INFLUENCE OF BATH TEMPERATURE AND PH VALUE ON PROPERTIES OF CHEMICALLY DEPOSITED Cu_4SnS_4 THIN FILMS

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ABSTRACT

Thin films of Cu_4SnS_4 semiconductors were prepared by chemical bath deposition technique in aqueous solutions. The effects of various bath temperatures (40, 50 and 60 °C) and pH values (pH 0.5, pH 1.0 and pH 1.5) on growth of 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 intense peak at $2\theta = 30.2^\circ$ which belongs to (221) plane of Cu_4SnS_4 . The films deposited at 50 °C were found to have the best photoresponse activity and smaller crystal size. At pH 1.5, the film showed well-covered entire substrate surface and the highest absorption values in AFM and optical study, respectively. The best condition to prepare good quality thin films can be carried out at 50 °C with pH 1.5. The bandgap value was found to be 1.4 eV with direct transition.

Keywords: Semiconductor, thin films, band gap, chemical bath deposition

INTRODUCTION

Interest on the preparation and study of physical properties of ternary chalcogenide compounds for their possible applications in optoelectronic devices, solar cells, infrared detectors and light emitting diodes has been increasing in the recent years. There are many techniques for preparing thin films such as plasma-enhanced chemical vapor deposition,¹ metal organic chemical vapor deposition,² thermal evaporation,³ chemical bath deposition,⁴ close spaced sublimation,⁵ vacuum evaporation,⁶ electrodeposition,⁷ molecular beam epitaxy,⁸ spray pyrolysis⁹ and sputter deposition¹⁰. Amongst these deposition techniques, chemical bath deposition is most commonly used because it is a simple, cost effective and convenient for larger area deposition of thin films. The chemical bath deposition method has been proved as a suitable method of preparing binary compounds like MnS ,¹¹ SnS ,¹² SnSe ,¹³ CdSe ,¹⁴ Sb_2S_3 ,¹⁵ PbS ¹⁶ and ternary semiconductors such as CdSSe ,¹⁷ CuInSe_2 ,¹⁸ $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ ¹⁹ and CuBiS_2 .²⁰

Here, we report the preparation and characterization of Cu_4SnS_4 thin films by chemical bath deposition. The effects of pH and bath temperatures on the properties of these films are investigated. 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 ($\text{Na}_2\text{S}_2\text{O}_3$), disodium ethylenediaminetetraacetic acid (Na_2EDTA) and hydrochloric acid (HCl). All the solutions were prepared in deionised water (Alpha-Q Millipore). 10 ml of CuSO_4 (0.05M) solution was added into 10 ml of SnCl_2 (0.05M) solution in 100 ml beaker. To it, 10 ml of Na_2EDTA (0.1M) solution was added and then solution was continuously stirred. 10 ml of $\text{Na}_2\text{S}_2\text{O}_3$ (0.05M) solution was then added into a beaker slowly. The resultant solution was stirred for few minutes. The indium doped tin oxide (ITO) glass was used as the substrate. The ultrasonically cleaned glass substrates were immersed vertically into acidic bath. In order to determine the optimum condition for the deposition process, the films were deposited at different bath temperatures (40 -60 °C) and pH values (pH 0.5 to pH 1.5). During deposition period the beaker was kept undisturbed. The substrates were removed from the baths after 2 hours. The deposited films were tested for adhesion by subjecting it 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_α ($\lambda=1.5418 \text{ \AA}$) radiation. Topography was measured by using an atomic force microscopy (Quesant Instrument Corporation, Q-Scope 250) operating in contact mode, with Si_3N_4 cantilever. Photoelectrochemical (PEC) experiments were performed using a $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox system, by performing linear sweep voltammetry between -500 to -1000 mV. The sequence of constant illumination and dark period were performed on the PEC 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 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

Fig. 1 shows the XRD patterns of the films deposited at different chemical bath temperatures. All the samples showed a polycrystalline in nature. There are six peaks occurred at $2\theta = 28.6^\circ$, 30.1° , 35.2° , 42.9° , 47.2° and 50.6° were detected for the films deposited at 40, 50 and 60 °C respectively. The corresponding d -spacing values are well in agreement with JCPDS data (Reference code: 010710129) of 3.12, 2.96, 2.54, 2.10, 1.92 and 1.80 Å which attributed to the (102), (221), (420), (331), (040) and (711) planes, respectively. All these peaks are related to the compound of Cu_4SnS_4 of orthorhombic structure ($a=13.5580 \text{ \AA}$, $b=7.6810 \text{ \AA}$, $c=6.4120 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$). As the chemical bath temperature is increased from 40 °C to 50 °C, the intensity of diffraction peak (211) increases and this peak becomes narrower indicating an improvement of the crystallinity.

Fig. 1. X-ray diffraction patterns of Cu_4SnS_4 films deposited at different chemical bath temperatures. [(a) 40 °C (b) 50 °C (c) 60 °C [Cu_4SnS_4 ($\blacktriangle$)] Larger label for a, b and c

Fig. 2 shows the three-dimensional representation of 20 μm X 20 μm area of the Cu_4SnS_4 films deposited at different chemical bath temperatures. The films deposited at 40 °C and 60 °C (Fig. 2a and 2c) revealed an incomplete coverage of the substrate surface and the grains are not distributed uniformly over the substrate. The growth of grains was focused at certain nucleation centers on the surface of substrate. However, the surface morphology of the Cu_4SnS_4 films deposited at 50 °C showed uniform grain size as seen in Fig. 2b. The indium tin oxide substrate was covered completely indicating more nucleation sites have formed and the numbers of grains have increased.

