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Structural, optical and electrical studies on pulse electrodeposited $CdIn_2S_4$ thin films

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Abstract

$CdIn_2S_4$ thin films were prepared by pulse electrodeposition technique over F:SnO_2 glass and stainless steel substrates in galvanostatic mode from an aqueous acidic bath containing $CdSO_4$, $InCl_3$ and $Na_2S_2O_3$. The growth kinetics of the film has been studied and the deposition parameters such as electrolyte bath concentration, bath temperature, time of deposition, deposition current and pH of the bath are optimized. X-ray diffraction (XRD) analysis of the as deposited and annealed films shows polycrystalline nature. Energy dispersive analysis by X-ray (EDAX) confirms nearly stoichiometric $CdIn_2S_4$ nature of the film. Scanning electron microscope (SEM) studies show that, the deposited films are well adherent and grains are uniformly distributed over the surface of the substrate. The optical transmission spectra show a direct band gap of 2.16 eV. Conductivity measurements have been carried out at different temperatures and electrical parameters such as activation energy, trapped energy state and barrier heights etc. have been determined.

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1. Introduction

For the past couple of decades there has been an increased interest in the use of photoelectrochemical (PEC) solar cells, which leads to the search for thin film polycrystalline materials with acceptable efficiency, some times approaching that of single crystals. Thin films have been attractive especially because of their varied applications as semiconducting devices, photovoltaics, optoelectronic devices, radiation detectors, laser materials, thermoelectric devices, solar energy converters, etc. [1–4]. Interest in the use of PEC solar cells for low-cost energy conversion has lead to an extensive research in the field for novel semiconductor materials [5–8]. Investigations have shown that the layered semiconducting cadmium chalcogenides (CdSe, CdS, CdTe), which absorb visible and near-IR light, are particularly promising for PEC solar energy conversion. The applications include intercalation compounds as well as long-life PEC solar cells. Polycrystalline electrodes are economically desirable for solar cell applications, where large area semiconductor substrates are necessary.

Ternary chalcogenides also have potential applications in solar energy conversion [9–12]. The optical and structural properties of chemically deposited nanocrystalline $CdIn_2S_4$ thin films have been studied by Pathan et al. [13]. Growth kinetics and temperature dependent optical properties of $CdIn_2S_4$ epilayers formed by hot wall epitaxy method have been reported [14,15]. Point defect study from low photoluminescence of $CdIn_2S_4$ thin film grown by hot wall epitaxy method has been studied [16]. Many workers have succeeded in depositing thin films of $CdIn_2S_4$ by vacuum evaporation [17,18]. The optical properties, photoluminescence study, Raman scattering of $CdIn_2S_4$ thin films have been reported by several workers [19–23]. Synthesis and characterization of $CdIn_2S_4$ nanorods by

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converting CdS nanorods via the hydrothermal route has been reported [24]. The shape of the X-ray K absorption spectrum of sulfur in the normal spinel $CdIn_2S_4$ has been determined using the FEFF 7 program [25].

The electrodeposition of ternary and other higher multinary compounds containing more than two constituent elements is rather complex owing to a large difference in the deposition potential of the constituent elements and due to the possibility of the formation of intermediate phases during electrodeposition. No attempt has been made so far to electrodeposit stoichiomatric ternary $CdIn_2S_4$ thin films.

In this report, an attempt is made to prepare $CdIn_2S_4$ films through electrodeposition technique on conducting glass and stainless steel substrates, and their characterization. Effect of post annealing treatment on the properties of these films is also reported.

2. Experimental

Thin films of $CdIn_2S_4$ were cathodically pulse electrodeposited on F:SnO_2 glass substrates and on stainless steel substrates under galvanostatic mode. The 'ON' times were 1, 2, 3, 4, and 5 s with corresponding 'OFF' times fixed at 1, 3, 7, 16 and 45 s which correspond to a duty cycle of 50%, 40%, 30%, 20%, and 10%, respectively. Graphite was used as the counter electrode in the electrolytic cell. The electrolyte was prepared by mixing solution of high purity AR grade $CdSO_4$ (0.1 M), $InCl_3$(0.1 M) and $Na_2S_2O_3$ (0.01 M) in the volume ratio of 1:2:4, respectively. The pH of the electrolytic solution was adjusted by addition of dilute H_2SO_4. The substrates were thoroughly cleaned with double distilled water. The distance between the working electrode and the counter electrode was kept constant (1 cm) during deposition. A detailed kinetics study was carried out at constant current density of 2.1 mA/cm^2. From the visual observation during pulse plating it was observed that formation of dark yellow thin film of $CdIn_2S_4$ takes place. Thickness of the pulse deposited $CdIn_2S_4$ thin films were measured by weight difference method. The films were found to be well adherent and uniform. Annealing of these films was carried out in vacuum in the temperature range 150–300 °C.

