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Original scientific paper

DEPOSITION AND CHARACTERIZATION OF Cu_4SnS_4 THIN FILMS BY CHEMICAL BATH DEPOSITION METHOD

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A low cost chemical bath deposition method has been used for the preparation of Cu_4SnS_4 thin films onto indium tin oxide glass substrate. The deposition parameters such as bath temperature (50 °C), deposition time (120 min), electrolyte concentration (0.05 M) and bath pH (1.5) were optimized to obtain good quality thin films. The structural, surface morphological and optical properties of thin films were studied by X-ray diffraction, an atomic force microscopy and an UV-Vis Spectrophotometer, respectively. The X-ray diffraction study revealed that the Cu_4SnS_4 films were polycrystalline in nature with the preferential orientation along the (221) plane. The atomic force microscopy results indicated that the films were smooth, uniform and the substrate surface was covered completely at these experimental conditions. These films exhibited *p*-type semiconductor behavior with the band gap energy about 1.57 eV.

Key words: thin film; chemical bath deposition; X-ray diffraction

ДЕПОЗИЦИЈА И КАРАКТЕРИЗАЦИЈА НА ТЕНКИ ФИЛМОВИ ОД Cu_4SnS_4 СО МЕТОД НА ХЕМИСКА ДЕПОЗИЦИЈА

Употребен е евтин метод на хемиска депозиција за добивање тенки филмови од Cu_4SnS_4 врз стаклен супстрат покриен со оксид на индиум и калај. За да се добие добар квалитет на тенките филмови, направена е оптимизација на параметрите на депозиција: температура на бањата (50 °C), време на депозиција (120 min), концентрација на електролитот (0,05 M) и pH на бањата (1,5). Структурните, површинско-морфолошките и оптичките својства на тенките филмови се проучени со рендгенска дифракција, со микроскопија заснована на (меѓу)атомски сили и со УВ-видлива спектрометрија. Истражувањето со рендгенската дифракција покажа дека филмовите од Cu_4SnS_4 се поликристални со преферирана ориентација наддолж (221) рамнината. Резултатите од микроскопијата заснована на (меѓу)атомски сили покажуваат постоење на рамни (мазни) и униформни филмови, како и целосно прекриена површина на супстратот при споменатите експериментални услови. Добиените филмови покажуваат *p*-тип на полуспроводничко однесување со енергетска ширина на забранетата зона од околу 1,57 eV.

Клучни зборови: тенки филмови; хемиска депозиција; рендгенска дифракција

1. INTRODUCTION

The investigation of thin films has received a great deal of attention during the last few years due to their important semiconducting properties. Thin films can be used as optoelectronic devices, photovoltaic cells, solar selective coatings and laser materials. Photovoltaic cells at present furnish the most important long duration power supply for satellite, space vehiclec and terrestrial applications. The solar energy is considered a major candidate for obtaining energy from the sun, since it can convert sunlight directly into electricity. In recent years, considerable efforts have been made

to find out low cost materials such as metal chalcogenide materials [1–3] for solar energy conversion application. There are several methods that can be used to prepare thin films such as chemical bath deposition [4], electrodeposition [5], molecular beam epitaxy [6], close spaced sublimation [7], sputter deposition [8], metal organic chemical vapor deposition [9] and plasma-enhanced chemical vapor deposition [10]. The properties of thin films depend on the deposition process and deposition parameters. Each deposition method has its own advantages and disadvantages. The chemical bath deposition method is preferred for its simplicity, inexpensive and capability to achieve large area coatings. Over the past several years, many researchers have prepared thin films such as ZnS [11], PbS [12], SnS [13], CdS [14], FeS_2 [15], $CuBiS_2$ [16], $PbSnS_3$ [17], $Cd_{1-x}Zn_xS$ [18] and $Cd_{0.5}Zn_{0.5}Se$ [19] by the chemical bath deposition method. Nair *et al*. [20] have reported the results on the formation of Cu_4SnS_4 thin films when a chemically deposited SnS-CuS layer is heated at 400 °C under a 300 mTorr pressure of nitrogen.

