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Effects of Bath Temperature on the Electrodeposition of Cu_4SnS_4 Thin Films

[1]Anuar, K., [1]S. M. Ho, [1]W. T. Tan, [1]S. Atan, [1]Z. Kuang, [1]M. J. Haron and [2]N. Saravanan

[1]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 Serdang,Selangor, Malaysia.
[2]Department of Bioscience and Chemistry, Faculty of Engineering and Science,
UniversitiTunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia.

Abstract: Thin films of Cu_4SnS_4 semiconductors were prepared by electrodeposition technique in aqueous solutions. The effects of various bath temperatures (25-50°C) on growth of these films were reported. The structure and morphology characteristics of thin films of Cu_4SnS_4 grown on indium tin oxide glass substrates were investigated by X-ray diffraction and atomic force microscopy techniques. The optical properties were measured to determine the transition type and band gap value. The thin films produced were found to be polycrystalline with orthorhombic structure. The X-ray diffraction data showed that the most prominent peak at $2q$ = 30.2° which belongs to (221) plane of Cu_4SnS_4. The atomic force microscopy image indicated that the films deposited at 25°C exhibited smaller crystal size with uniformly distributed on indium tin oxide substrates. The bandgap value was found to be 1.68 eV with direct transition.

Key words: Thin films, electrodeposition, band gap energy, semiconductor

INTRODUCTION

The solar cell made of polycrystalline thin film is one of the most promising low cost candidates for terrestrial photovoltaic applications. There are many techniques for preparing thin films such as chemical bath deposition[11], vacuum evaporation[2], electrodeposition[3], molecular beam epitaxy[4], close spaced sublimation[5], thermal evaporation[6], spray pyrolysis[7], sputter deposition[8], metal organic chemical vapor deposition[9] and plasma-enhanced chemical vapor deposition[10]. The preparation of thin films by the electrodeposition is currently attracting a great deal of attention, as the method is simple, inexpensive, no requirement of sophisticated instruments and possibility for large-scale production. At present, electrodeposition has been proved as a suitable method of preparing binary compounds like CdS[11], ZnS[12], CdSe[13], PbS[14], SnS[15], SnSe[16], Cu_2S[17] and ternary semiconductors such as $CdIn_2S_4$ [18], $SnS_{0.5}Se_{0.5}$ [19], $CuInS_2$ [20], $CuInSe_2$ [21], ZnCuTe[22].

In this work, we investigated the influence of the bath temperature (25-50 °C) on structural, morphological and optical properties of electrodeposited Cu_4SnS_4 films. The structure of the film was studied by technique. The morphology and optical absorption properties were determined by using atomic force microscope and UV-Visible Spectrophotometer, respectively.

MATERIALS AND METHODS

All the chemicals used for the deposition were analytical grade. It includes copper sulfate ($CuSO_4$), tin chloride ($SnCl_2$), sodium thiosulfate ($Na_2S_2O_3$) and hydrochloric acid (HCl). All the solutions were prepared in deionised water (Alpha-Q Millipore). The deposition bath contained 0.01mol/L of $CuSO_4$, $SnCl_2$ and $Na_2S_2O_3$.The pH of the bath was adjusted to 1.5 by using HCl. The electrodeposition was carried out in a conventional three-electrode cell. The indium-doped tin oxide (ITO) was used as the working electrode. The ITO was cleaned ultrasonically in ethanol and distilled water before use. The counter electrode and reference electrode was The photoresponse in the anodic region indicated the n-type semiconductor. The films deposited at 25 °C are considered as the optimum bath temperature to produce good quality thin films. made from platinum wire and Ag/AgCl, respectively. The EG&G Princeton Applied Research potentiostat driven by a software model 270 Electrochemical Analysis System was used to control electrodeposition process and to monitor current and voltage profiles. The deposition was carried out at -600 mV versus Ag/AgCl for 45 min. In order to determine the optimum condition for the deposition process, the films were deposited at different bath temperatures (25-50 °C). After deposition, the deposited films were tested for adhesion by subjecting it to a steady stream of distilled

Corresponding Author: Anuar Kassim, Department of Chemistry, Faculty of Science,Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
E-mail: anuar@fsas.upm.edu.my

water. The deposited films were kept for further analysis.

