

Electrochemical growth and studies of indium-rich CuInTe₂ thin films

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Abstract: CuInTe₂ thin films were electrochemically deposited on fluorine-doped tin oxide (<10 Ω/□) coated glass. The electrochemical bath used for the electrodeposition of CuInTe₂ thin films consisted of aqueous solution mixture of 0.025 M CuCl₂, 0.1 M InCl₃ and pre-reacted 0.01M tellurium with HNO₃. Linear and cyclic sweep voltammograms were analysed to find out the suitable deposition potentials and growth parameters. Acetonitrile was added as a supporting electrolyte and growth was carried out at the constant deposition potentials of -350 mV and -450 mV with and without stirring. X-ray diffraction (XRD) results obtained in this work show films that were grown under stirring conditions are more oriented in the (112) direction. CuInTe₂ were also analyzed by scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX). SEM study revealed the formation of uniformly covered nanoflakes of 40-50 nanometers in width and compositional analysis show that CuInTe₂ film grown had an excess of indium content, but (Cu %+In%):Te% is close to stoichiometry.

Keywords: CuInTe₂, Electrodeposition, XRD, SEM, Thin Films, Solar Energy Materials

1. Introduction

Ternary chalcopyrite semiconductors thin films are of considerable interest because of their potential for application in variety of opto-electronic devices such as lightemitting diodes, infrared detectors, optical parametric oscillators, upconverters and IR generators [1-3]. CuInTe₂ belongs to the category of I-III-VI₂ chalcopyrite semiconductors, which have a direct band gap varying between 0.92 eV and 1.02 eV, which falls in the optimum range for terrestrial solar energy conversion. The direct band gap nature of this semiconductor minimizes the requirement for long minority carrier diffusion lengths and owing to its high absorption coefficient, it requires only a few tenth to a few micron of thickness to make devices, thus minimizing the cost of material [4-8]. CuInTe₂ crystallizes in the tetragonal chalcopyrite structure; however, sometimes, the cubic sphalerite phase, a disordered form of the chalcopyrite is observed. CuInTe₂ results from the stacking of two cubic zinc blend structures along the z-axis. The primitive cell for this structure is made up of eight tetrahedrons with shared vertices, so that the whole cell is just two stacked cubic structures. By

convention, the short edge is labelled 'a' and the long edge is labelled 'c'. This gives rise to the condition that, given perfect tetragonal symmetry, $c/a = 2$. A chalcopyrite primitive cell contains three different atoms, two cations (A and B) and one anion (C). If these atoms arranged so that each C anion has two a cations and two B cations as nearest neighbours, the resulting structure is chalcopyrite. In CuInTe₂, each group I (Cu) or group III (In) atom has four bonds to the group VI atom (Se or Te). In turn each Te atom has two bonds to Cu and two to In. The tetrahedral structure becomes distorted due to differing bond strength between I-VI and III-VI atoms, so the value of c changes relative to a. The measure of this distortion can be described by the quantity, $(2 - c/a)$. In the past, CuInTe₂ have been grown using various techniques such as flash evaporation [9-10], pulsed laser deposition [11], three-source co-evaporation technique [12], bridgeman technique [13], thermal vacuum evaporation [14] and electrodeposition [15-17]. In the present work, we report the growth and characterization of CuInTe₂ thin films using the electrodeposition technique. Electrodeposition is a simple technique with high material utilization and is suitable for fabricating large-area devices without

requiring a vacuum system. It is an isothermal process, which can be used to control the composition, morphology and film thickness by only varying the electrical parameters [18-20]. In electrodeposition, liquid phase changes to solid phase, and nature prefers this transition whereas in other techniques like MBE and MOCVD, the phase changes occur directly from gas to solid during the materials growth process [21]. Growth of semiconductor compounds using dry techniques requires high growth temperature whereas electrodeposition can be done at room temperature. Apart, from this electrodeposition has also few cons like this technique always requires a conductive (metal) surface and the coating bath should be checked and maintained frequently in order to get a reproducible process.