In the present study, we describe the deposition of Cu_4SnS_4 thin films onto indium tin oxide glass substrate using the chemical bath deposition technique. We report for the first time chemical bath deposition of Cu_4SnS_4 thin films in the presence of Na_2EDTA at 50 °C in a strong acidic medium (pH = 1.5). The deposition parameters were optimized to obtain good quality thin films. The structural and morphological properties of thin films were investigated by the X-ray diffraction and the atomic force microscopy, respectively. Meanwhile, the optical properties of thin films were studied by the UV-Visible Spectrophotometer.

2. EXPERIMENTAL

Preparation of samples

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared using deionised water (Alpha-Q Millipore). The chemicals used were copper sulfate ($CuSO_4$), tin chloride ($SnCl_2$), sodium thiosulfate ($Na_2S_2O_3$), disodium ethylenediaminetetraacetic (Na_2EDTA) and hydrochloric acid (HCl). The copper sulfate, tin chloride and sodium thiosulfate were acted as a source of copper, tin and sulfide ion, respectively. The Na_2EDTA was used as a complexing agent to chelate with Cu^{2+} and Sn^{2+} to obtain Cu-EDTA and Sn-EDTA complex solutions. The presence of Na_2EDTA was found to improve the lifetime of the deposition bath as well as the adhesion of deposited films on the indium tin oxide glass substrate. Before deposition, the indium tin oxide (ITO) glass substrate was degreased with ethanol for 10 min, followed by ultrasonically cleaned with distilled water for another 15 min. Depositions of Cu_4SnS_4 thin films were carried out by using the following procedure: Firstly, 10 ml of $CuSO_4$ (0.05 M) and 10 ml of $SnCl_2$ (0.05 M) solutions were complexed with 10 ml of Na_2EDTA (0.1 M), respectively and stirred for several minutes to get clear and homogeneous solutions. Thereafter, 10 ml of $Na_2S_2O_3$ (0.05 M) was added under stirring conditions. Finally, hydrochloric acid was added to make the solution acidic and the pH was maintained at 1.5. The clean ITO glass substrate was then placed vertically inside the beaker without disturbing it. This beaker was then kept in constant temperature water bath. The beaker was allowed to stand for 120 min at 50 °C constant temperature. After completion of film deposition, the ITO glass substrate was removed from the beaker and cleaned with distilled water. Then the deposited films were dried in the desiccator and subjected to further analyses.

Characterization method

The structural characterization of the films was carried out using a Philips PM 11730 X-ray diffractometer with CuK_α radiation (λ = 1.5418 Å) in scanning the angle (2θ) from 20 ° to 60 °. The surface morphology of the films was investigated by atomic force microscopy (Quesant Instrument Corporation, Q-Scope 250). It was operated in a contact mode with the Si_3N_4 cantilever. The value of root mean square (RMS) roughness was calculated from the height values in the atomic force microscopy (AFM) image using the commercial software. The elemental composition of the films was studied by scanning the electron microscope (JEOL JSM 6400) attached with energy dispersive analysis of the X-ray (EDAX) analyzer. The photoelectrochemical experiment was performed in $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox system by running linear sweep voltammetry (LSV) between –400 to –1000 mV versus Ag/AgCl (silver-silver chloride electrode). A halogen lamp (300 W, 120 V) was served as the light source. The voltage scan speed was 10 mV/s and the light was manually chopped. The absorption was recorded in the range of 350–

800 nm using the Perkin-Elmer Lambda 20 UV-Vis 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. Thus, the absorbance measurement included only the contribution from Cu_4SnS_4 thin films. From the analyses of absorption spectrum, the band gap energy (E_g) was determined.

3. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) pattern of thin films deposited onto the indium tin oxide glass substrate at optimized deposition parameters is shown in Fig. 1. This pattern contains eight diffraction peaks indicating that these films are polycrystalline in nature. The XRD peaks are at 2θ = 22.3 °, 28.9 °, 30.2 °, 35.2 °, 39.1 °, 47.0 °, 50.6 ° and 57.0 °. Fig. 1 shows that the films exhibit a high intensity peak at 2θ = 30.2 °. All other peaks and their relative planes are listed in Table 1. The comparisons of observed *d*-spacing values with standard *d*-spacing values (JCPDS Reference code: 010710129) [21] clearly indicate the formation of orthorhombic phase of Cu_4SnS_4. The lattice parameter values are a = 1.3558 nm, b = 0.7681 nm, c = 0.6412 nm.

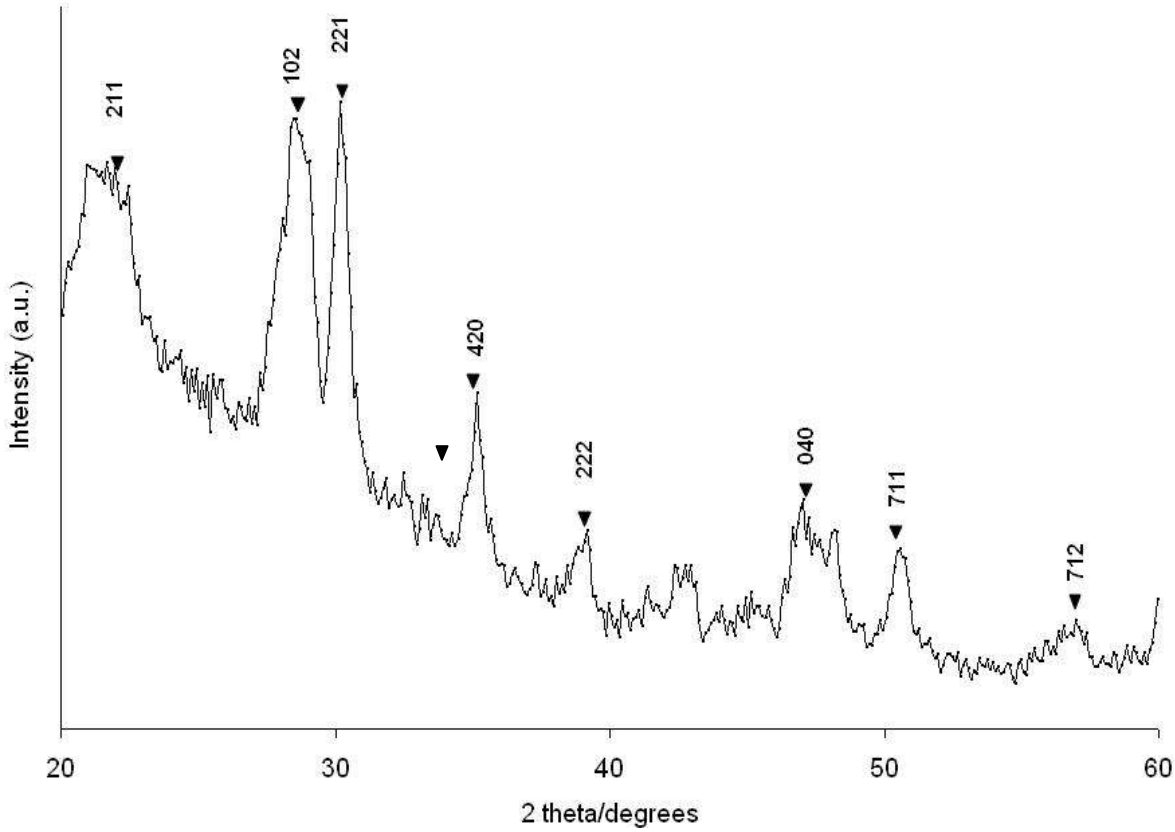


Fig. 1. X-ray diffraction pattern of Cu_4SnS_4 thin films deposited at optimized deposition parameters. (Cu_4SnS_4)

