

Effects of Electrolytes Concentration on The Chemically Deposited Cu_4SnS_4 Thin Films

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Cu_4SnS_4 thin films have been deposited on indium tin oxide glass substrates from aqueous acidic bath using chemical bath deposition. The disodium ethylenediaminetetraacetic acid was used as a complexing agent. Deposition at different concentrations was attempted in order to study the effect of electrolytes concentration on the film properties and to get good quality photosensitive materials. The structure and surface morphology of films were studied by X-ray diffraction and atomic force microscopy. The optical properties were measured to determine transition type and band gap value. The X-ray diffraction analysis showed the presence of polycrystalline in nature. Also, the films exhibited orthorhombic structure with a sharp (221) plane. The films prepared using higher concentration showed better photosensitivity compared with lower concentration. The AFM images of these films showed the surface of substrate was covered completely. Optical absorption shows the presence of direct transition with band gap energy of 1.7 eV.

Key Words: Bandgap energy, Semiconducting material, Chemical bath deposition, Solar cells, Thin films.

INTRODUCTION

Thin films have attracted much interest due to their varied applications such as solar cells, optoelectronic devices, laser materials and thermoelectric devices. Recently, ternary compounds have received much attention in the field of solar cells owing to their interesting properties of band gap. There are many methods for preparing thin films such as chemical bath deposition¹, vacuum evaporation², electrodeposition³, molecular beam epitaxy⁴, close spaced sublimation⁵, thermal evaporation⁶, spray pyrolysis⁷, sputter deposition⁸, metal organic chemical vapour deposition⁹ and plasma-enhanced chemical vapour deposition¹⁰. Chemical bath deposition is a relatively inexpensive, simple and convenient method for large area deposition and a variety of substrates can be used to grow thin films. It does not require complicated instrumen-

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tation. The thin film materials prepared by chemical bath deposition such as CdS¹¹, SnSe¹², MnS¹³, Sb₂S₃¹⁴, ZnSe¹⁵, PbSe¹⁶, CuInSe₂¹⁷, Cd_{0.5}Zn_{0.5}Se¹⁸ and CuBiS₂¹⁹ have been reported.

In the present study, we describe chemical bath deposition technique for the deposition of Cu₄SnS₄ thin films from aqueous solution containing CuSO₄, SnCl₂ and Na₂S₂O₃. The effect of the electrolytes concentration on the film properties was investigated. The films have been characterized by X-ray diffraction for structure determination, atomic force microscope for surface morphology study and UV-visible spectrophotometer for optical absorption properties study.

EXPERIMENTAL

Preparation of films: All the chemicals used for the deposition were analytical grade. It includes copper sulfate, tin chloride, sodium thiosulfate, disodium ethylene diaminetetraacetic acid (Na₂EDTA) and hydrochloric acid. All the solutions were prepared in deionized water (Alpha-Q Millipore). The indium doped tin oxide glass was used as the substrate. The ultrasonically cleaned glass substrate was immersed vertically into chemical bath. The disodium ethylenediaminetetraacetic acid was used to chelate with Cu²⁺ and Sn²⁺ to obtain Cu-EDTA and Sn-EDTA solutions. The chemical bath comprised of Cu-EDTA, Sn-EDTA and sodium thiosulfate solutions. In order to investigate the effect of electrolytes concentration on the film properties, deposition at various concentrations was carried out. The first set of experiment was carried out using constant concentration of 0.05 M of CuSO₄, SnCl₂ and varying concentrations of Na₂S₂O₃ (0.01 and 0.05 M) solutions. The second set of experiment was carried out using fixed concentration of 0.05 M of CuSO₄, Na₂S₂O₃ and varying concentrations of SnCl₂ (0.01 and 0.05 M) solutions. The third set of experiment was carried out using constant concentration of 0.05 M of SnCl₂, Na₂S₂O₃ and varying concentrations of CuSO₄ (0.01 and 0.05 M) solutions. The pH was adjusted to 1.5 using HCl. The deposition was carried out at 50 °C for 2 h. After the deposition, the films were washed with distilled water and kept for analysis.

