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EFFECTS OF DEPOSITION PERIOD ON THE CHEMICAL BATH DEPOSITED Cu_4SNS_4 THIN FILMS

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ABSTRACT

Cu_4SnS_4 thin films were prepared by simple chemical bath deposition technique. The influence of deposition period on the structural, morphological and optical properties of films was studied. The films were characterized using X-ray diffraction, atomic force microscopy and UV-Vis Spectrophotometer. X-ray diffraction patterns indicated that the films were polycrystalline with prominent peak attributed to (221) plane of orthorhombic crystal structure. The films prepared at 80 min showed significant increased in the intensity of all diffractions. According to AFM images, these films indicated that the surface of substrate was covered completely. The obtained films also produced higher absorption characteristics when compared to the films prepared at other deposition periods based on optical absorption studies. The band gap values of films deposited at different deposition periods were in the range of 1.6-2.1 eV. Deposition for 80 min was found to be the optimum condition to produce good quality thin films under the current conditions.

Key words: Thin film, chemical bath deposition, band gap energy.

INTRODUCTION

Interest on the preparation and study of physical properties of thin film semiconductors for their possible applications in optoelectronic devices, solar cells, infrared detectors and light emitting diodes has been increasing in the recent years. The properties of thin films prepared by different methods are critically dependent on the nature of preparation technique. In the past few decades, several techniques such as chemical bath deposition, vacuum evaporation, electrodeposition, molecular beam epitaxy, close spaced sublimation, thermal evaporation, spray pyrolysis, sputter deposition and plasma-enhanced chemical vapor deposition have been used in the deposition of thin films. Chemical bath deposition technique is relatively simple, cost effective and can be applied in large area deposition at low temperature. This method does not require vacuum and sophisticated instrumentation.

The vast preparation and studies of metal chalcogenides thin films using chemical bath deposition method can be classified into two categories. Examples of binary compounds are MnS[1], SnS[2], SnSe[3], CdSe[4], Sb_2S_3[5], PbS[6], CdS[7] and ZnSe[8]. Meanwhile, $CuInSe_2$[9], $Cd_{0.5}Zn_{0.5}Se$[10] and $CuBiS_2$[11] are examples of ternary metal chalcogenides. Here, we report the preparation and characterization of Cu_4SnS_4 thin films by chemical bath deposition method. Nair and co-workers[12] reported the formation of Cu_4SnS_4 thin films by heating sequentially deposited SnS and CuS films (both obtained by chemical bath deposition) at 400 °C in a nitrogen atmosphere. In this work, copper tin sulphide thin films have been deposited on indium tin oxide glass substrates from aqueous solutions containing $CuSO_4$, $SnCl_2$, $Na_2S_2O_3$. The Na_2EDTA was used

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as complexing agent during deposition. To date, there have been no reports in the literature on the investigation of deposition period (40-180 min) on the properties of Cu_4SnS_4 thin films. The structure of the film was studied by X-ray diffraction. The morphology and optical absorption properties were determined by using atomic force microscope and UV-Visible Spectrophotometer, respectively.

EXPERIMENTAL

All the chemicals used for the deposition were analytical grade. It includes copper sulfate ($CuSO_4$), tin chloride ($SnCl_2$), sodium thiosulfate ($Na_2S_2O_3$), disodium ethylenediaminetetraacetic acid (Na_2EDTA) and hydrochloric acid (HCl). All the solutions were prepared in deionised water (Alpha-Q Millipore). The indium doped tin oxide (ITO) glass was used as the substrate. Before deposition, the glass slides were degreased with ethanol for 10 min. Then, ultrasonically cleaned with distilled water for another 10 min and dried in desiccators. Deposition of Cu_4SnS_4 thin films was carried out at 50 C at pH 1.5 by using following procedure: 10 ml of $SnCl_2$ (0.05M) and $CuSO_4$ (0.05M) were taken in a 100 ml beaker, respectively. Then, 10 ml of 0.1 M Na_2EDTA as complexing agent was added into both beakers with constant stirring. To it, 10 ml of $Na_2S_2O_3$ (0.05M) was added slowly. The resultant solution was stirred for few minutes. The cleaned glass substrates were immersed vertically into beaker. In order to determine the optimum conditions for the deposition process, the films were deposited at different deposition periods (40-180 min). After completion of deposition, the deposited films were tested for adhesion by subjecting them to a steady stream of distilled water.

