

# Characterization of Defects Levels and Their Influence on the Photoconductivity of p-Type CuInSe<sub>2</sub> Thin Films

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**Abstract**— Polycrystalline thin films of slightly Cu rich p-type CuInSe<sub>2</sub> with thickness of the order of 150nm were deposited on glass substrates by reactive evaporation at a temperature of 473±5K and pressure 10<sup>-5</sup>mbar. The prepared thin films were characterized by X-ray diffractometry, energy dispersive X-ray spectroscopy and scanning electron microscopy. Special focus is given on the good photoresponse of the film. The defect level identified during electrical conductivity measurement was explained based on the stoichiometry of the film and the estimated formation energies of defect levels possible in the compound. The slow non-exponential decay of photocurrent observed in the film was interpreted as due to the effect of trapping of charge carriers.

**Keywords**— CuInSe<sub>2</sub>, thin films, reactive evaporation, trap, photoconductivity.

## I. INTRODUCTION

CuInSe<sub>2</sub> (CIS) is recognized as a highly efficient, low cost, radiation resistant and stable absorber layer in solar cell fabrication due to its near-optimum band gap for harvesting solar energy, high optical absorption coefficient, long term thermal, environmental and electrical stability, reasonable work function and potential low cost methods in its preparation [1]. A wide variety of preparation techniques such as pulsed laser deposition [2], electroless deposition [3], chemical bath deposition [4], flash evaporation [5], spray pyrolysis [6], metal organic chemical vapour deposition [7] have been employed for the deposition of CIS absorber layer with varying degrees of success. Most interestingly, it is possible to dope CIS as n-type and p-type simply by the introduction of native defects and thereby form stable homojunctions in solar cells [8]. However, deviations from the ideal stoichiometry of CIS give rise to several donor and acceptor levels which influence its

optoelectronic properties [9].

The presence of intrinsic point defects such as vacancies, interstitials and antisite defects plays a dominant role on the optical and electrical properties of CIS. The cation vacancies or anion interstitials leads to p-type conductivity, whereas, the anion vacancies or cation interstitials leads to n-type conductivity of the film [10]. Therefore, depending on the deposition methods, especially for vacuum evaporated thin films, there are possibilities for the incorporation of a number of such defects that contribute significantly to electro-optical properties of CIS [11]. Thus it is desirable to have knowledge of the origin and nature of these defects for a better understanding of the performance of CIS based solar cells.

Hence, the present paper gives special attention on defect analysis and also on the role of the defects as shallow traps in photoconductivity of reactive evaporated CIS thin films. The as-prepared CIS thin films were characterized using X-ray diffractometry (XRD), energy dispersive X-ray spectroscopy (EDAX) and scanning electron microscopy (SEM). Results of these studies are described and interpreted.

## II. EXPERIMENTAL DETAILS

Thin films of CuInSe<sub>2</sub> were prepared by reactive evaporation, a variant of Gunther's three temperature method [12]. This technique is found to be the most successful industrial process to prepare polycrystalline CIS thin films for high efficiency solar cells, because this method provides good quality stoichiometric films with excellent reproducibility and high deposition rates.

In the present work, high purity copper (99.999%) and high purity indium (99.999%) were evaporated separately from molybdenum boats, in the

atmosphere of high purity selenium (99.99%), which was evaporated from a glass crucible kept in a molybdenum basket. After attaining a pressure of  $10^{-5}$  mbar, the vapours were allowed to deposit on glass substrates kept at a high temperature of  $473 \pm 5$  K. The details of the experimental procedure have been discussed elsewhere [13]. CuInSe<sub>2</sub> thin films were obtained with the following optimized deposition conditions:

Impingement rate of copper :  $3.5 \times 10^{15}$  atoms  $\text{cm}^{-2}\text{s}^{-1}$   
 Impingement rate of indium :  $3.3 \times 10^{15}$  atoms  $\text{cm}^{-2}\text{s}^{-1}$   
 Impingement rate of selenium:  $4.1 \times 10^{15}$  atoms  $\text{cm}^{-2}\text{s}^{-1}$

The structure of the film was analysed by XRD using Rigaku D MaxC X-Ray Diffractometer for  $2\theta$  varying from  $10^\circ$  to  $70^\circ$  with Cu-K $\alpha$  (1.5404Å) as the radiation source. The composition of the film was determined by EDAX using LINK 10000, Cambridge Instruments. The surface morphology of the film was observed by SEM using Cambridge Instrument Model no: S-360 machine. The electrical conductivity of the film was measured in the temperature range 300-423K by d.c four probe method in a conductivity cell at a pressure of  $10^{-3}$  mbar. The room temperature photoconductivity of the sample was measured by Keithley 2611A source meter. The sample was illuminated using an FSH lamp (82V, 300W). The thickness of the film was 150nm, measured using Veeco Dektak 6M Stylus Profiler. Hot probe analysis revealed the p-type conductivity of the film.