Characterization of films: X-Ray diffraction analysis was carried out, using a Philips PM 11730 diffractometer for the 2θ ranging from 20° to 60° with CuK_α (λ = 1.5418 Å) radiation. An atomic force microscopy study was done using Q-Scope 250 provided by Quesant Instrument Corporation. Optical absorption study was carried out using the Perkin-Elmer UV/Vis Lambda 20 spectrophotometer. The film-coated indium doped tin oxide glass was placed across the sample radiation pathway while the uncoated ITO glass was put across the reference path. The absorption data were manipulated for the determination of the band gap energy.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the films deposited at various CuSO₄ concentrations (0.01 and 0.05 M) and constant Na₂S₂O₃, SnCl₂ at 0.05 M. The film prepared using 0.01 M CuSO₄ showed three peaks at 2θ = 30.1°, 35.3° and 50.5° corres-

ponding to interplanar distances of 2.96, 2.54 and 1.80 Å, respectively. These peaks are in good agreement with the JCPDS data (Reference code: 010710129) for Cu_4SnS_4 ($a = 13.5580$ Å, $b = 7.6810$ Å, $c = 6.4120$ Å, $\alpha = \beta = \gamma = 90^\circ$). As the concentration of CuSO_4 was increased to 0.05 M, the intensity of peak corresponding to (221) plane increased. Also, the additional peak corresponding to 2.67 Å at $2\theta = 33.2^\circ$ was obtained.

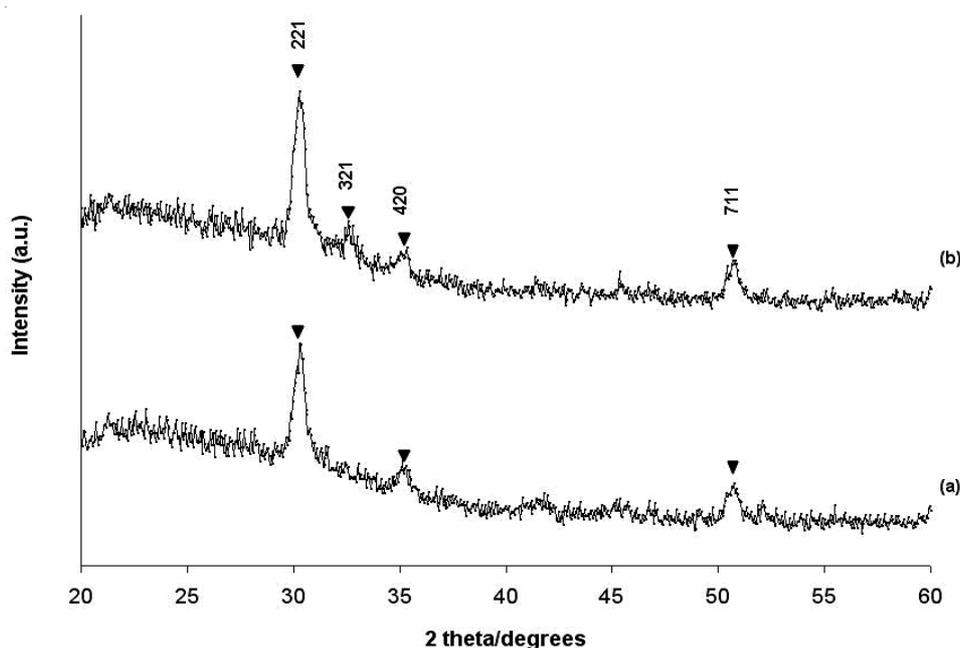


Fig. 1. XRD patterns of samples prepared at various CuSO_4 concentrations: [a] 0.01 M [b] 0.05 M. Concentration of SnCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ are fixed at 0.05 M. [Cu_4SnS_4 (▼)]

Fig. 2 shows the XRD patterns of the films deposited at various SnCl_2 concentrations (0.01 and 0.05 M) and fixed $\text{Na}_2\text{S}_2\text{O}_3$, CuSO_4 at 0.05 M. Each pattern contains several diffraction peaks indicating that the films are polycrystalline in nature. There are three Cu_4SnS_4 peaks at $2\theta = 30.1^\circ$, 35.1° and 50.5° for the sample prepared at lower concentration of SnCl_2 (0.01 M). The corresponding interplanar distances are well in agreement with the JCPDS data of 2.96, 2.55 and 1.80 Å. When the concentration of SnCl_2 was increased to 0.05 M, the intensity of (221) plane increased. This is accompanied by the appearance of two other peaks of Cu_4SnS_4 at $2\theta = 28.6^\circ$ and 46.4° with interplanar distances of 3.14 and 1.95 Å.