X-ray diffraction analysis was carried out, using a Philips PM 11730 diffractometer for the 2θ ranging from 20° to 60° with CuK_a (ë=1.5418 Å) radiation. Surface topography was measured by using an atomic force microscopy (Quesant Instrument Corporation, Q-Scope 250) operating in contact mode, with Si_3N_4 cantilever. 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 (E_g).

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction (XRD) patterns of Cu_4SnS_4 thin films deposited at different deposition periods. The XRD patterns from all the samples have shown a major diffraction peak at 2θ=30.2° which is corresponding to (221) orientation of orthorhombic structure of Cu_4SnS_4. In addition to the (221) plane, we also observed other diffraction peaks at 2θ = 28.5°, 35.2°, 47.2° and 50.6° which are attributed to (102), (420), (040) and (711) planes, respectively. In particular, the film deposited for 80 min showed higher intensity for all diffraction peaks indicating that this deposition period is favorable for the Cu_4SnS_4 films growth. The observed *d*-spacing values were compared with standard *d*-spacing values[13] (Reference code: 01-071-0129) and are in good agreement with standard *d*-spacing values. On the other hand, the presence of the indium tin oxide peaks[14] (Reference code: 01-089-4598) in the XRD patterns is due to the glass substrate used during deposition. There is only single peak occurred at 2θ = 21.3° corresponding to (211) plane was detected as shown in figure 1(a)-(d). According to XRD patterns, the higher intensity of Cu_4SnS_4 peaks could be observed as compared to the substrate peaks.

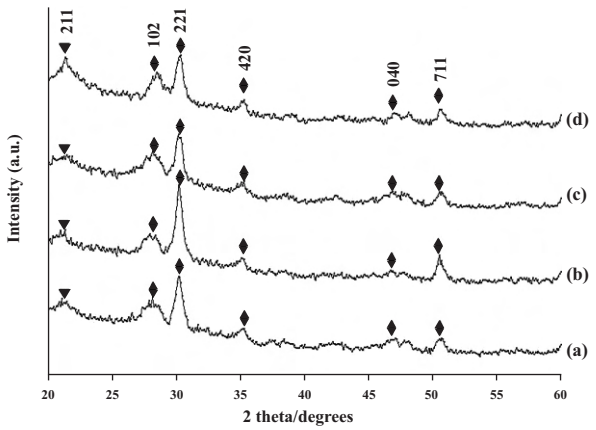

Figure 1. X-ray diffraction patterns of Cu_4SnS_4 thin films deposited at different deposition periods (a) 40 min (b) 80 min (c) 150 min (d) 180 min [Cu_4SnS_4 ♦, indium tin oxide▼]

Figure 2 shows three-dimensional AFM images (20 m X 20 m) for Cu_4SnS_4 thin films deposited onto ITO glass substrates at different deposition periods. The films deposited at 40 min showed incomplete coverage of material over the surface of substrates (figure 2a). It is also pointed out that the film formation was irregular and the film thickness was estimated to be 960 nm. As the deposition time was increased to 80 min, more surface coverage was noticed. There are more materials to be deposited onto substrate and thicker film (2422 nm) to be formed (figure 2b). However, thinner films could be observed when the deposition time was increased further to 150 min (664 nm) and 180 min (322 nm), respectively, as shown in figure 2(c) and 2(d).

