



RESEARCH ARTICLE

ELECTRICAL CHARACTERIZATION OF CuInSe₂ THIN FILMS FOR SOLAR CELL APPLICATIONS

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ABSTRACT

Copper indium diselenide (CuInSe₂) thin films were deposited by using electrochemical deposition technique. The electrochemical parameters were optimized with the aid of cyclic voltammetry for slow scan rate. CuInSe₂ thin films were electrodeposited on FTO coated glass substrates at -0.6 V and -0.8 V versus Ag/AgCl reference electrode. The films were thermally treated at 400 °C for 15 minutes to improve the homogeneity and degree of crystallinity. The electrical properties have been studied with the help Autolab potentiostat/Galvanostat.

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INTRODUCTION

One of the leading examples of photovoltaic cell is CIS/CIGS based solar cell. CIS absorber layer having chalcopyrite crystal structure with optimal band gap 1.05 eV and high optical absorption coefficient $\sim 10^5$ /cm² suitable for high efficiency thin film solar cell development. It consist of elements from different group from the periodic table; Cu from Group I, In from Group III and Se from Group VI. The crystal structure of CuInSe₂ is shown in Figure 1. CIS and CIGS are polycrystalline form, non-radiative recombination centers can be strongly suppressed, leading to its ability to be used in photovoltaic applications. Copper indium diselenide (CuInSe₂) thin films have been deposited by electrodeposition technique on FTO coated glass substrates of sheet resistance 15–20 Ω/sqcm. In the electrodeposition process, conventional three-electrode electrochemical cell was consisting of FTO as a working electrode, graphite as a counter electrode and Ag/AgCl as a reference electrode (Pandey *et al*, 1996). Following flow chart1 shows the procedure to electrodeposits CIS thin films in various precursors.

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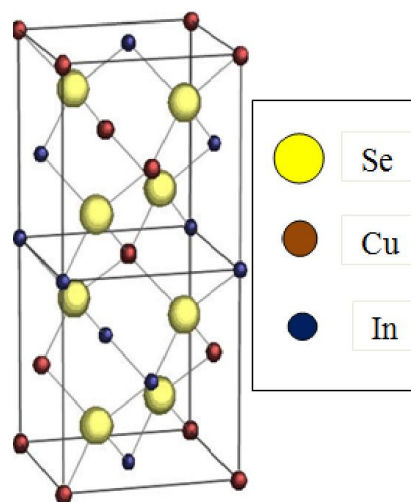
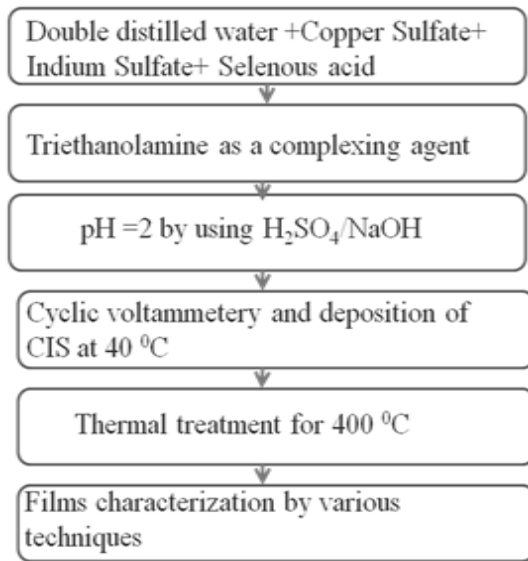


Fig. 1. The chalcopyrite crystal structure of CuInSe₂

The ionic source for Cu, In and Se were used as CuSO₄ 5H₂O, In₂(SO₄)₃ 5H₂O and H₂SeO₃, with chemical composition 0.02 M, 0.04 M and 0.008 M, respectively. For co-deposition of Cu In and Se, Triethanolamine (TEA) was used as complexing agent. The role of TEA is to form the complex with noble element and slow down the deposition rate of the same.

Triethanolamine is also helps to improve the adhesion of film (Rabchynski *et al.*, 2004; Dhanwate *et al.*, 2013).



The above precursors were dissolved in double distilled water with continuous moderate stirring. The pH of bath was adjusted ~ 2 using H₂SO₄ or NaOH. Cyclic voltammetry and deposition of CuInSe₂ layers were carried out using $\mu 3$ AUT 70762 AUTOLAB potentiostat/galvanostat of working temperature ~ 40 °C without stirring. A typical current density-voltage (J-V) characteristic of ITO/CIS/Al Schottkey barrier diodes are shown in Figure 2. JV curve clearly shows that the improvement in conductivity after heat treatment which indicates the annealed sample of CIS is more conducting which may be helpful to produce light efficiency solar cells (Massaccesi *et al.*, 1996). The improvement in current indicates the decrease in grain boundaries and defects. Defect enhances recombination process. More defects mean more space charge combinations. If there were no defects present, the total diode current would be diffusion current and n, ideality factor could be 1; this will be ideal diode case (Asabe *et al.*, 2008). More defects drives n more than 1.