Fig. 3 shows the XRD patterns of the films deposited at various $\text{Na}_2\text{S}_2\text{O}_3$ concentrations (0.01 M and 0.05 M) with constant CuSO_4 , SnCl_2 at 0.05 M. There are five Cu_4SnS_4 peaks at $2\theta = 26.5^\circ$, 30.1° , 33.1° , 35.1° and 50.7° , corresponding to d-spacing

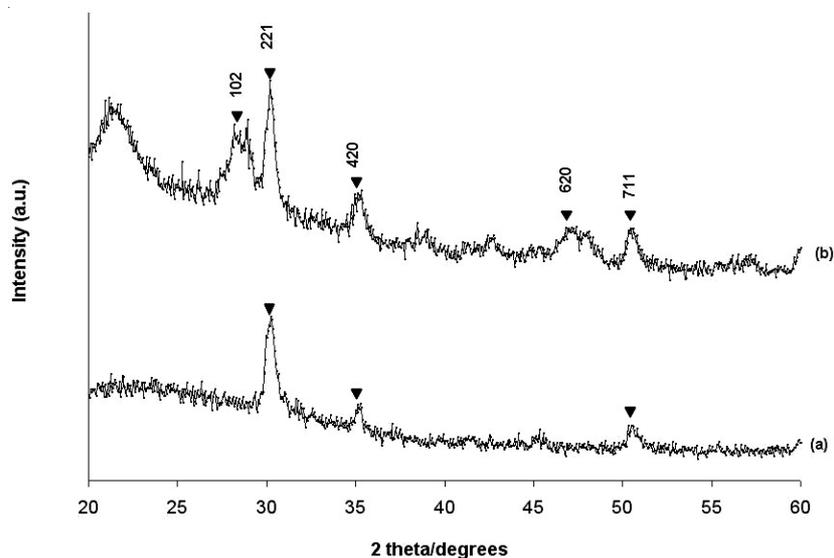


Fig. 2. XRD patterns of samples prepared at various SnCl_2 concentrations: [a] 0.01 M [b] 0.05 M. Concentration of CuSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ are fixed at 0.05 M [Cu_4SnS_4 (\blacktriangledown)]

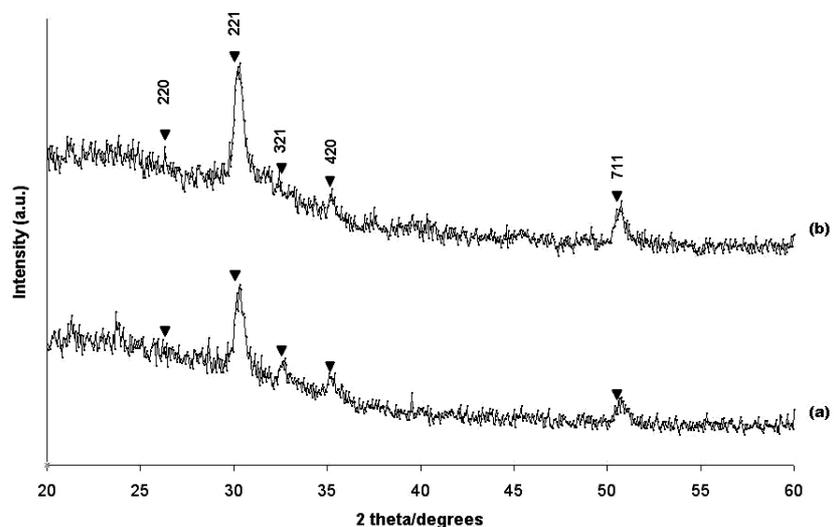


Fig. 3. XRD patterns of samples prepared at various $\text{Na}_2\text{S}_2\text{O}_3$ concentrations: [a] 0.01 M [b] 0.05 M. Concentration of CuSO_4 and SnCl_2 are fixed at 0.05 M [Cu_4SnS_4 (\blacktriangledown)]

