. We can see that the morphologies of films show a clear dependence on the solution concentration. The films prepared using lower concentration (0.05 M and 0.1 M) reveal incomplete coverage of the substrate surface and the grains are not distributed uniformly over the substrate. However, the films obtained using higher concentration (0.2 M), the grains coalescence take place. It is observed that all of these films have a homogeneous and uniform surface. The SEM micrograph (Figure 2c) shows that the substrate is covered completely indicating more nucleation sites have formed and the number of grains has increased. The size of each granule does not differ from each other, varying from 3-5 μm . On the other hand, the grain size increases as the solution concentration increases from 0.05 M to 0.2 M accordingly to SEM micrographs. The increase in grain size in the films with increase in solution concentration is clearly exhibited by the sharp intense peaks in the X-ray diffraction patterns.

The compositional analysis of the thin films is investigated by energy dispersive analysis of X-ray (EDAX) technique. The quantitative elemental analysis is carried out only for Cu and S. The Table 1 shows the ratio of Cu to S obtained from the EDAX analysis. It is observed that the atomic percentage of the thin films is altered as the thin films are prepared at different solution concentrations. For the thin films prepared using 0.05 M and 0.1 M of copper sulphate, thiourea and tartaric acid, the Cu:S ratio is 0.81 and 0.91, respectively. When the ratio close to 1, improved in grain size is observed for the films deposited using 0.2 M. This might be due to the better orientation of grains in the films under these experimental conditions. Therefore, the solution concentration has significant influence on the composition of the deposited films.

Figure 3 shows the absorbance spectra of CuS thin films prepared at various solution concentrations. The spectra clearly indicate that lower wavelengths correspond to maximum absorption compared to higher wavelengths. The absorbance of the films produced in the visible region indicating the possibility of these materials to be used in the photoelectrochemical cells. The films deposited using 0.2 M of copper sulphate, thiourea and tartaric acid produced the largest absorption value (Figure 3c) as compared with other solution concentrations. This response associated with the formation of regular grain sizes which normally related the higher surface area. This observation is

consistent with the results from scanning electron micrographs as shown in Figure 2c.