2. Experimental Details

CuInTe₂ thin films were grown using three electrodes namely, glass coated fluorine doped tin oxide (SnO₂) as substrate or working electrode, carbon rod as the counter electrode and silver chloride (AgCl) as reference electrode. First the SnO₂ layers were prepared on glass slides to form working electrode used in this work by spray pyrolysis method, which is a simple and low-cost technique and can be used to grow high-conducting and transparent layers of SnO₂. This process basically consists of a compressor, oxygen gas filters, which are connected through a flow meter to a glass sprayer contained the fluorine doped SnCl₂ solution. Glass slides cleaned with chromic acid, liquid soap and distilled water followed by ultrasonic cleaning were used as substrate. Oxygen as a carrier gas was passed through the sprayer containing SnCl₂ and then spray was carried over the substrates, which were kept on hot plate. Inside the heating Cl₂ evaporates and reaction occurs within each particle to form SnO₂ particles. By this process SnO₂ film can grow uniformly at very low flow rates. These films were grown at various substrate temperatures ranging from 300°C--500°C. The electrochemical bath used for the electrodeposition of CuInTe₂ thin films consisted of aqueous solution of mixture of cupric chloride (CuCl₂·2H₂O) 0.025 M, indium chloride (0.1M) and pre-reacted tellurium (0.01M) with HNO₃, and acetonitrile was added as a supporting electrolyte. Indium chloride (InCl₃) was prepared by heating metallic indium with concentrated HCl at around 60°C. The process yields a concentrated solution of InCl₃ and by adding the distilled water, required concentration can be obtained. Linear and cyclic sweep voltammograms were analysed to find out the suitable deposition potentials and growth parameters. The deposition was performed at the constant potentials of -350 mV and -400 mV versus AgCl. The pH of the bath was maintained at around 1.4 and deposition was carried out with and without magnetic stirrer. The compositional ratio selected for the deposition of CuInTe₂ thin films was 1:4:2 with 10 ml volume of acetonitrile added to obtain highly adhesive films and to obtain the final bath. A computer-controlled potentiostat (EG &G PARC model Versastat II) was used for

the cyclic and linear voltammetry studies, as well as for the electrochemical deposition of the CuInTe₂ thin films. Ternary films grown by the electrodeposition method generally have poor crystallinity. The crystallinity of prepared films can be improved by annealing them either in vacuum or in an inert atmosphere. In our case, CuInTe₂ films were grown at room temperature for 15 min after which they were subjected to annealing in vacuum at 200 °C for 1 hr. For stirring conditions, magnetic stirrer with a controllable speed was used to supply the agitation in the electrolytic bath. Teflon coated magnetic stir bar immersed in a solution was used for stirring and speed of magnetic stirrer was kept constant at 250 rpm for the growth of CuInTe₂ thin films under stirring. Structural studies of the films were carried out on a Bruker D8 Advance X-ray diffractometer. Cu-K_α radiation of wavelength 1.5406 Å was used in the XRD studies. The SEM and EDAX studies were performed on a Philips FE-SEM/EDAX Model-Quanta 200 FEG microscope.

3. Results and Discussion

We have shown in this work that deposition parameters such as growth potential and stirring play an important role in the growth of CuInTe₂ films. The linear voltammogram (LSV) and cyclic sweep voltammogram (CV) for a bath containing a mixture of aqueous solutions of CuCl₂·2H₂O, InCl₃ and pre-reacted tellurium with acetonitrile as a supporting electrolyte are shown in Figure 1(a) and 1(b), respectively.

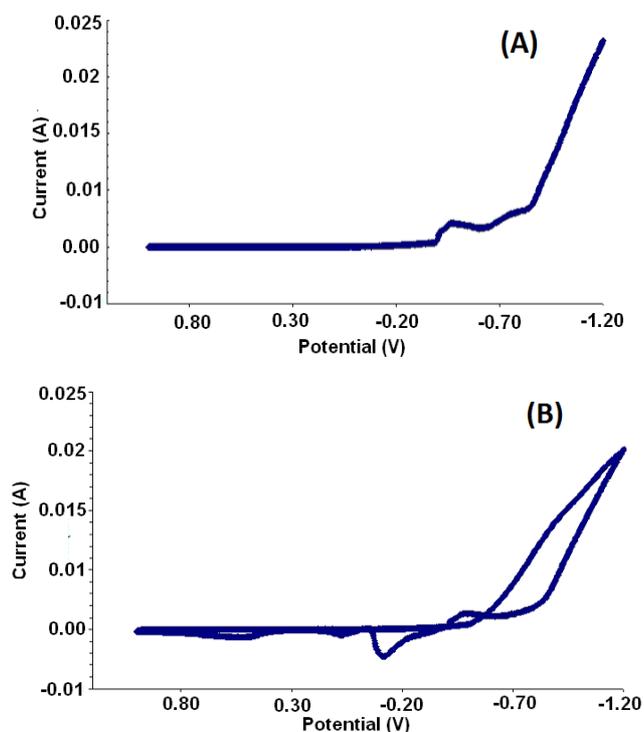


Fig. 1(a) & 1(b). Linear and cyclic Sweep voltammogram of the copper, indium and tellurium ions with using acetonitrile.