values 3.36, 2.96, 2.68, 2.55 and 1.79 Å for the samples prepared at 0.01 M and 0.05 M of $\text{Na}_2\text{S}_2\text{O}_3$. Comparison between the films deposited at 0.01 and 0.05 M of $\text{Na}_2\text{S}_2\text{O}_3$ showed that the intensity of the peaks increased indicating greater crystallinity as the concentration was increased. This could be seen in the (221) plane which is more intense.

Fig. 4 shows the AFM images of films prepared at different CuSO_4 concentrations (0.01 M and 0.05 M) and constant SnCl_2 , $\text{Na}_2\text{S}_2\text{O}_3$ at 0.05 M. The film prepared using 0.01 M CuSO_4 showed low appearance of grains over the substrate. The size of the grains varies from one another and randomly distributed over ITO substrate. However, the film prepared using 0.05 M CuSO_4 indicated better morphology compared to the lower concentration. The grain size of these films was much bigger and has complete coverage over the substrate surface. This result is consistent with the observation from XRD.

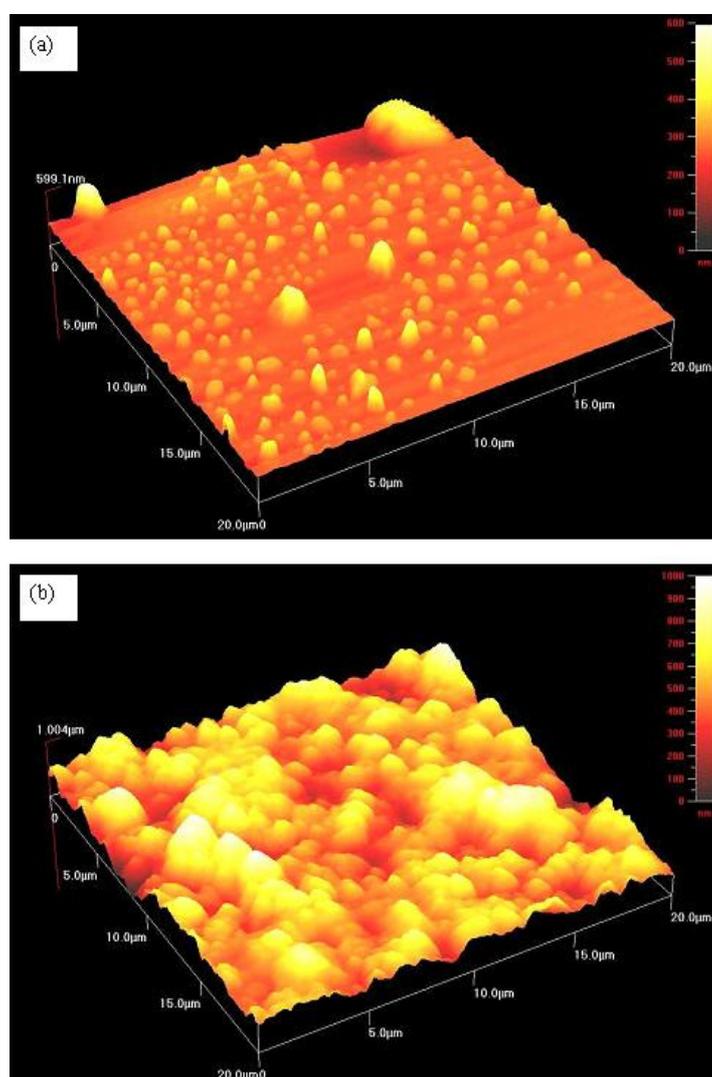


Fig. 4. Atomic force microscopy images of Cu_4SnS_4 films deposited at various CuSO_4 concentrations: [a] 0.01 M [b] 0.05 M. Concentration of $\text{Na}_2\text{S}_2\text{O}_3$ and SnCl_2 are fixed at 0.05 M