X-ray diffraction analysis was carried out, using a Philips PM 11730 diffractometer for the 2θ ranging from 25° to 60° with CuK_α (λ=0.15418 nm) radiation. Topography was measured by using an atomic force microscopy (Quesant Instrument Corporation, Q-Scope 250) operating in contact mode, with a commercial Si_3N_4 cantilever. Photoelectrochemical (PEC) experiments were p erformed using a $[Fe(CN)_6]^{3-}$ /$[Fe(CN)_6]^{4-}$ redox system, by performing linear sweep voltammetry between 300 to 1000 mV. The sequence of constant illumination, chopped illumination and dark period were performed on the P.E.C cell to study the effect on photoactivity behavior. A halogen lamp (300 W, 120 V) was used for illuminating the electrode. 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 I.T.O glass was put across the reference path. From the analyses of absorption spectra, the band gap energy was determined.

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction (XRD) patterns for the films deposited at various bath temperatures. The XRD patterns are found to be polycrystalline with orthorhombic structure. There are six peaks at 2*q* =30.2°, 35.4.°, 42.9°, 47.4°, 50.7° and 57.5 °C were detected for films deposited from 25°C to 35 °C. The corresponding interplanar distances are well in agreement with JCPDS data (Reference code: 010710129) of 0.296, 0.255, 0.210, 0.192, 0.180 and 0.161 nm which attributed to the (221), (420), (331), (040), (711) and (532) planes, respectively. All these peaks are related to the compound of Cu_4SnS_4 of orthorhombic structure (a =13.5580 Å, b = 7.6810 Å, c =6.4120Å, α = β = γ =90°). However, raising the bath temperature further to 40 °C and above, resulted in the disappearance of (532) plane could be observed in X.R.D patterns. The most prominent peak obtained at 2*q* =30.2° corresponding to interplanar distance of 0.296 nm. As the bath temperature increased, the intensity of the peak (221) increased. This indicates that the grain size increases when the bath temperature is increased.

The Cu_4SnS_4 thin films were morphologically characterized using atomic force microscopy (AFM). Fig. 2 shows the three-dimensional representation of a 20 mm X 20 mm area of the Cu_4SnS_4 thin films deposited at different bath temperatures. It is observed that the films deposited at 25 °C have a homogeneous, uniform surface and well cover the substrate (Fig. 2a). As the bath temperature was increased to 50 °C (Fig. 2b), decreasing in the number of grains could be observed. The grain size of Cu_4SnS_4 material is much bigger with diameter around 1 mm. This result is consistent with the observation from X-ray diffraction patterns.

Fig. 3 shows the absorption spectra of Cu_4SnS_4 films at various bath temperatures. The films show a gradually increasing absorbance throughout the visible region, which makes it possible for this material to be used in a photoelectrochemical cell. The film deposited at 25°C showed gradual increasing of absorption starting from 650 nm downward. This film showed higher absorption characteristics when compared to the films prepared at other bath temperatures. Thus, this bath temperature is more preferable in the preparation of Cu_4SnS_4 films of better quality on ITO substrate. The optical absorption values are in line with AFM results, the larger grain sizes could be obtained in the films deposited at higher temperature that produce lower absorption results.

Fig. 4 shows the difference between photocurrent (I_p) and darkcurrent (I_d) for the Cu_4SnS_4 thin films in contact with 0.01M Fe^{2+}/Fe^{3+} redox couple. An increase in current could be observed as the films were illuminated. The current change upon illumination indicates semiconductor behavior of the materials. The fact that photocurrent occurs on the positive potential region reflects that the films prepared are n-type. This indicates that the majority carriers generated are electrons.

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:

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

where *v* is the frequency, *h* is the0 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 $(Ahv)^{2/n}$ as a function of *hv*. Extrapolation of the line to the base line, where the value of $(Ahv)^{2/n}$ is zero, will give E_g. The $(Ahv)^{1/2}$ versus *hv* plot is a straight line (Fig. 5) indicating that the energy band gap of Cu_4SnS_4 is direct and intercept on the *hv* axis yield a band gap of 1.68 eV for the film deposited at 25 °C.

Conclusion: The polycrystalline Cu_4SnS_4 thin films can be deposited on indium tin oxide glass substrates by the electrodeposition technique. The Cu_4SnS_4 thin films have orthorhombic structure and preferred orientation in the
(221) plane. The AFM images indicated that higher bath temperature leads to larger crystal size. The films deposited at 25 °C have a homogeneous, uniform surface and well cover the substrate. These films also produced higher absorption values. The band gap energy was found to be 1.68 eV with direct transition.The photoresponse in the anodic region indicated the n-type semiconductor. The films deposited at 25°C are considered as the optimum bath temperature to produce good quality thin films.