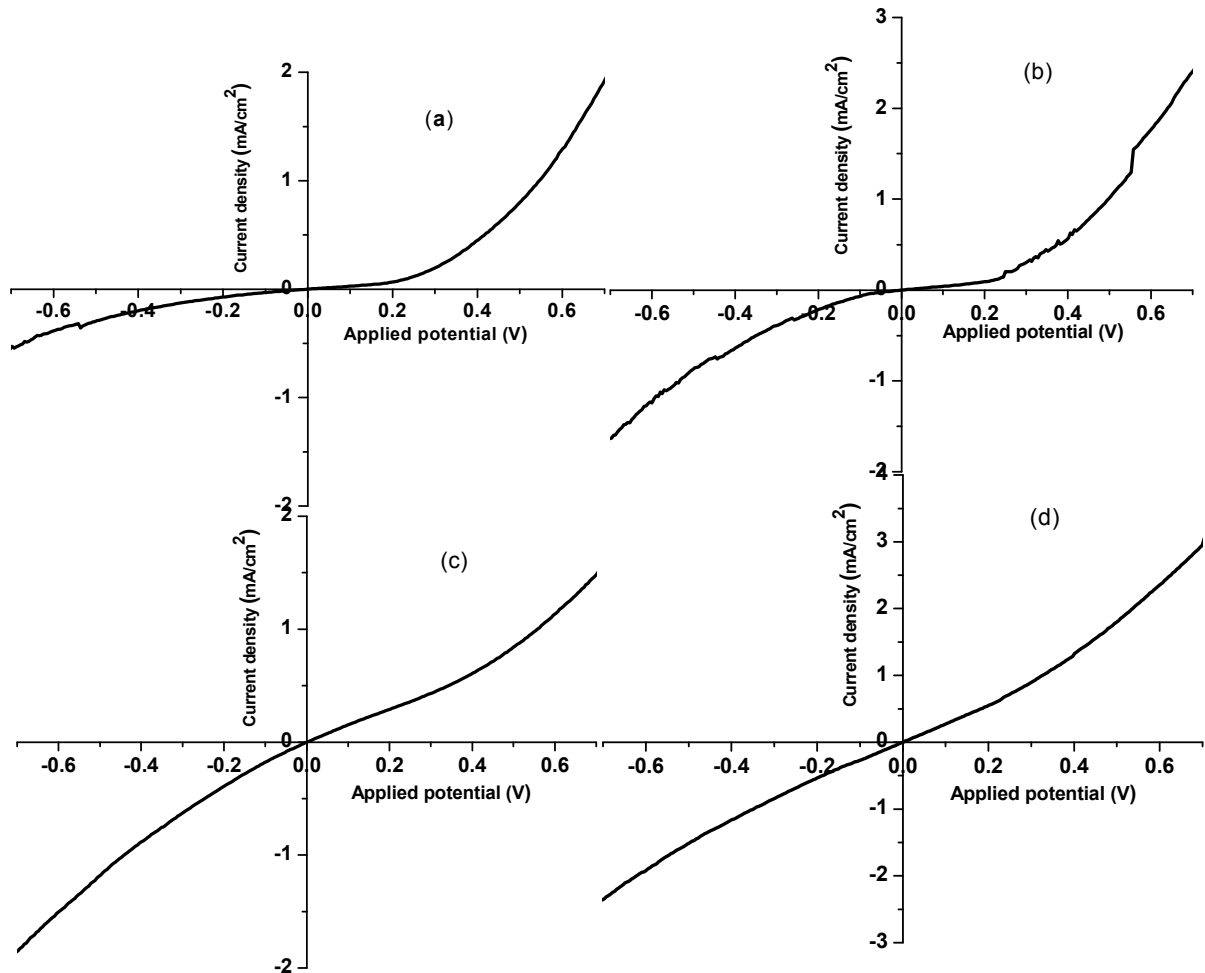


Fig. 2. J-V characteristics of CIS thin films a) -0.6 V, as-deposited, b) -0.6 V, annealed, c) -0.8 V, as-deposited and d) -0.8 V, annealed at 400 °C for 15 minutes

Table 1. Calculated values of Barrier potential and Ideality factor

Deposition potential	Condition	Barrier Height (eV)	Ideality Factor
-0.6 V	As-deposited	1.111	2.6
-0.6 V	Annealed	1.094	2.2
-0.8 V	As-deposited	1.074	2.1
-0.8 V	Annealed	1.053	1.9

