

# SYNTHESIS AND CHARACTERIZATION OF CuInSSe THIN FILMS BY CBD TECHNIQUE



## Physics

**KEYWORDS:** xrd, sem/edax, CuInSSe, Thin film

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### ABSTRACT

Nanocrystalline copper indium sulphoselenide (CuInSSe) thin films were deposited on glass substrate by (CBD) chemical bath deposition technique. The CuInSSe films were co-deposited from an aqueous solutions containing  $\text{CuCl}_2$ ,  $\text{InCl}_3$ , thiourea and  $\text{SeO}_2$ , and the Cu/In ratio was kept at 1.0. EDC was used as a complexing agent. The XRD, Scanning Electron Microscope (SEM), Energy Dispersive Analysis of X-Ray (EDAX) and Optical transmission studied were used to characterize the grown thin films. The deposition parameters such as pH, temperature and time were optimized.

### INTRODUCTION

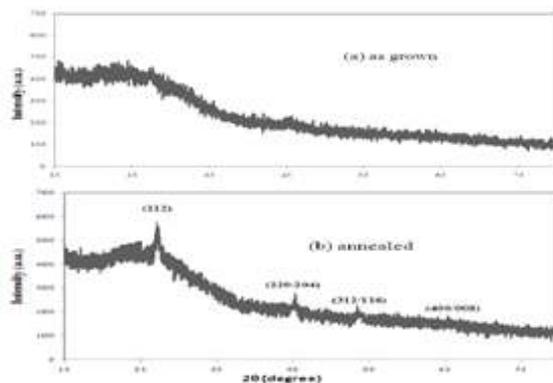
Ternary and quaternary chalcopyrite compounds have the potential for photovoltaic applications since their optical band gap lies in the range 0.8–2.0 eV, and they can be grown either n or p type [1]. Among the various materials, chalcopyrite such as  $\text{CuInS}_2$ ,  $\text{CuInSe}_2$  (CIS),  $\text{CuIn(S,Se)}_2$  (CISS), and  $\text{Cu(In,Ga)Se}_2$  (CIGS) have attracted considerable attention because of their direct band gap. These chalcopyrites have much higher absorption coefficients and only require very thin layers (1–2  $\mu\text{m}$ ) to absorb a significant fraction of the incident solar radiation [2]. Few researchers have reported on the fabrication of CuInSSe thin films using various techniques like as; sputtering [3], sulfurization and selenization [4], electrodeposition [5], spray pyrolysis [6], and solution growth technique [7]. Among these fabrication methods, CBD is a simple and low cost technique, which has been used to grow several binary and ternary alloys and semiconductors. For achieving low cost, large area production of thin films, this method is very attractive for its simplicity in instrumentation, operation, and high efficiency of material utilization. In present study, we have fabricated polycrystalline CuInSSe thin films on glass substrates using CBD method. The structural, morphological, compositional, and optical properties of the annealed CuInSSe films are investigated.

### EXPERIMENTAL

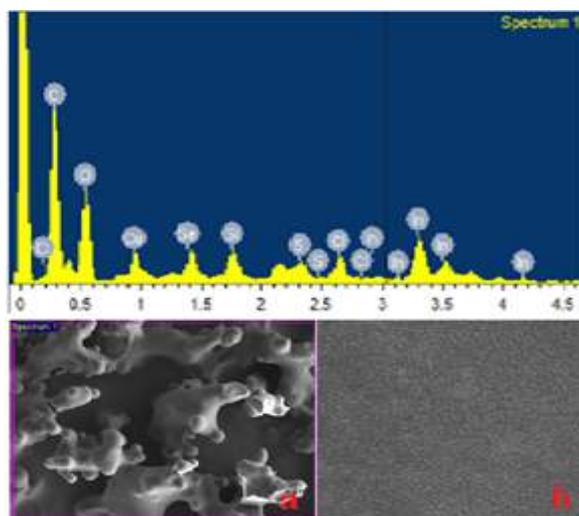
We have used glass slide as a substrate. Before deposition, the glass substrates were cleaned first by a mild soap solution, then degreased with acetone, etched with 5% of HCl for 30 min, and ultrasonically cleaned by de-ionized water and finally dried in air. The substrate cleaning is very important in the deposition of thin films. Chemicals used for the deposition of CuInSSe thin films were analytical grade.  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (CDH),  $\text{InCl}_3$  (CDH),  $\text{NH}_2 \cdot \text{CS} \cdot \text{NH}_2$  (CDH) and  $\text{SeO}_2$  (CDH) dissolved in distilled water were used as the starting solutions. The atomic ratio of Cu:In:(S+Se) in the solution was kept at 1:1:4. For the deposition of CuInSSe thin films, 20 ml of 0.05 M aqueous solution of  $\text{CuCl}_2$  was taken in a 100 ml capacity glass beaker, and 20 ml of 0.05  $\text{InCl}_3$  was added with constant stirring. Then 20 ml of 0.2 M aqueous solution of (S+Se) was added in the mixer of (Cu+In). A few mgs of ethylene diamine dihydrochloride (EDC) was added to the solution to prevent the precipitation of the selenium salt. The pH of the solution was adjusted to 10 by adding liquor ammonia. A cleaned glass substrate was positioned vertically in glass beaker with constant stirring. The films are obtained at 70 °C bath temperature for 80 minutes. The Deposited films are washed by deionized water and dried then annealed at 400 °C for 1/2 hour in vacuum. A Philips D8 advance X-ray diffractometer employing  $\text{Cu-K}\alpha$  radiation of wavelength 1.5406 Å was used for structural studies. The Scanning Electron Microscope (SEM) and Energy Dispersive Analysis of X-Ray (EDAX) studies were carried out using a Philips FE-Quanta 200 microscope and optical transmission spectra were obtained using a UV-VIS Spectrophotometer (Shimadzu UV-2450).