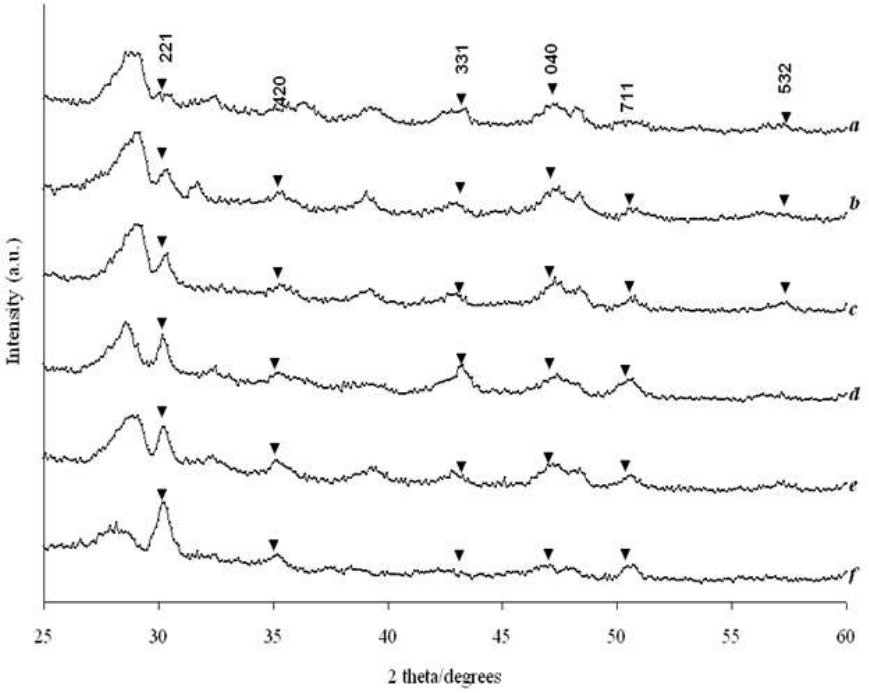


Fig. 1: X-ray diffraction patterns of Cu_4SnS_4 thin films deposited at various bath temperatures (a) 25 °C (b) 30°C (c) 35 °C (d) 40 °C (e) 45 °C (f) 50 °C [Cu_4SnS_4 (▲)]