Fig. 2. Atomic force microscopy images of Cu_4SnS_4 films deposited at different chemical bath temperatures [(a) 40 °C (b) 50 °C (c) 60 °C]. [Scan area: 20 μm X 20 μm].

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 50 °C showed gradual absorption at 450 nm downward. The spectrum reveals that this film has higher absorbance characteristic as compared with the films prepared at 40 °C and 60 °C. 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.

Fig. 3: Optical absorbance versus wavelength of the Cu_4SnS_4 films deposited at different chemical bath temperatures (40 °C; 50 °C; 60 °C). Changed to same symbols.

Fig. 4 shows the different between photocurrent (I_p) and darkcurrent (I_d) for the films deposited at different chemical bath temperatures. The film deposited at 50 °C showed the highest photoresponse activity if compared with other deposition temperatures. This could be due to sufficient semiconducting material deposited onto the surface of substrate. The photocurrent occurs on the negative potential indicates the films are p-type and they can be deployed as a photocathode in a photoelectrochemical cell for reduction reactions.

Fig. 4: Comparison of photosensitivity of the films deposited at different chemical bath temperatures (40 °C; 50 °C; 60 °C). Changed to same symbols

Fig. 5 shows the XRD patterns of Cu_4SnS_4 thin films deposited at different pH ranging from 0.5 to 1.5. The XRD patterns are found to be polycrystalline with orthorhombic structure. There are two peaks can be observed at diffraction angles of 30.3° and 50.6° on the XRD pattern obtained on the films prepared at pH 0.5. These two peaks are assigned to interplanar distances of 2.95 and 1.81 Å which corresponding to (221) and (711) planes respectively. When the pH value was increased from 1 to 1.5, the number of peaks related with Cu_4SnS_4 formation increased. There are three additional Cu_4SnS_4 peaks could

be detected at $2\theta = 28.6^\circ$, 33.5° and 47.1° which attributed to the (102), (321) and (040) planes.

Fig. 5: X-ray diffraction patterns of Cu_4SnS_4 thin films deposited at 50°C in different pH solutions (a) pH 0.5 (b) pH 1.0 (c) pH 1.5.

Fig. 6 shows the three-dimensional representation of a $20\ \mu\text{m} \times 20\ \mu\text{m}$ area of the Cu_4SnS_4 thin films deposited at different pH of the chemical bath. The irregular surface of film and discontinuous distribution of grains was detected for the film grown at pH 0.5 (Fig. 6a) and pH 1 (Fig. 6b) respectively. However, the film shows uniform, dense and well-covered entire substrate surface (Fig. 6c) when the solution pH is increased from 1 to 1.5.

Fig. 6: Atomic force microscopy images of Cu_4SnS_4 thin films deposited at 50°C in different pH solutions (a) pH 0.5 (b) pH 1.0 (c) pH 1.5 [Scan area: $20\ \mu\text{m} \times 20\ \mu\text{m}$].

Fig. 7 shows the absorption spectra of Cu_4SnS_4 films at different pH values. The films show a gradually increasing absorbance throughout the visible region. The films grown at pH 1.5 are thicker and have higher absorption characteristics.

This response also associated with the fact that more polycrystalline Cu_4SnS_4 materials were formed at this pH value. Thus, pH 1.5 is more preferable in the preparation of Cu_4SnS_4 films of better quality on ITO substrate.

Fig. 7: Optical absorbance versus wavelength of the Cu_4SnS_4 films deposited at 50°C in different pH solutions. Changed to same symbols.

Fig. 8 indicates the different between photocurrent (I_p) and darkcurrent (I_d) for the films deposited at different pH of the chemical bath. The photoresponse for the films deposited at pH 0.5 was the lowest because of least Cu_4SnS_4 crystallite formation. It is observed that the samples prepared at higher pH (pH 1.5) values have the highest photoresponse activity.

Fig. 8: Comparison of photosensitivity of the films deposited at 50°C in different pH solutions. Changed to same symbols

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with Stern relationship²¹ 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. 9) indicating that the energy band gap of Cu_4SnS_4 is direct and intercept on the $h\nu$ axis yield a band gap of 1.4 eV for the film prepared in 50°C at pH 1.5.

Fig. 9: Plot of $(Ah\nu)^{2n}$ versus $h\nu$ when $n=4$ for Cu_4SnS_4 films deposited at 50 °C in pH 1.5.

CONCLUSIONS

Cu_4SnS_4 thin films have been chemically deposited on indium tin oxide substrates from aqueous solution containing CuSO_4 , SnCl_2 , $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2EDTA . The thin films produced were found to be polycrystalline with orthorhombic structure. The X-ray diffraction pattern showed that the most intense peak at $2\theta = 30.2^\circ$ which belongs to (221) plane of Cu_4SnS_4 . The films deposited at 50 °C were found to have the best photoresponse activity and smaller crystal size. At pH 1.5, the film showed well-covered entire substrate surface and the highest absorption values in AFM and optical study, respectively. Deposition at 50 °C with pH 1.5 is the optimum condition to prepare good quality thin films under the current condition. The bandgap value was found to be 1.4 eV with direct transition. The photoresponse in the cathodic region indicate the p-type semiconductor.

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