The compositional analysis of the films is investigated by the energy dispersive analysis of the X-ray (EDAX) technique. The EDAX spectrum of the Cu_4SnS_4 thin films deposited under optimized deposition conditions is shown in Fig. 2. The quantitative elemental analysis is carried out only for Cu, Sn and S. The atomic percentage (%) for these elements is 49.1, 12.6 and 38.3 %, respectively. The ratio of 4:1:3 of copper (Cu), tin (Sn) and sulphur (S) has been confirmed by EDAX analysis. We can conclude that the sulphur concentration is slightly less as compared to stoichiometric of Cu_4SnS_4.

Table 1

Comparison of the JCPDS d-spacing data for Cu_4SnS_4 thin films to experimentally observed values for the sample deposited at optimized deposition parameters

2θ (°)	*hkl*	*d*-spacing	
		Observed	JCPDS value
22.3	211	3.99	3.98
28.9	102	3.08	3.12
30.2	221	2.96	2.96
35.2	420	2.55	2.54
39.1	222	2.30	2.31
47.0	040	1.93	1.92
50.6	711	1.80	1.80
57.0	712	1.61	1.62

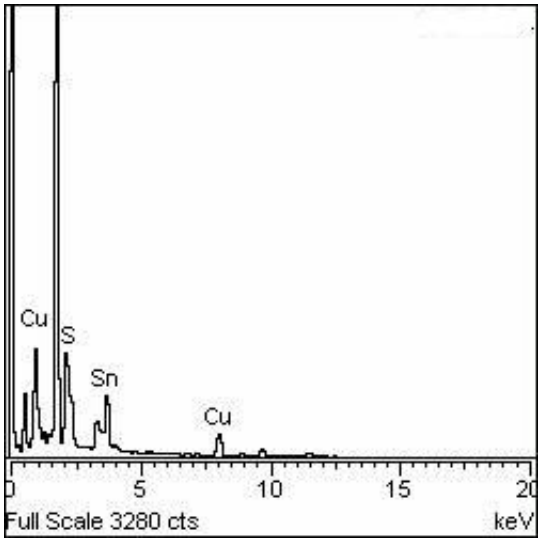
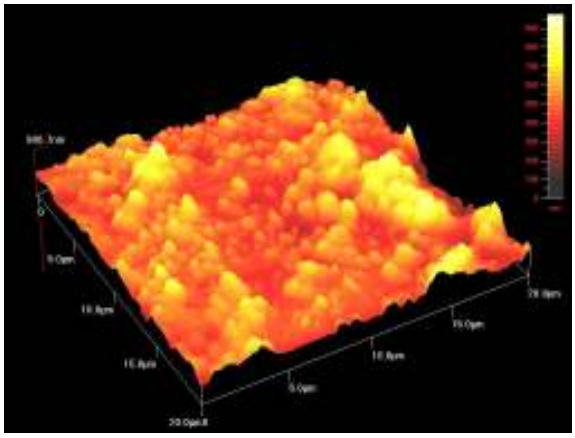
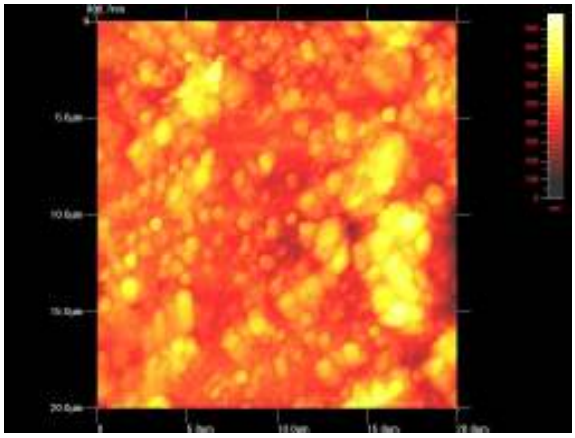