The X-ray diffraction (XRD) patterns for as-deposited and annealed $CdIn_2S_4$ thin films were recorded by Philips X-ray diffractometer Model 1710 with Cr-Kα radiation in the span of angle between 10° and 100°.

The surface morphology was studied by using JEOL, JXA—840 reflection Scanning Electron Microscope at a magnification of 5000 × at potential 15 kV.

The optical absorption studies were carried using UV–VIS–IR spectrophotometer Model Hitachi 119 in the spectral range 380–1250 nm. The electrical conductivity measurements were carried out using Keithley 2000 electrometer in the temperature range 300–620 K.

3. Results and discussion

3.1. Growth kinetics

A detailed study of kinetics was carried out at a constant current density 2.1 mA/cm^2 by changing the pH of the electrolyte and bath temperatures. The film thickness was slowly built up at the initial stages linearly and finally saturated to a maximum of about 1–2 μm for about 15–60 min keeping the bath temperatures as 30, 40 and 50 °C, respectively, for different pH of the electrolyte. Fig. 1 shows the growth kinetics of $CdIn_2S_4$ thin film deposited at 40 °C and different pH values viz. 2, 2.5 and 3. For pH = 2, growth of the film is slow and film thickness increases marginally, For pH = 2.5, the film thickness is linear up to 60 min of deposition time and reaches a value of 0.6 μm after which the thickness built up is nearly constant. For pH = 3, the film growth is fast and linear up to about 40 min of deposition time and the thickness reached is about 1.4 μm. The growth rate is somewhat reduced in the deposition range of 60–80 min. The films deposited at 30 and 50 °C also show the same trend and for pH = 3, thickness of about 1.2–1.62 μm is obtained. From these observations, it can be concluded that $CdIn_2S_4$ thin films of uniform and maximum thickness (1.4 μm) are formed under the optimized conditions of 40 °C bath temperature, 40 min of deposition time and pH 3 of the electrolytic bath. The growth kinetics was also studied by keeping the optimum conditions cited above and changing the duty cycle as 10%, 20%, 30%, 40%, and 50%. The variation of thickness as function of duty cycle is shown in Fig. 2. Thickness of the film is found increasing for all duty cycles up to 60 min. The maximum thickness is obtained for the duty cycle of 30%. The film deposited at current density of 2.1 mA/cm^2 was found to be uniform, thick and well adherent to the substrate. For other higher and lower values of current densities, the thickness of the film was less. Hence 2.1 mA/cm^2 was considered as optimized current density. The optimized electrodeposition parameters are given in Table 1.

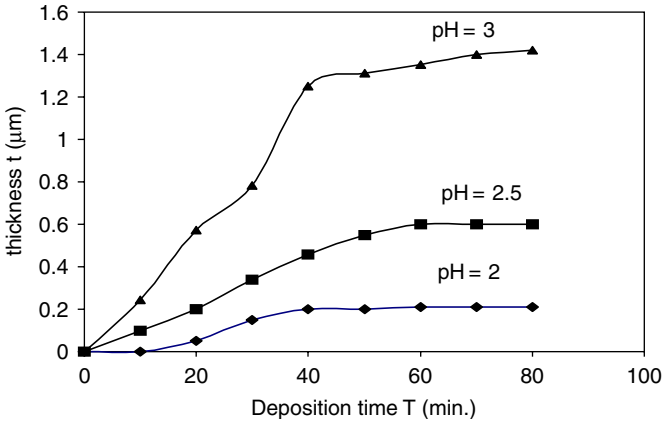

Fig. 1. Growth kinetics of $CdIn_2S_4$ thin films deposited at a current density of 2.1 mA/cm^2 (direct current) for different pH.