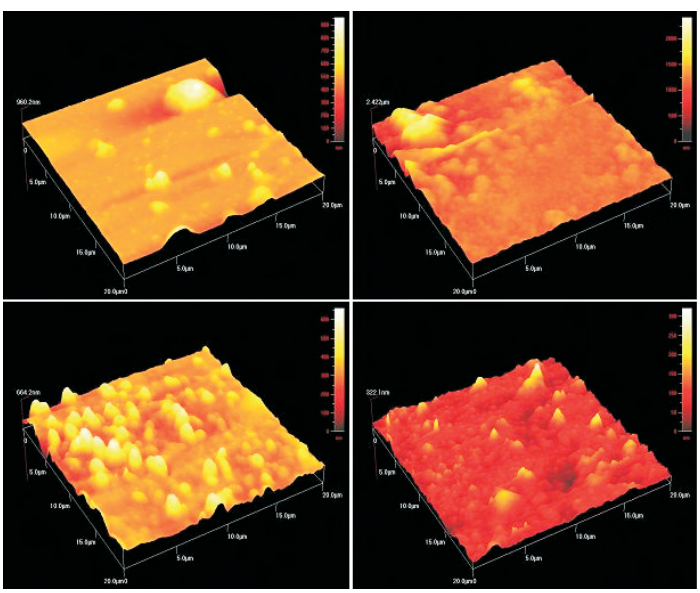

Figure 2: Atomic force microscopy images of Cu_4SnS_4 thin films deposited at different deposition periods (a) 40 min (b) 80 min (c) 150 min (d) 180 min

The optical properties of Cu_4SnS_4 thin films were measured in the range of 300-800 nm using UV-Vis Spectrophotometer. Figure 3 presents the absorbance spectra of Cu_4SnS_4 thin films deposited at different deposition periods. The results showed that the film deposited at 80 min produced higher absorption characteristics as compared with other deposition periods. This could be due to thicker films formed onto surface of the substrate.

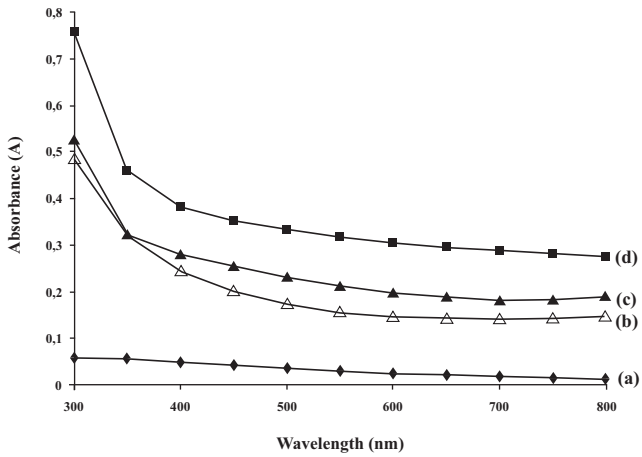

Figure 3: Optical absorbance versus wavelength of the Cu_4SnS_4 thin films deposited at different deposition periods (a) 80 min (b) 150 min (c) 180 min (d) 80 min

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with Stern[15] relationship of near-edge absorption:

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

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. Figure 4 shows the plots of $(Ah\nu)^2$ versus $h\nu$ for the Cu_4SnS_4 thin films deposited at various deposition periods. For all of the deposited thin films, $(Ah\nu)^2$ is a linear function of $h\nu$, as expected for a direct band gap semiconductor. The band gap values of the films can be obtained by linear extrapolation of the curves to zero absorption. It is found that the band gap energy decreases from 2.05 to 1.6 eV as the deposition time is increased from 40 to 80 min. However, the band gap energy increases (1.8 to 2.1 eV) when the deposition time is increased further from 150 to 180 min. The observed variation in the band gap values is an indication of the effects of deposition period on the properties of the semiconductor.