These studies are used to determine the conditions suitable for the electrodeposition of an alloy. It was observed that the deposition potentials of the constituent ions should be brought close to each other either by adjusting the ionic concentrations or by adding suitable supporting electrolyte. The reduction potential of each constituent is different, but in our case we added acetonitrile (10 cc) to merge the peaks of all constituents and to form a narrow plateau region. The LSV curve (Figure 1(a)) shows the potential corresponding to the sharp peak region extends from -250 mV to -450 mV indicating the voltage range suitable for the electrodeposition of CuInTe_2 from this bath. Hence deposition of CuInTe_2 thin films was carried within this potential range at -350 mV and -450 mV. CuInTe_2 films were also attempted after the deposition potential of -450 mV but the films could not be grown with this bath. The reverse scan in CV (Figure 1(b)) gives information regarding the species, which are stripped from the substrate and hence contain information regarding the deposit. It also shows the stripping/dissolution waves for all the three elements suggesting that all three elements Cu, In, and Te can be deposited from this bath. Structural studies of the electrodeposited CuInTe_2 thin films were studied by XRD. Figure 2 and 3 show the XRD patterns of CuInTe_2 thin films grown at the deposition potential of -350 mV and -450 mV versus AgCl, (a) without stirring, (b) with stirring, respectively.

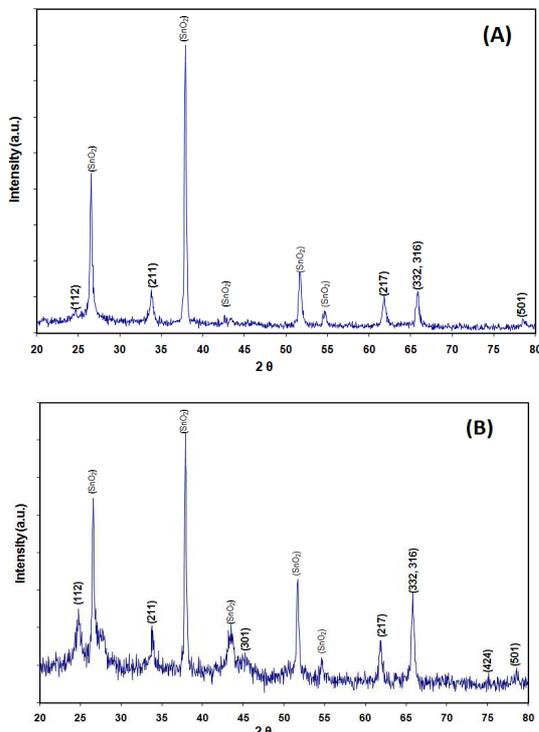


Fig. 2(a) & 2(b). XRD pattern of annealed CuInTe_2 films grown at the deposition potential of -350 mV vs AgCl (a) without stirring (b) with stirring.

The peaks are indexed and it can be seen that the main peaks are those of CuInTe_2 corresponding to (112), (211),

(301), (217), (332,316) and (501) or of the substrate SnO_2 . CuInTe_2 exhibit the chalcopyrite structure and it can be seen that the chalcopyrite peak (112) is present in Figures 2 and 3. XRD patterns reveal that those films, which were grown under stirring condition, are more prominent (Fig. 2(b) & 3(b)) in chalcopyrite peak to those which were grown without stirring (Fig. 2(a) and 3(a)).

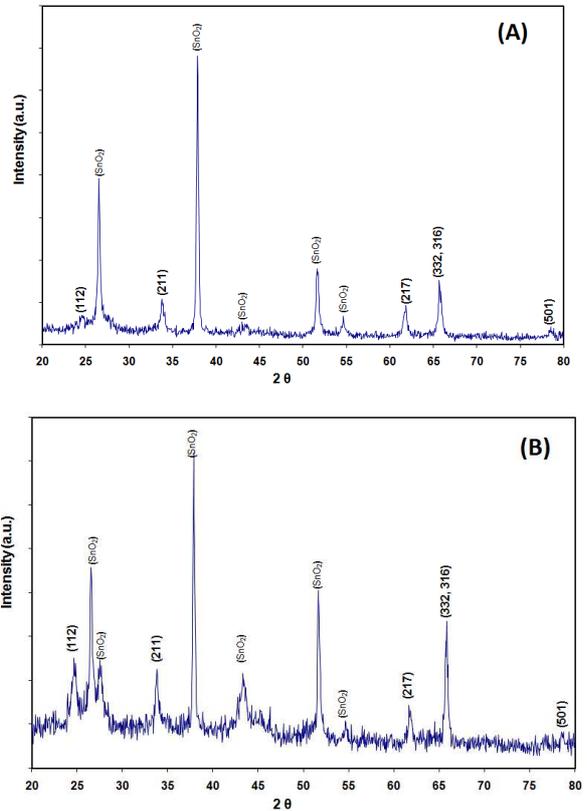


Fig. 3(a) & 3(b). XRD pattern of annealed CuInTe_2 films grown at the deposition potential of -450 mV vs AgCl (a) without stirring (b) with stirring.