Fig. 2. EDAX spectrum of Cu_4SnS_4 thin films deposited at optimized deposition parameters

Surface morphology is observed with the atomic force microscopy (AFM) technique. Figs. 3a and 3b show two-dimensional and three-dimensional images of films deposited onto the indium tin oxide glass substrate at optimized deposition parameters, measured over an area of 20 μm × 20 μm. Fig. 3a shows that the small spherical grains of approximately 0.8–1 μm size are uniformly distributed over the surface of substrate. Fig. 3b indicates the formation of hill-like structure which shows the growth of thin films during the deposition process. The AFM images show that the grains are distributed to cover the surface of the substrate completely.



a)



b)

Fig. 3. Two-dimensional (a) and three-dimensional (b) AFM images of Cu_4SnS_4 thin films deposited at optimized deposition parameters

The root mean square (RMS) roughness which is defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness [22]. The surface roughness is small (67 nm) and is unavoidable due to the three-dimensional growth of films. The thickness of the films is also studied using AFM images. At the right side of the images, an intensity strip is shown, which indicates the depth and height along the *z*-axis. The thickness is measured from the AFM images and is found to be 980 nm.

Figure 4 shows the optical absorption spectrum of Cu_4SnS_4 thin films in the wavelength region from 350 to 800 nm. As seen in the Figure 4, the spectrum of thin films shows high absorption

(at wavelengths less than 750 nm) throughout the visible region indicating that these materials can be used for photoelectrochemical cells

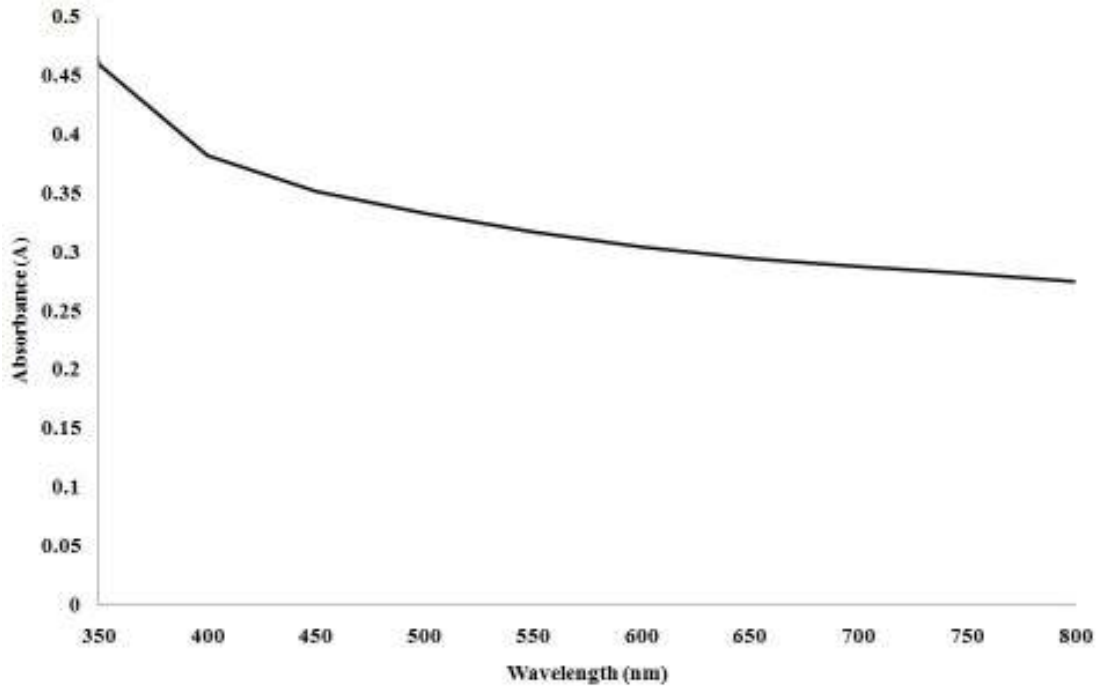


Fig. 4. Optical absorbance versus wavelength of Cu_4SnS_4 thin films deposited at optimized deposition parameters