Fig. 5 shows the AFM images of films prepared at different SnCl_2 concentrations (0.01 M and 0.05 M) and constant $\text{Na}_2\text{S}_2\text{O}_3$, CuSO_4 at 0.05 M. The AFM image of film prepared using 0.01 M SnCl_2 showed the surface of substrate was not covered completely. This observation suggests an incomplete nucleation step with irregular growth rate of the grains. However, there seems increase in the number of grains for the film deposited at 0.05 M SnCl_2 . The surface of the ITO glass substrate was covered completely as can be seen in Fig. 5b.

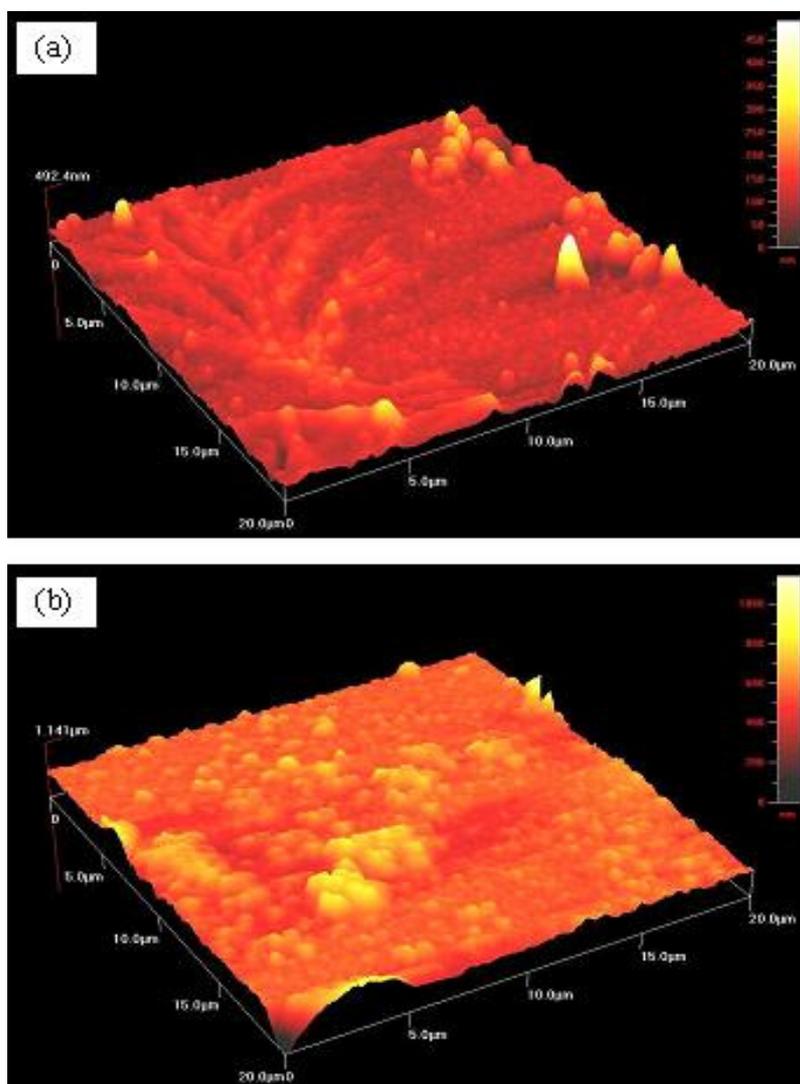


Fig. 5. Atomic force microscopy images of Cu_4SnS_4 films deposited at various SnCl_2 concentrations: [a] 0.01 M [b] 0.05 M. Concentration of $\text{Na}_2\text{S}_2\text{O}_3$ and CuSO_4 are fixed at 0.05 M

Fig. 6 shows the AFM images of films prepared at different $\text{Na}_2\text{S}_2\text{O}_3$ concentrations (0.01 and 0.05 M) and constant SnCl_2 , CuSO_4 at 0.05 M. The images pointed out that the deposits are crystalline and their grain size varies with the variation of $\text{Na}_2\text{S}_2\text{O}_3$ concentrations. The sample prepared at 0.01 M of $\text{Na}_2\text{S}_2\text{O}_3$ exhibits smaller crystal size (Fig. 6a) while sample prepared at 0.05 M of $\text{Na}_2\text{S}_2\text{O}_3$ leads to bigger crystal size (Fig. 6b). The sample prepared at higher concentration showed the surface of the substrate was covered completely. The size of the grains varied from 1 to 2 μm . The improvement of crystallinity of the film is consistent with the results of XRD.