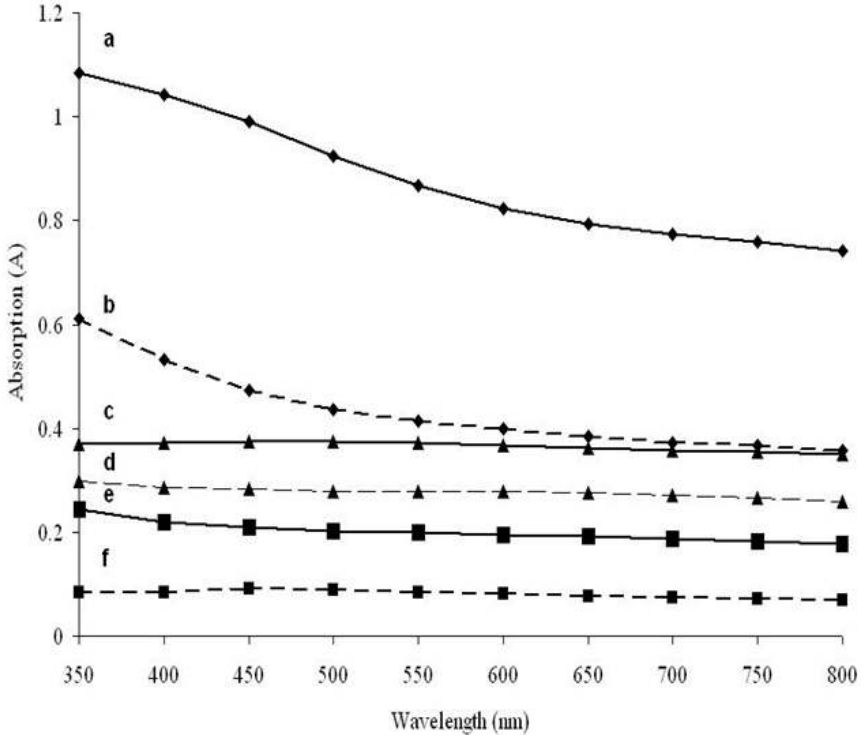
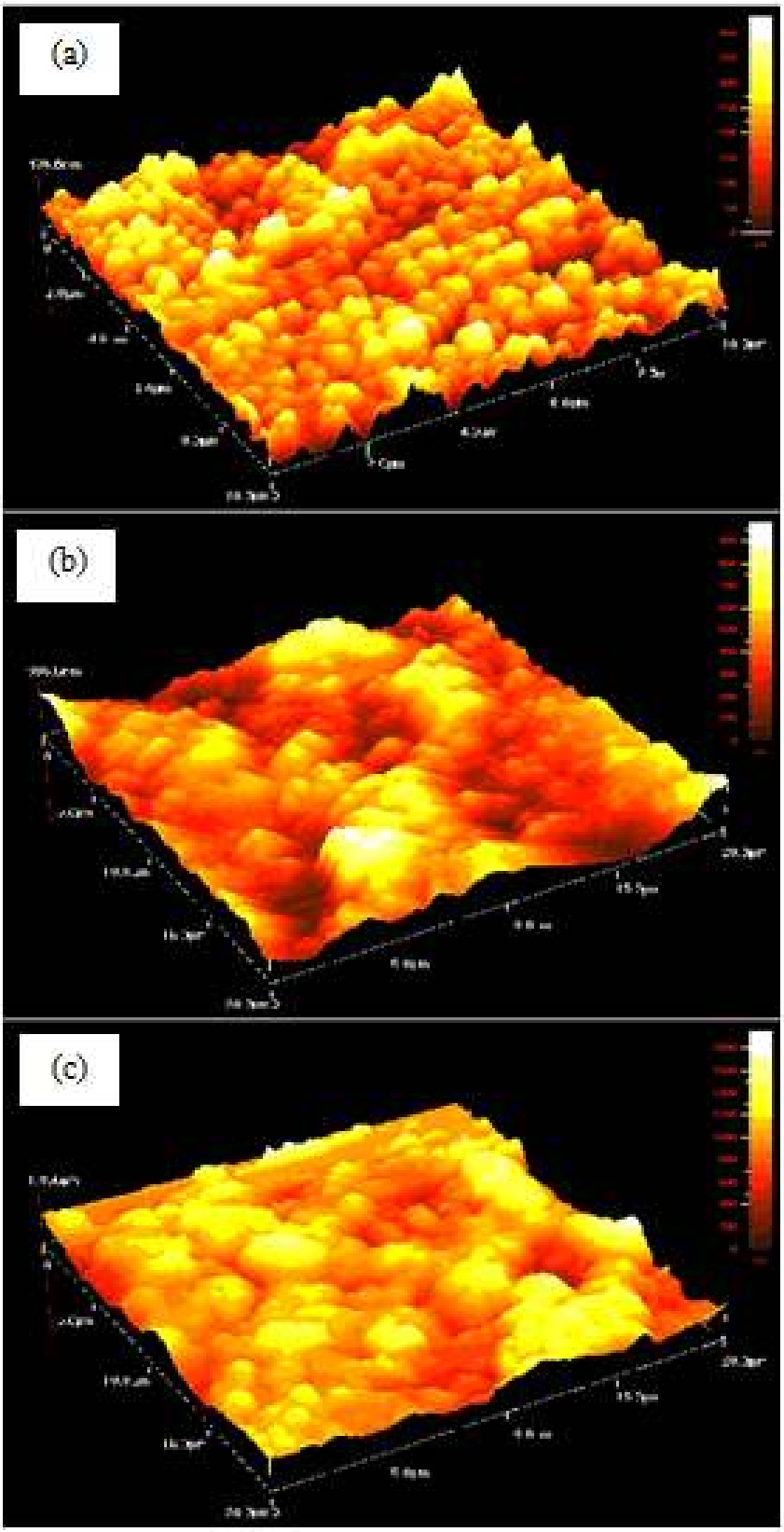