### III. RESULTS AND DISCUSSION

#### A. Structural analysis

Fig. 1 shows the XRD pattern of the prepared CuInSe<sub>2</sub> thin film.

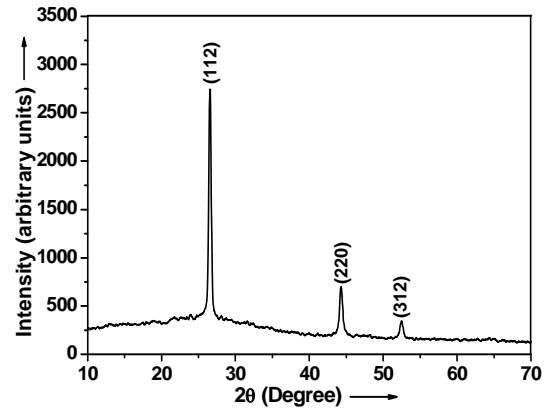


Fig. 1 XRD pattern of the prepared CuInSe<sub>2</sub> thin film

The observed inter planar spacing and (*hkl*) planes of the prepared sample were very well indexed with that of tetragonal CuInSe<sub>2</sub> (JCPDS File No. 40-1487). XRD pattern revealed the formation of polycrystalline CuInSe<sub>2</sub> thin film with preferential orientation along the (112) plane. The average crystallite size was calculated using Scherrer formula [14] and was obtained as 52 nm.

#### B. Compositional and morphological analysis

Fig. 2 and Fig. 3 show the EDAX spectrum and SEM image of the as-deposited CuInSe<sub>2</sub> thin film.

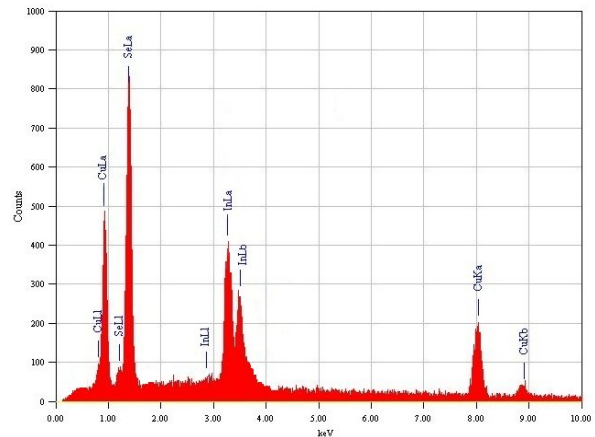


Fig. 2 EDAX spectrum of a typical CuInSe<sub>2</sub> thin film

Analysis of EDAX spectrum shown in Fig. 2 revealed that the prepared thin films of CuInSe<sub>2</sub> are slightly Cu rich, non-selenium deficient with an average atomic

percentage of Cu = 25.75%, In = 23.87% and Se = 50.38%.

The SEM image shown in Fig. 3 confirmed the significantly smooth surface of the prepared film. The surface of the film was densely packed with needle shaped crystallites without having any discontinuity. The average grain size calculated from SEM was about 150nm, an expected outcome of clustering or agglomeration of particles. This is because the grain size measurements from SEM will of course lead to a value greater than the crystallite size measured from XRD.

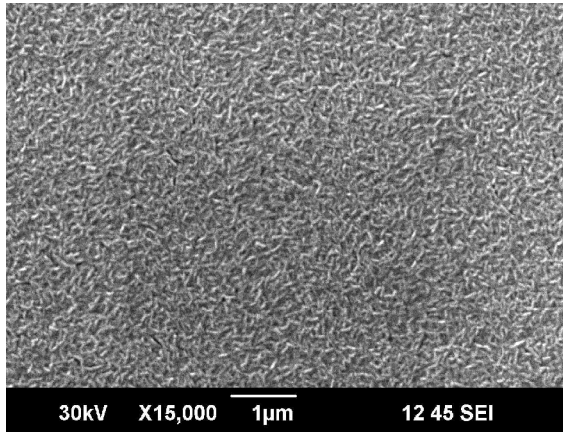


Fig. 3 SEM image of the prepared CuInSe<sub>2</sub> thin film

### C. Electrical conductivity

Fig. 4 shows the variation of ln(I) with inverse of temperature of the CIS thin film for three continuous heating-cooling cycles. The increase in current with temperature ascertained the semiconducting nature of the film.