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References

1. Badera N., Godbole B., Srivastava S.B., Vishwakarma P.N., Chandra L.S.S., Jain D., Sathe V.G. and Ganesan V. (2008). Photoconductivity in $Cd_{1-x}Mn_xS$ thin films prepared by spray pyrolysis technique. *Solar Energy Materials and Solar Cells*, **92**: 1646-1651.
2. Shen Y., Xu N., Hu W., Xu X., Sun J., Ying Z. and Wu J. (2008). Bismuth doped ZnSe films fabricated on silicon substrates by pulsed laser deposition. *Solid-State Electronics*, **52**: 1833-1836.
3. Murali K.R., Srinivasan K. and Trivedi D.C. (2004). Structural and photoelectrochemical properties of CdSe thin films deposited by the vacuum evaporation technique. *Material Science and Engineering, B*, **111**: 1-4.
4. Moses E.R., Delphine A.S.M., Sanjeeviraja C. and Jayachandran M. (2010). Growth of ZnSe thin layers on different substrates and their structural consequences with bath temperature. *Physica B: Condensed Matter*, **405**: 2485-2491.
5. Ahamed M.G., Basheer S., Balu A.R., Nagarethiam V.S., Thayumanavan A., Murali K.R., Sanjeeviraja C. and Jayachandran M. (2010). Structural, optical and electrical properties of electron beam evaporated CdSe thin films. *Crystal Research and Technology*, **45**: 387-392.
6. Ezema F.I., Ekwealor A.B.C., Asogwa P.U., Ugwuoke P.E., Chigbo C. and Osuji R.U. (2007). Optical properties and structural characterizations of Sb_2S_3 thin films deposited by chemical bath deposition technique. *Turkish Journal of Physics*, **31**: 205-210.
7. Pathan H.M., Salunkhe P.V., Sankapal B.R. and Lokhande C.D. (2001). Photoelectrochemical investigation of Ag_2S thin films deposited by SILAR method. *Materials Chemistry and Physics*, **72**: 105-108.
8. Gopakumar N., Anjana P. and Vidyadharan P.P. (2010). Chemical bath deposition and characterization of CdSe thin films for optoelectronic applications. *Journal of Materials Science*, **45**: 6653-6656.
9. Anuar K., Nani R. and Ho S.M. (2011). Atomic force microscopy studies of zinc sulphide thin films. *International Journal of Advanced Engineering Sciences and Technologies*, **7**: 169-172.
10. Raniero L., Ferreira C.L., Cruz L.R., Pinto A.L. and Alves R.M.P. (2010). Photoconductivity activation in PbS thin films grown at room temperature by chemical bath deposition. *Physica B: Condensed Matter*, **405**: 1283-1286.
11. Anuar K., Ho S.M., Ngai C.F. and Saravanan N. (2010). XRD and SEM investigation of the influence of pH and bath temperature on nickel sulphide thin films. *SIGMA*, **13**: 99-105.
12. Ubale A.U. (2010). Effect of complexing agent on growth process and properties of nanostructured Bi_2S_3 thin films deposited by chemical bath deposition method. *Materials Chemistry and Physics*, **121**: 555-560.
13. Babu P., Reddy M.V., Revathi N. and Reddy K.T.R. (2011). Effect of pH on the physical properties of $ZnIn_2Se_4$ thin films grown by chemical bath deposition. *Journal of Nano and Electronic Physics*, **3**: 85-91.
14. Joshi R.K., Subbaraju G.V., Sharma R. and Sehgal H.K. (2004). $Pb_{1-x}Fe_xS$ nanoparticle films grown from acidic chemical bath. *Applied Surface Science*, **239**: 1-4.
15. Chaudhari J.B., Deshpande N.G., Gudage Y.G., Ghosh A., Huse V.B. and Sharma R. (2008). Studies on growth and characterization of ternary $CdS_{1-x}Se_x$ alloy thin films deposited by chemical bath deposition technique. *Applied Surface Science*, **254**: 6810-6816.
16. Song W.C. and Lee J.H. (2009). Growth and characterization of $Zn_xCd_{1-x}S$ films prepared by using chemical bath deposition for photovoltaic devices. *The Journal of the Korean Physical Society*, **54**: 1660-1665.
17. Takeuchi Y., Kudoh Y. and Sato G. (1985). The crystal structure of covellite CuS under high pressure up to 33kbar. *Zeitschrift fur Kristallographie*, **173**: 119-128.
18. Isac L., Duta A., Kriza A., Manolache S. and Nanu M. (2007). Copper sulfides obtained by spray pyrolysis-possible absorbers in solid-state solar cells. *Thin Solid Films*, **515**: 5755-5758.

19. Ali Yildirim M., Ates A. and Astam A. (2009). Annealing and light effect on structural, optical and electrical properties of

CuS, CuZnS and ZnS thin films grown by the SILAR method. *Physica E: Low-dimensional Systems and Nanostructures*, **41**, 1365-1372.

Table 1: Compositional analysis of CuS thin films deposited at various solution concentrations

	Copper (Atomic %)	Sulfur (Atomic %)	Cu:S ratio
0.05 M	44.68	55.32	0.81
0.1 M	47.65	52.35	0.91
0.2 M	48.38	51.62	0.94

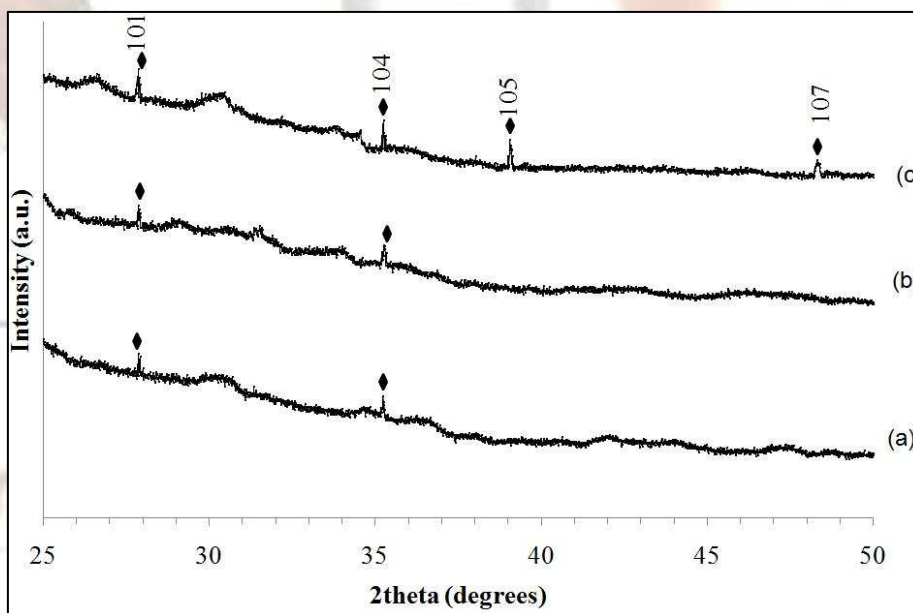


Fig. 1: X-ray diffraction patterns of CuS thin films deposited at different solution concentrations (a) 0.05 M (b) 0.1 M (c) 0.2 M (CuS)