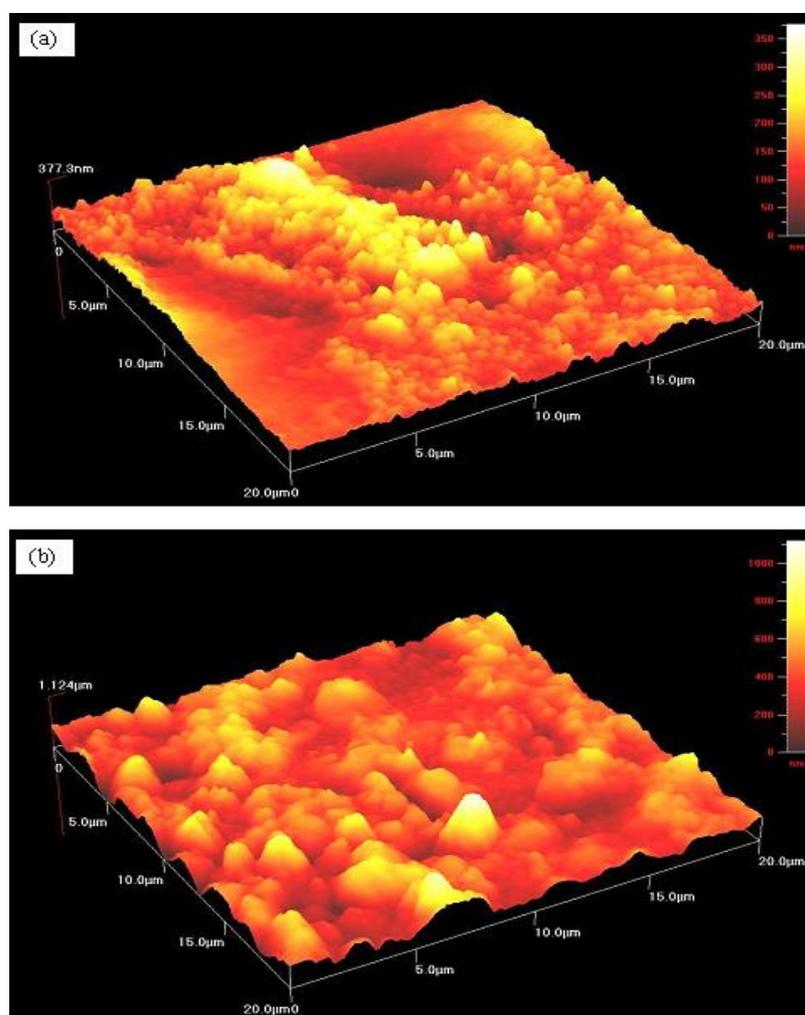


Fig. 6. Atomic force microscopy images of Cu_4SnS_4 films deposited at various $\text{Na}_2\text{S}_2\text{O}_3$ concentrations: [a] 0.01 M [b] 0.05 M. Concentration of SnCl_2 and CuSO_4 are fixed at 0.05 M

Figs. 7-9 show the photoresponse of the films prepared using different concentrations of CuSO_4 , SnCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$, respectively. The current change with the illumination confirms that the films possess semiconducting behaviour. The films prepared using higher concentration (Figs. 7b, 8b and 9b) showed better photosensitivity compared with lower concentration (Figs. 7a, 8a and 9a). This is probably due to the improved crystal compactness or density of the deposit. The fact that the photocurrent occurs on the negative potential indicates the films prepared are *p*-type semiconductor.