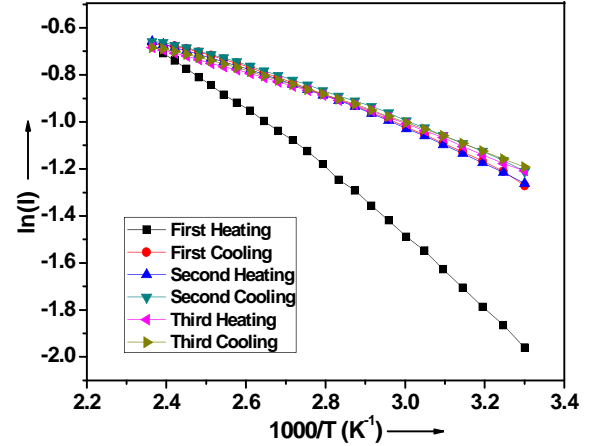


Fig. 4 Variation of ln(I) with temperature

As already mentioned, for films deposited by vacuum evaporation, there are possibilities for the incorporation of a number of defects in the film during its formation. The prepared film being polycrystalline in nature, generally have lattice defects such as vacancies, interstitials and antisites. The seven relevant defects that are possible to occur in CIS are: the vacancies  $V_{Cu}$ ,  $V_{In}$  and  $V_{Se}$ , the cation-cation antisites  $Cu_{In}$  and  $In_{Cu}$ , and the anion-cation antisites  $Cu_{Se}$  and  $In_{Se}$  [15]. The EDAX analysis showed that the prepared thin films were slightly Cu rich with an excess of Se. Since the films were of p-type, this deviation from ideal stoichiometry could lead to the existence of any of the acceptor type defects such as indium vacancy ( $V_{In}$ ), selenium interstitial ( $Se_i$ ), copper on indium antisite ( $Cu_{In}$ ) or selenium on indium antisite ( $Se_{In}$ ). So a systematic analysis of defects that are possible to occur in the sample was carried out by an examination of activation energy. It was observed that the film exhibited a thermally activated electrical conductivity ( $\sigma$ ) described by Arrhenius relation [16]

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{K_B T}\right) \quad (1)$$

where  $\sigma_0$  is a pre-exponential constant,  $E_a$  is the thermal activation energy,  $K_B$  is the Boltzmann constant and  $T$  is the absolute temperature. The activation energy which was calculated from the ln(I) versus 1000/T plot was

0.05eV. This value was in fairly good agreement with the energy of the defect level assigned to  $\text{Cu}_{\text{In}}$  ( $\sim 50\text{meV}$ ) by Polity *et al.* [15] in their study of defects in electron irradiated  $\text{CuInSe}_2$  by positron lifetime spectroscopy. Briefly, the  $\text{Cu}_{\text{In}}$  is a shallow acceptor defect responsible for p-type conductivity in slightly Cu rich, non-selenium deficient  $\text{CuInSe}_2$  thin films [17]. Hence the p-type conductivity of the as-prepared CIS thin film can be assigned to  $\text{Cu}_{\text{In}}$  defect, consistent with EDAX results.

The order of formation energies of the defects in stoichiometric/slightly Cu rich-In poor p-type  $\text{CuInSe}_2$  thin films was calculated by Zhang *et al.* [18] and is given as  $\text{Cu}_{\text{In}} < \text{V}_{\text{Cu}} < \text{V}_{\text{In}} < \text{Cu}_i < \text{In}_{\text{Cu}}$ . The defects such as  $\text{Se}_i$  and  $\text{Se}_{\text{In}}$  possess higher formation energies than  $\text{Cu}_{\text{In}}$ . Therefore, considering the order of formation energies, the possibilities of forming the  $\text{Cu}_{\text{In}}$  defect in the prepared film is higher than the other possible defects  $\text{V}_{\text{In}}$ ,  $\text{Se}_i$  and  $\text{Se}_{\text{In}}$  [15]. Hence taking into account, the stoichiometry of the film and observation of defect transition energy level at energy consistent with literature data, the defect level observed at 50meV in the present study was assigned to that of antisite defect  $\text{Cu}_{\text{In}}$ . It was thus very likely that these defects were possible candidates that give rise to shallow traps in the band gap of the material thereby leading to a non exponential decay of photocurrent observed during the photoconductivity measurements.

#### D. Photoconductivity

Fig. 5 and Fig. 6 shows the the photoresponse curve of  $\text{CuInSe}_2$  thin film at room temperature and the dependence of life time  $\tau_d$  on time. The film showed a good photo response. Photosensitivity (S) is defined as

$$S = \frac{I_L - I_D}{I_D} \quad (2)$$

where  $I_L$  is the photocurrent and  $I_D$  is the dark current. The photosensitivity of the prepared CIS thin film is calculated as 0.6 at room temperature. On illumination, the photocurrent is found to increase, indicating that the prepared film is photoconducting in nature thereby

affirming the possible use of reactive evaporated CIS thin films in photovoltaic devices.