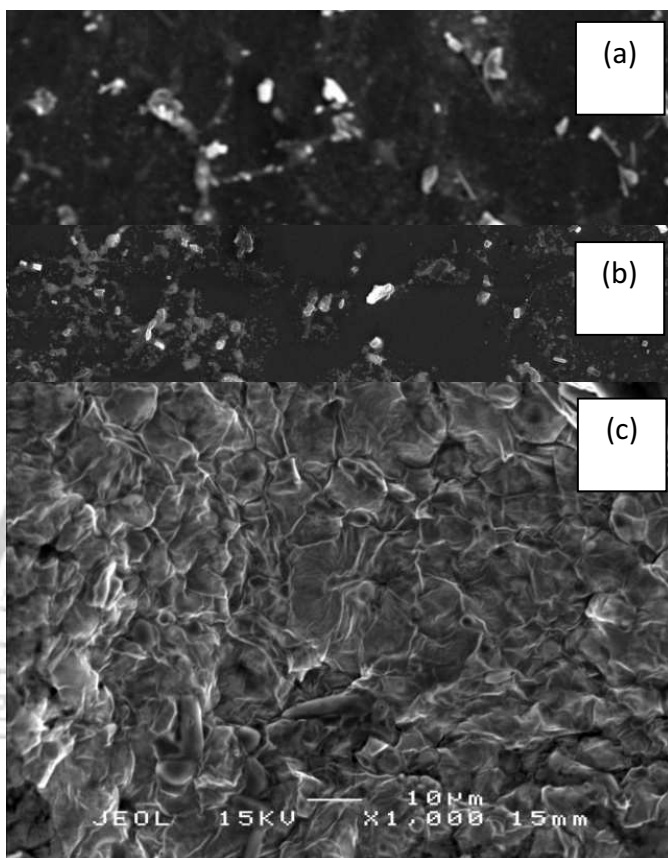


Fig. 2: Scanning electron micrographs of CuS thin films deposited at different solution concentrations (a) 0.05 M (b) 0.1 M (c) 0.2 M

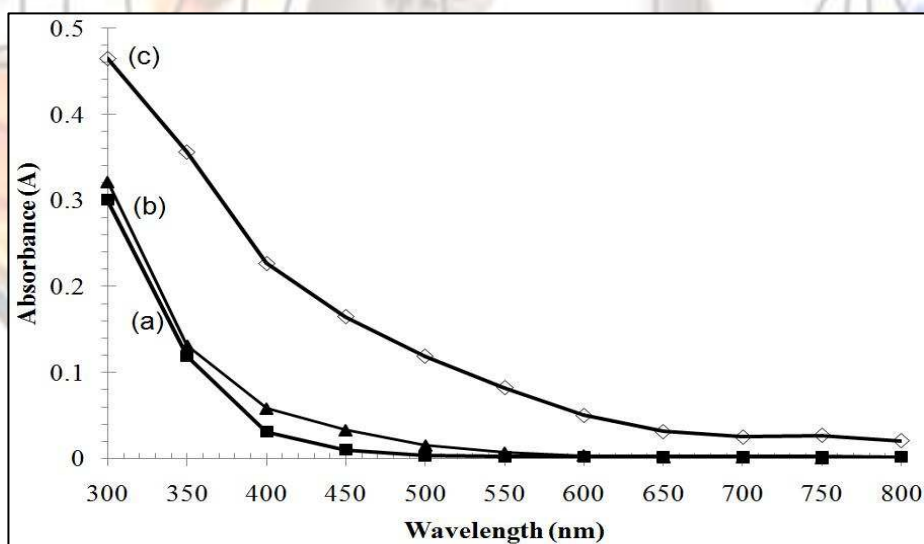


Fig. 3: Absorbance versus wavelength spectra of CuS thin films deposited at different solution concentrations (a) 0.05 M (b) 0.1 M (c) 0.2 M