The band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with the Stern [23] relationship of near-edge absorption (Equation 1):

$$A = \frac{[k\left(hv - E_g\right)^{n/2}]}{hv} \qquad (1)$$

where v is the frequency, h is the Planck's constant, k equals a constant while n carries value which is either 1 or 4. The plot of $(Ahv)^2$ versus hv for the films deposited at optimized deposition conditions is shown in Fig. 5. The band gap energy is obtained by extrapolating the linear portion of $(Ahv)^{2/n}$ versus hv to the energy axis at $(Ahv)^{2/n} = 0$. The line to determine the band gap is plotted using Microsoft Excel software (least square method). The R^2 value obtained from the graph shown is 0.962 which is almost to the value of 1. This value shows that all the data is fitted well by using this least square method. The linear nature of the plot indicates the existence of direct transition [24]. The band gap value is found to be 1.57 eV.

Figure 6 shows the photoresponse of Cu_4SnS_4 thin films in contact with the $[Fe(CN)_6]^{3-}$ /$[Fe(CN)_6]^{4-}$ redox system. The current-potential response when lights are shone and chopped at an almost constant frequency is overlaid on the results of this test carried out in dark condition for a better delineation of photocurrent and darkcurrent. The photocurrent can be explained by the fact that once transition of electrons occurs, holes are left in the valence band with a lifetime adequate for them to participate in electrochemical reaction at the electrode/electrolyte interface [25]. The current changes with the illumination indicating the films possess semiconductor behavior. The fact that photocurrent occurs on negative potential indicates that the films prepared are of *p*-type and they can be deployed as photocathode in the photoelectrochemical cell.

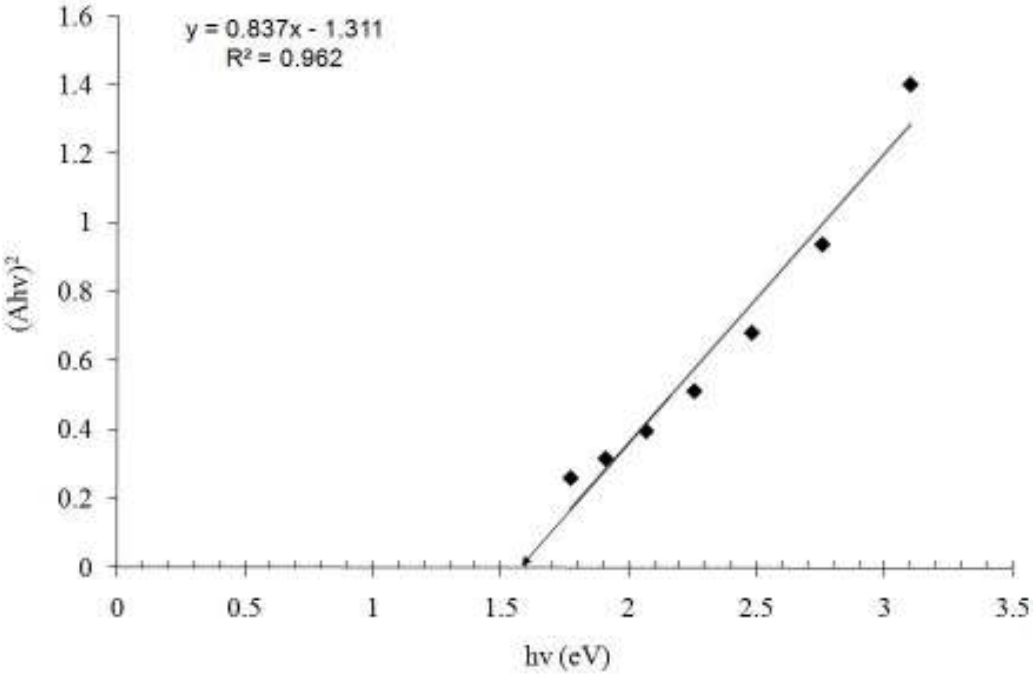


Fig. 5: Plot of $(Ahv)^2$ versus hv of Cu_4SnS_4 thin films deposited at optimized deposition parameters