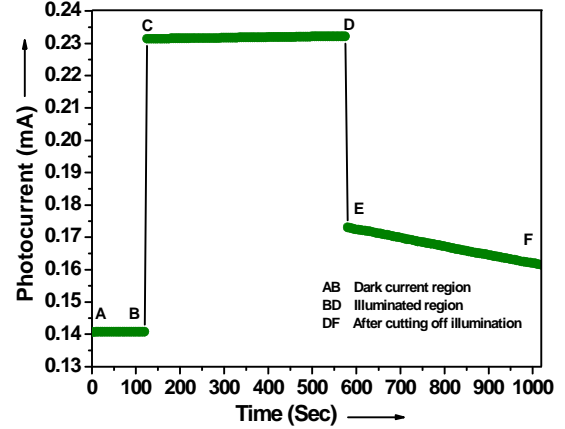


Fig. 5 Photoresponse curve of  $\text{CuInSe}_2$  thin film

In Fig. 5, the region AB represents the dark current. The increase in photocurrent on illumination can be related to the photogeneration of carriers. Soon after an increase, photocurrent showed only a slight increase from C to D during the illumination time. On the other hand, the decay of photocurrent involves two different regions- the fast decay region from D to E and the slow decay region from E to F. The fast decay was due to the sudden decrease in photo generated carriers reaching the inter-grain barrier. The slow decay was due to the gradual emptying of charge carriers from shallow traps that are likely to be present in the film. The slow non-exponential decay of photocurrent with time after cutting of illumination and the observed decrease in slope of the curve with increase in decay time clearly manifested the effect of trapping of the carriers in the defects within the band gap of the film [19].

Since the prepared sample was proved to be of p-type, the acceptor-type antisite defect  $\text{Cu}_{\text{In}}$  can be considered as a possible candidate to act as shallow traps. The stoichiometry of the film and data of electrical conductivity measurement supports this assignment. Using the differential life-time concept as suggested by Fuhs and Stuke [20] the non-exponential decay process was analysed. The life-time  $\tau_d$  is given by

$$\tau_d = - \left[ \frac{1}{I_{ph}^*} \left( \frac{dI_{ph}}{dt} \right) \right]^{-1} \quad (3)$$

where  $I_{ph}^*$  is the maximum photocurrent at  $t=0$  for a given applied voltage and was found to vary with time.

As seen from Fig. 6, the differential lifetime increased with time. This confirmed the presence of traps in the bandgap of the material, having different time constants and thereby resulting in the non-exponential decay of photocurrent.

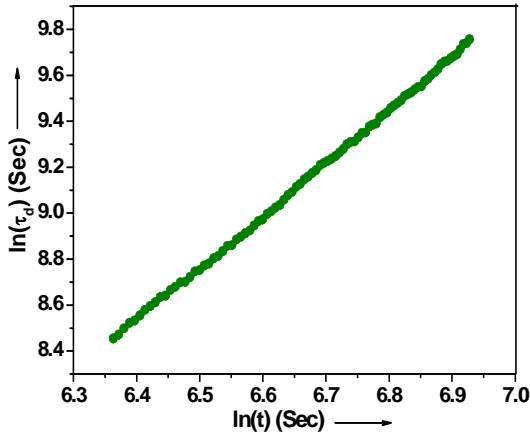


Fig. 6 Variation of  $\ln(\tau_d)$  with  $\ln(t)$  of CuInSe<sub>2</sub> thin film

Thus it can be concluded from the present study that the Cu<sub>in</sub> antisite was the dominating acceptor type defect in the investigated compound. This defect was considered to be responsible for the origin of shallow traps that readily traps minority carriers to prevent recombination with majority carriers and thereby enhancing the photocurrent. Therefore, the electrical conductivity measurement can be used as one sensitive method to track predominant native point defects related to the deviations from ideal stoichiometry of compound thin films.

#### IV. CONCLUSIONS

Polycrystalline thin films of CuInSe<sub>2</sub> were successfully deposited under optimized deposition conditions by Gunther's three temperature method. The composition of the film was found to be slightly Cu rich from EDAX studies. The defect level observed at 50meV during

electrical conductivity measurement was assigned to that of the antisite Cu<sub>in</sub>- an acceptor type intrinsic defect with low formation energy which is very likely to occur in the compound under study. The sample stoichiometry and the close correlation between calculated and estimated energy values of intrinsic defects levels supported this assignment. The observed non-exponential decay of photocurrent revealed the presence of shallow traps that are probable to originate from the Cu<sub>in</sub> antisite defect.

#### V. ACKNOWLEDGEMENTS

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