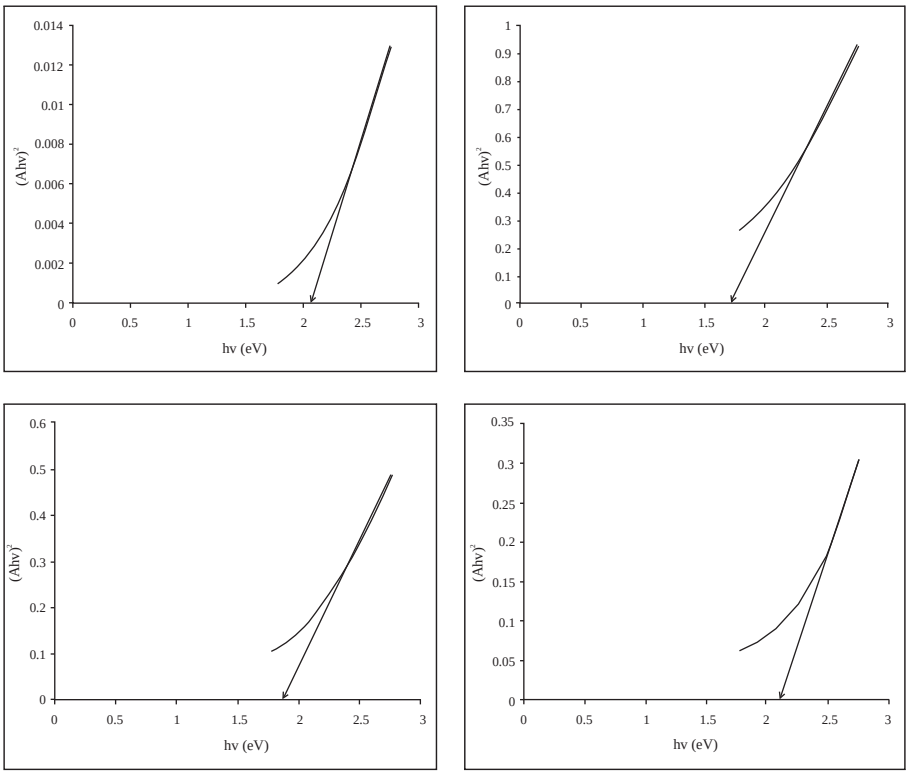

Figure 4: Plots of $(Ahv)^2$ versus hv for Cu_4SnS_4 thin films deposited at different deposition periods (a) 40 min (b) 80 min (c) 150 min (d) 180 min

Figure 5 shows the difference between photocurrent (I_p) and darkcurrent (I_d) response for the Cu_4SnS_4 thin films deposited at various deposition periods in contact with $[Fe(CN)_6]^{3-}$ /$[Fe(CN)_6]^{4-}$ redox system solution. When the deposition time was increased from 40 to 80 min, the difference in the photoresponse increased. This is due to more Cu_4SnS_4 grains are exposed towards the redox system. The results are match with AFM analysis. The decrease in the difference between the photocurrent and darkcurrent could be observed as the deposition time was increased to 180 min. The current change with illumination exhibits semiconductor behaviour of the materials. Apparently, the photocurrent occurs on negative potential shows the films prepared are of *p*-type material.

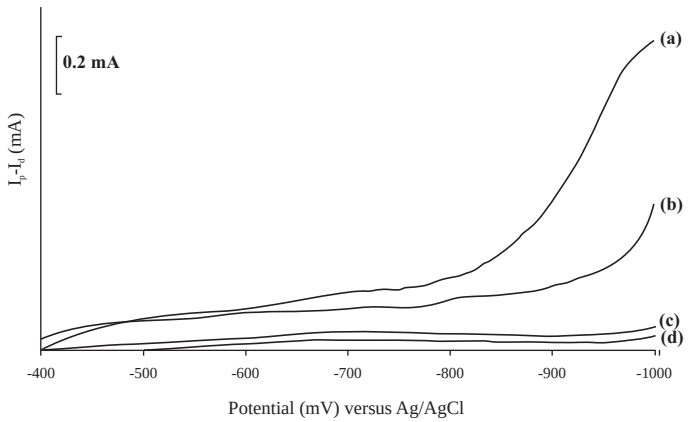

Figure 5: Difference between photocurrent and darkcurrent for the Cu_4SnS_4 thin film deposited at various deposition periods (a) 80 min (b) 150 min (c) 180 min (d) 40 min

CONCLUSIONS

Cu_4SnS_4 thin films were deposited by chemical bath deposition technique from aqueous solutions consisting of copper sulphate, tin chloride and sodium thiosulfate. X-ray diffraction patterns indicated that the films were polycrystalline with prominent peak attributed to (221) plane of orthorhombic crystal structure. The films prepared at 80 min showed significant increased in the intensity of all diffractions. According to AFM images, these films indicated that the surface of substrate was covered completely. The obtained films also produced higher absorption characteristics when compared to the films prepared at other deposition periods based on optical absorption studies. The band gap values of films deposited at different deposition periods were in the range of 1.6-2.1 eV. Deposition for 80 min was found to be the optimum condition to produce good quality thin films under the current conditions.

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