SEM micrographs provide valuable information on the surface morphology of CuInTe_2 thin films. Figures 4 and 5 shows the SEM micrograph along with the EDAX analysis (shown in inset) of the CuInTe_2 films grown at the constant deposition potential of -350 mV and -450 mV versus AgCl, (a) without stirring, (b) with stirring, respectively. It can be clearly seen from the SEM micrographs that there is a formation of uniformly covered nanoflakes of 40-50 nanometers in width. Compositional analysis show that CuInTe_2 film grown had an excess of indium content (Figures 4(a) and 4(b)), but $(\text{Cu} \% + \text{In} \%):\text{Te} \%$ is close to stoichiometry. It was found that the CuInTe_2 films prepared with stirring marginally affected the composition of Cu:In:Te in such a way that, the indium content decreased but there was again formation of nano flakes of 30-40 nm in width. When the deposition of CuInTe_2 films was carried out at the negative potential of -450 mV, the copper content increased in the film (Figures 5(a) and 5(b)) and final composition of Cu:In:Te was approached to the stoichiometric ratio of 1:1:2.

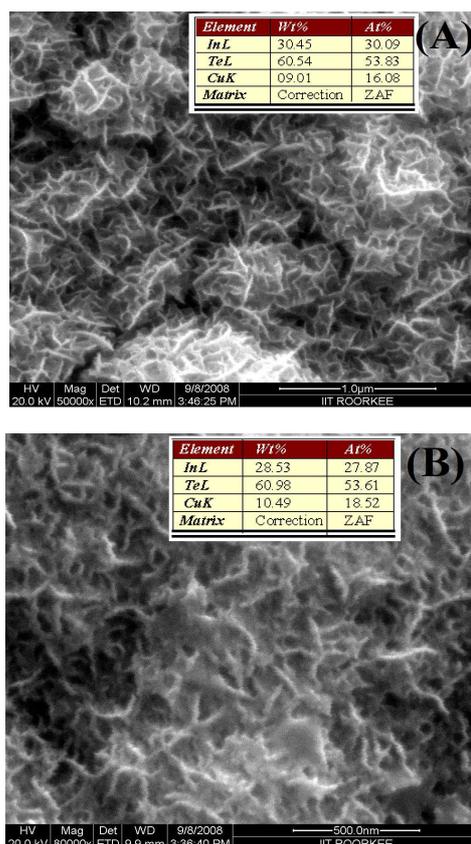


Fig. 4(a) & 4(b). SEM micrographs along EDAX in inset of the CuInTe₂ films grown at the deposition potential of -350 mV (a) without stirring, (b) with stirring

4. Conclusion

Single-phase CuInTe₂ thin films were obtained by the electrodeposition technique at different constant deposition potential with and without stirring conditions. It was observed that the CuInTe₂ films grown at the more cathodic deposition potential under stirring condition were more stoichiometric as well more crystalline to those which were grown without stirring. The overall SEM studies show that growth of nanoflakes having 30-40 nm width is uniform over the substrate.

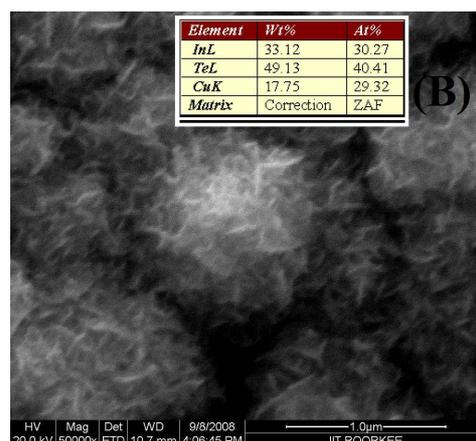
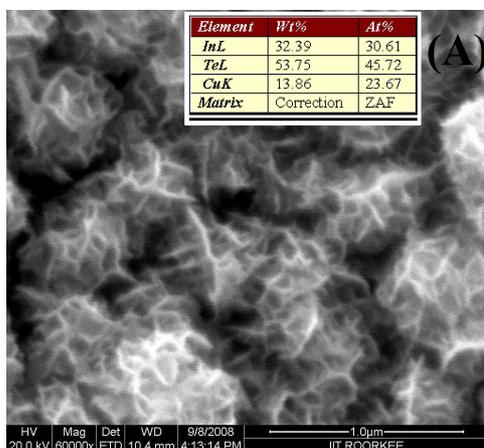


Fig. 5(a) & 5(b). SEM micrographs along EDAX in inset of the CuInTe₂ films grown at the deposition potential of -450 mV (a) without stirring, (b) with stirring

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