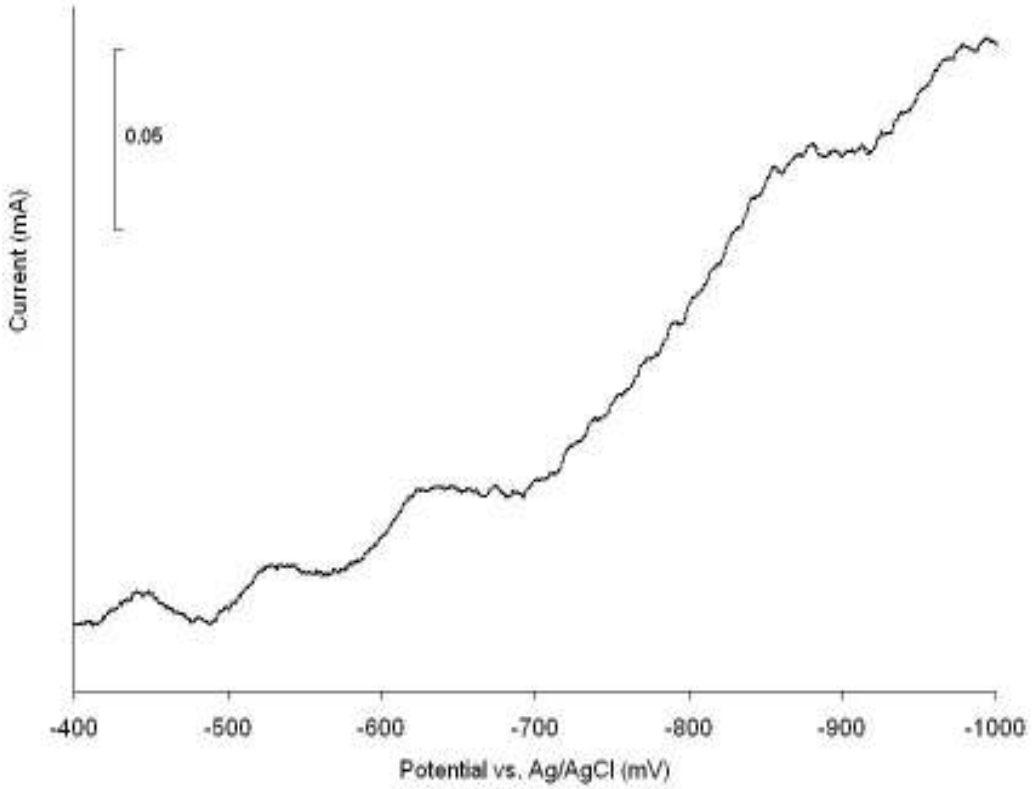


Fig. 6. The photosensitivity of Cu_4SnS_4 thin films deposited at optimized deposition parameters

4. CONCLUSION

Cu_4SnS_4 thin films were successfully deposited onto the indium tin oxide glass substrate using the chemical bath deposition method. The chemical bath consisted of $CuSO_4$, $SnCl_2$ and $Na_2S_2O_3$ as the starting materials while Na_2EDTA was used as the complexing agent. The X-ray diffraction study revealed that Cu_4SnS_4 films were polycrystalline in nature with the preferential orientation along (221) plane. The atomic force microscopy results indicated that the films were smooth, uniform and the substrate surface was covered completely at this experimental condition. These films exhibited *p*-type semiconductor behavior with the band gap energy which was about 1.57 eV.

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