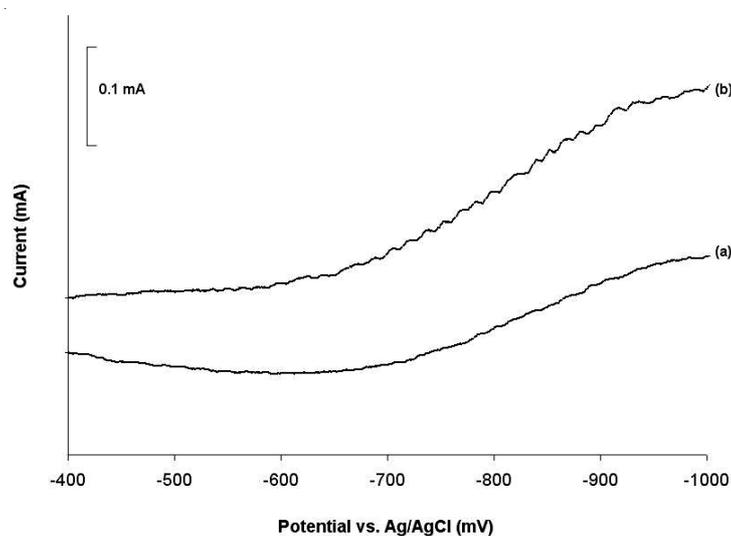


Fig. 7. Photoresponse of the Cu_4SnS_4 films deposited at various CuSO_4 concentrations ([a] 0.01 M and [b] 0.05 M). Concentration of SnCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ are fixed at 0.05 M

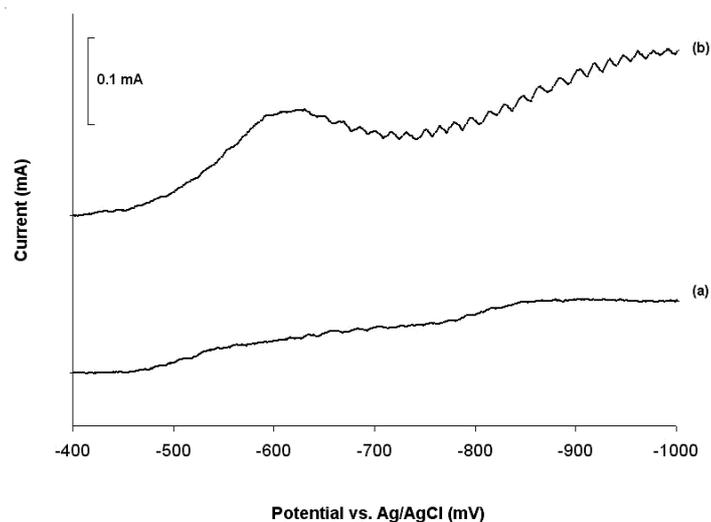


Fig. 8. Photoresponse of the Cu_4SnS_4 films deposited at various SnCl_2 concentrations ([a] 0.01 M and [b] 0.05 M). Concentration of CuSO_4 and $\text{Na}_2\text{S}_2\text{O}_3$ are fixed at 0.05 M

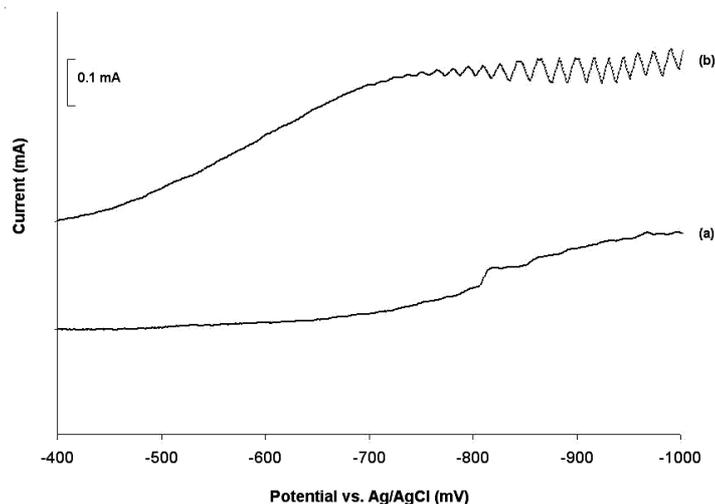


Fig. 9. Photo-response of the Cu_4SnS_4 films deposited at various $\text{Na}_2\text{S}_2\text{O}_3$ concentrations ([a] 0.01 M and [b] 0.05 M). Concentration of SnCl_2 and CuSO_4 are fixed at 0.05 M