Fig. 3: Optical absorbance versus wavelength of the Cu_4SnS_4 films deposited at various bath temperatures (a) 25 °C (b) 30 °C (c) 35 °C (d) 40 °C (e) 45 °C (f) 50 °C


(a)
(b)
(c)

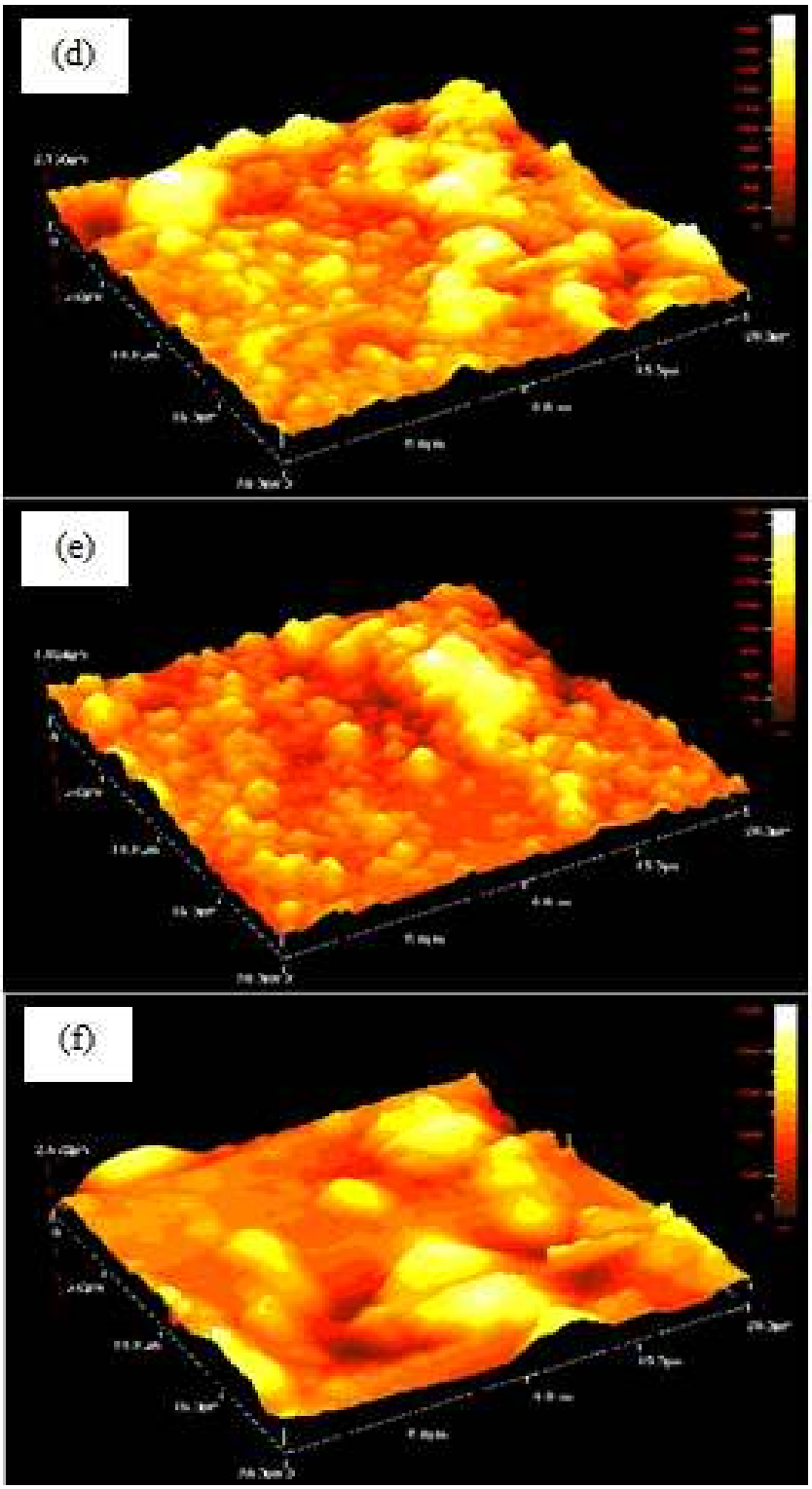


Fig. 2: Atomic force microscopy images of Cu_4SnS_4 thin films deposited at various bath temperatures (a) 25 °C (b) 30 °C (c) 35 °C (d) 40 °C (e) 45 °C (f) 50 °C