### RESULT AND DISCUSSION

Fig. 1 shows the XRD spectras of the (a) grown and (b) annealed CuInSSe thin films by CBD method. No peaks are observed for the (a) grown films of CuInSSe and for annealed (b) the patterns show that the films are single phase, polycrystalline, chalcopyrite structure in nature and having a preferred (112) orientation [8]. The main peaks at  $27.3^\circ$ ,  $45.4^\circ$ ,  $53.4^\circ$  and  $65.6^\circ$   $2\theta$  indicate that the synthesized material is CuInSSe and having the good agreement with the reported value (JCPDS 036-1311). No peaks were found from any other phases. The crystallite size calculated (for the (112) peak) using the Debye Scherrer formula is found to be 30–40 nm.



**Figure 1: XRD patterns of (a) grown and (b) annealed CuInSSe thin films by CBD.**



**Figure 2: SEM/EDAX micrographs of (a) grown and (b) annealed CuInSSe thin films by CBD**

Fig. 2 shows SEM and corresponding EDAX spectra of the (a) grown and (b) annealed CuInS<sub>2</sub> thin films by CBD method. The SEM micrograph reveals that the surface of the grown films has covered by particles with large grain size (a) while the size of the grain is reduced (b) after annealing the grown films at temp. 400°C for 1/2 hour in vacuum. It is clear from the EDAX micrograph that the element compositions of the annealed CuInS<sub>2</sub> thin films as follows: Cu = 23.12%; In = 26.25%; S = 28.37%; and Se = 22.26%.

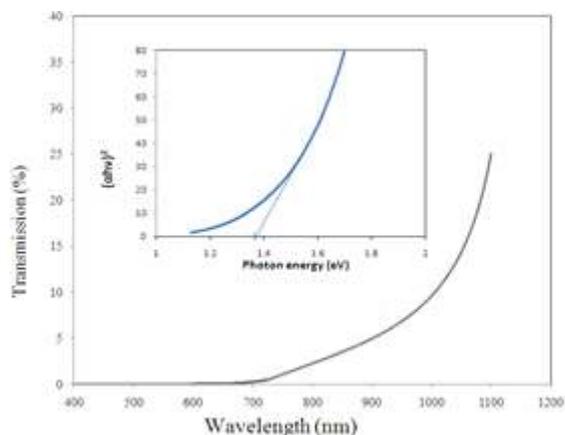


Figure 1: Transmission spectra and  $(\alpha h\nu)^2$  versus  $h\nu$  plot of annealed CuInS<sub>2</sub> thin films.

Fig. 4 shows the transmission spectra of annealed CuInS<sub>2</sub> thin films, which were recorded in the range 300–1200 nm. The presence of direct band gap was determined from  $(\alpha h\nu)^2$  against  $h\nu$  plots, obtained from the transmittance spectra. The band gap value of the films is found to be 1.38 eV

## CONCLUSIONS

Nanocrystalline CuInS<sub>2</sub> thin films were obtained on glass substrates using the chemical bath deposition technique. The grown thin films are p-type, and single phase with the chalcopyrite structure. The band gap value of the films is found to be 1.38 eV.

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