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance *versus* wavelength with Stern relationship of near-edge absorption:

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

where ν is the frequency, h is the Planck's constant, k equals a constant while n carries the value of either 1 or 4. The value of n is 1 and 4 for the direct transition and indirect transition, respectively. The band gap, E_g , could be obtained from a straight line plot of $(A h\nu)^{2/n}$ as a function of $h\nu$. Extrapolation of the line to the base line, where the value of $(A h\nu)^{2/n}$ is zero, will give E_g . The $(A h\nu)^{1/2}$ *versus* $h\nu$ plot is a straight line (Fig. 10) indicating that the energy band gap of Cu_4SnS_4 is direct and intercept on the $h\nu$ axis yield a band gap of 1.7 eV for the film prepared at 0.05 M of $\text{Na}_2\text{S}_2\text{O}_3$, SnCl_2 and CuSO_4 .

Conclusion

The Cu_4SnS_4 thin films have been successfully chemically deposited on an indium tin oxide glass substrate from aqueous solutions containing CuSO_4 , SnCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$. X-Ray diffraction data revealed the formation of polycrystalline Cu_4SnS_4 film with a preferred orientation along the (221) plane. The films prepared using higher concentration show better photosensitivity compared with lower concentration. The AFM images of these films showed the surface of substrate was covered completely. It is also clear that the grain size increases with the increase of electrolytes concentration. The films exhibited *p*-type semiconductor behaviour with band gap energy of 1.7 eV. Deposition at concentration of 0.05 M of CuSO_4 , SnCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ proved to offer a reasonably good Cu_4SnS_4 thin film.

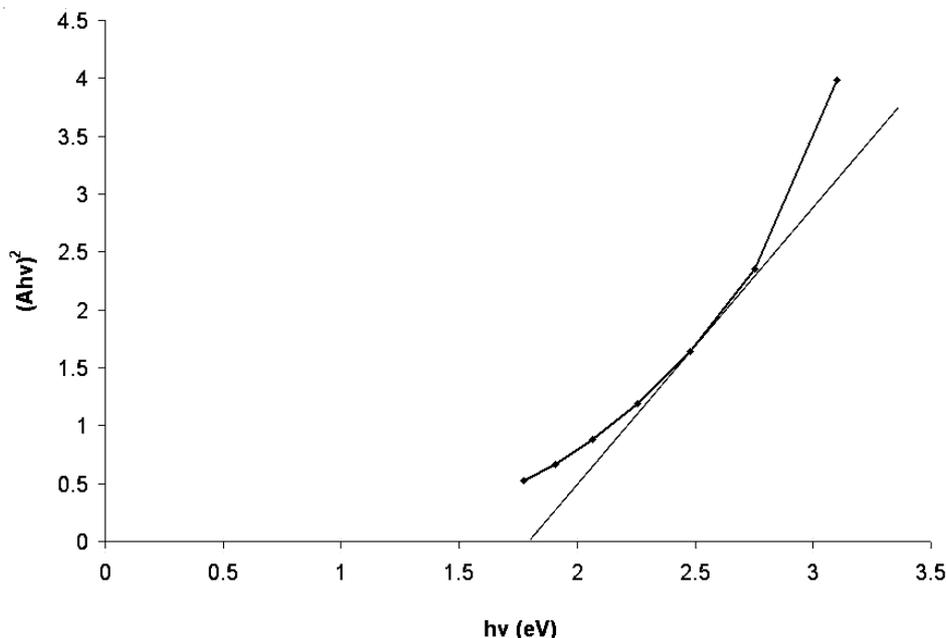


Fig. 10. Plot of $(Ahv)^{2/n}$ versus hv when $n = 4$ for Cu₄SnS₄ films prepared at 0.05 M of Na₂S₂O₃, CuSO₄ and SnCl₂ solutions

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