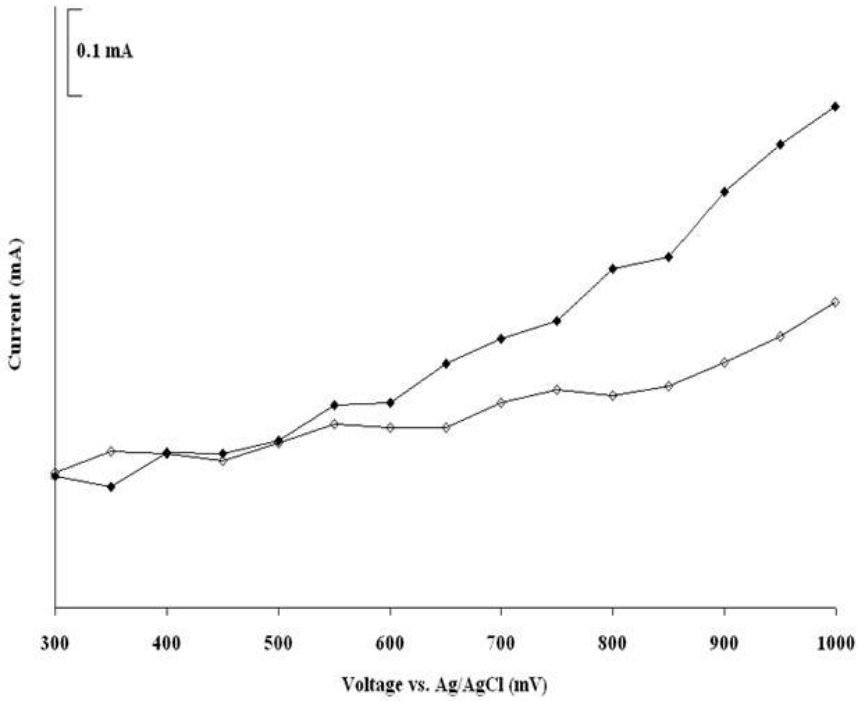


Fig. 4: Photoresponse of Cu_4SnS_4 thin films deposited at 25 °C. The difference between photocurrent and darkcurrent (♦ photocurrent, ◊ darkcurrent)

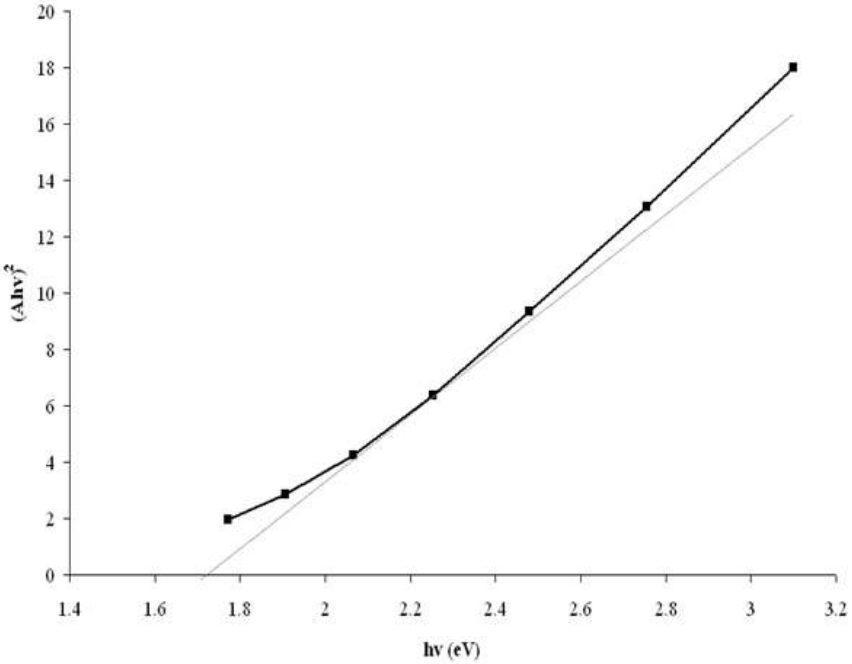


Fig. 5: Plot of $(Ahv)^{2/n}$ versus hv when n=4 for Cu_4SnS_4 thin films prepared using 0.01M $Na_2S_2O_3$, $CuSO_4$ and $SnCl_2$ solutions at 25 °C

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