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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 pyrolysis[1], pulsed laser deposition[2], vacuum evaporation[3], electrodeposition method[4], electron beam evaporation[5], chemical bath deposition[6] and SILAR method[7]. 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 CdSe[8], ZnS[9], PbS[10], NiS[11], Bi_2S_3[12], $ZnIn_2Se_4$[13], $Pb_{1-x}Fe_xS$[14], $CdS_{1-x}Se_x$[15] and $Zn_xCd_{1-x}S$[16] prepared using chemical bath deposition method have been reported by many researchers.

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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 ($CuSO_4$) and thiourea ($CS(NH_2)_2$) acted as a source of Cu^{2+} and S^{2-} 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

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 CuK_α (λ=1.5418 Å) radiation source. Data were collected by step scanning from 25° to 50° with a step size of 0.05° (2θ). 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 2θ=27.7° 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 Å, b=3.768 Å, c=16.27 Å). The presence of the hexagonal structure has been already reported for the CuS thin films prepared using spray pyrolysis technique[18] 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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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

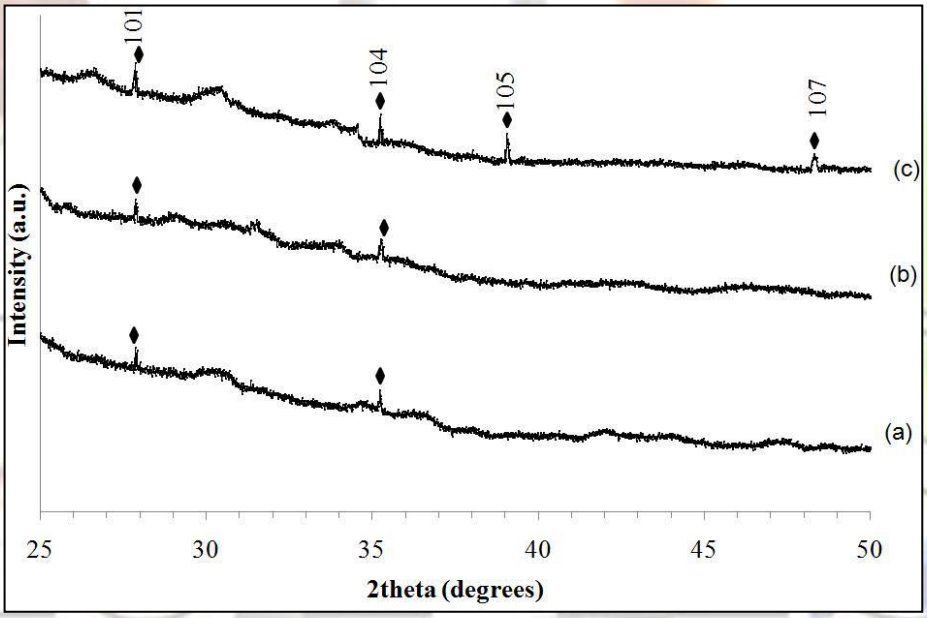

Fig. 1: X-ray diffraction patterns of CuS thin films deposited at different solution concentrations (a) 0.05 M (b) 0.1 M (c) 0.2 M (CuS)

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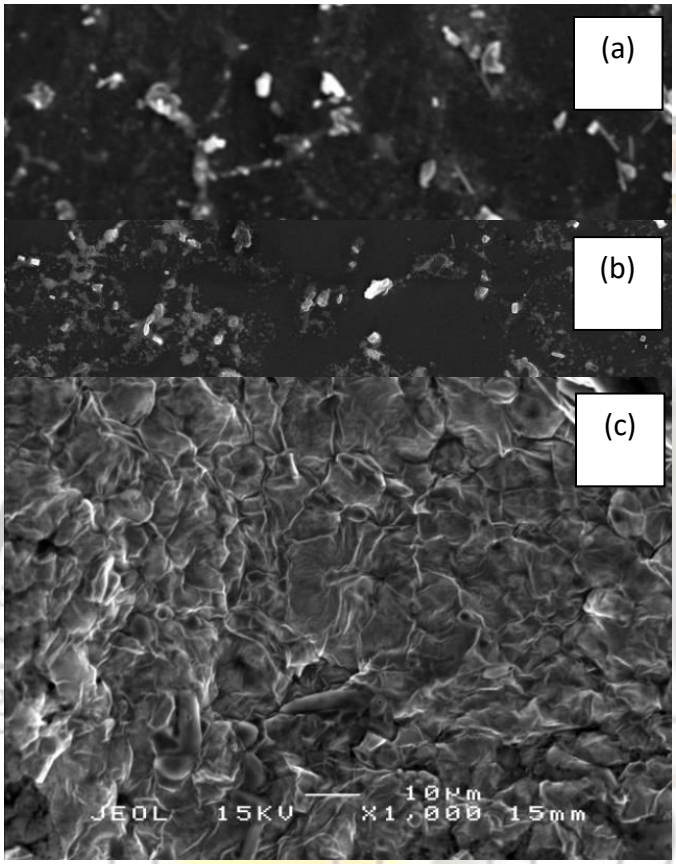

Fig. 2: Scanning electron micrographs of CuS thin films deposited at different solution concentrations (a) 0.05 M (b) 0.1 M (c) 0.2 M

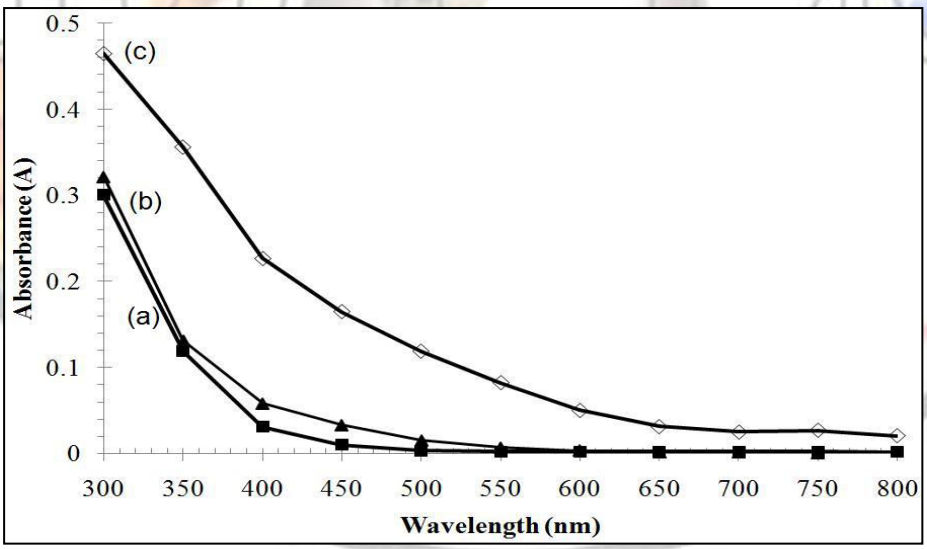

Fig. 3: Absorbance versus wavelength spectra of CuS thin films deposited at different solution concentrations (a) 0.05 M (b) 0.1 M (c) 0.2 M