Table 2. Calculated values of carrier concentrations and flat band potentials

Deposition potential	Condition	Flat band potential (V)	Carrier concentration (/cm ³)
-0.6 V	As-deposited	0.25	3 X 10 ¹⁵
-0.6 V	Annealed	0.18	5 X 10 ¹⁷
-0.8 V	As-deposited	0.28	1 X 10 ¹⁶
-0.8 V	Annealed	0.22	2 X 10 ¹⁸

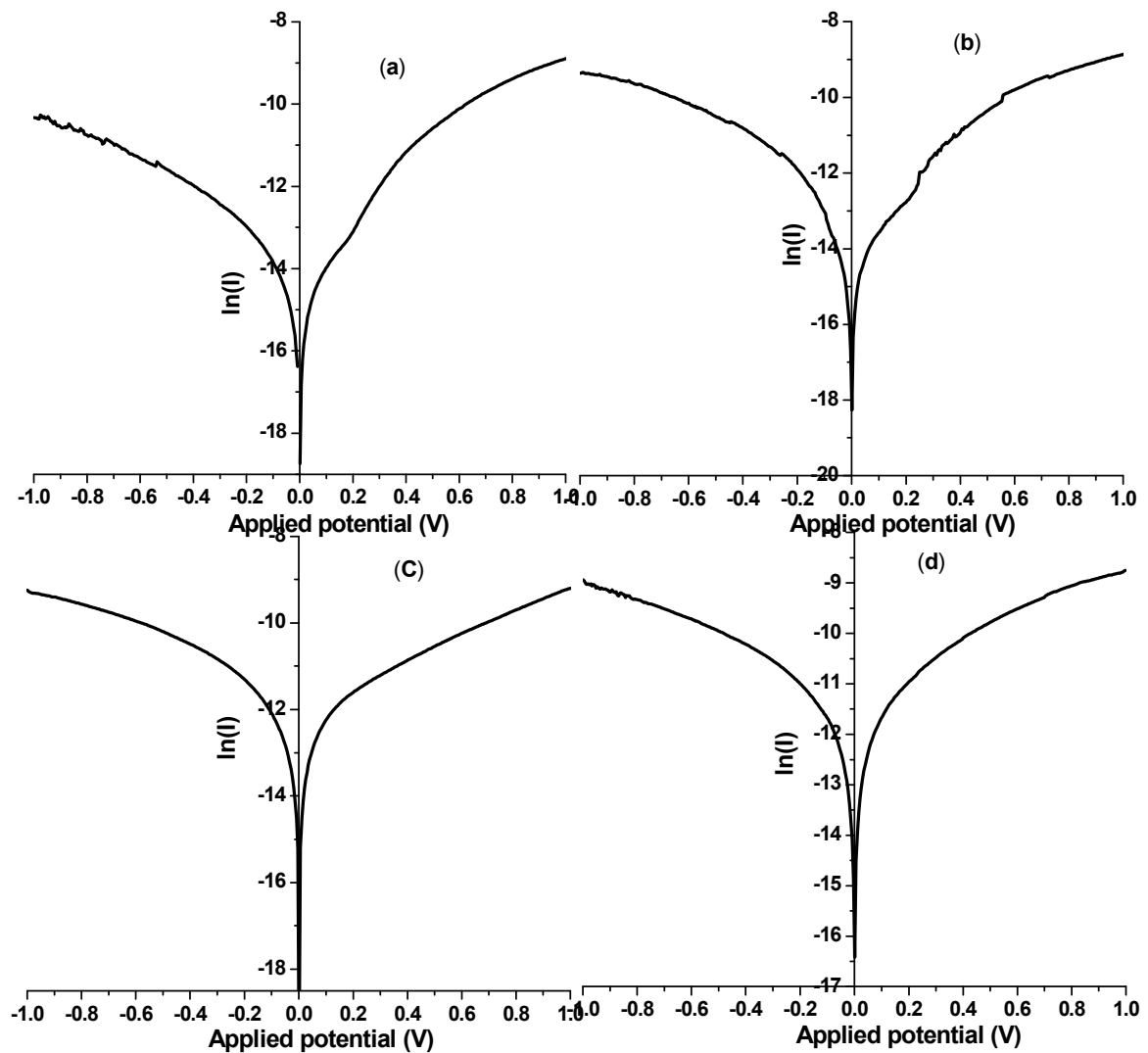


Fig. 3. Plot of $\ln(I)$ versus V of CIS of a) -0.6 V, as-deposited, b) -0.6 V, annealed, c) -0.8 V, as-deposited and d) -0.8 V, annealed at 400 °C for 15 minutes

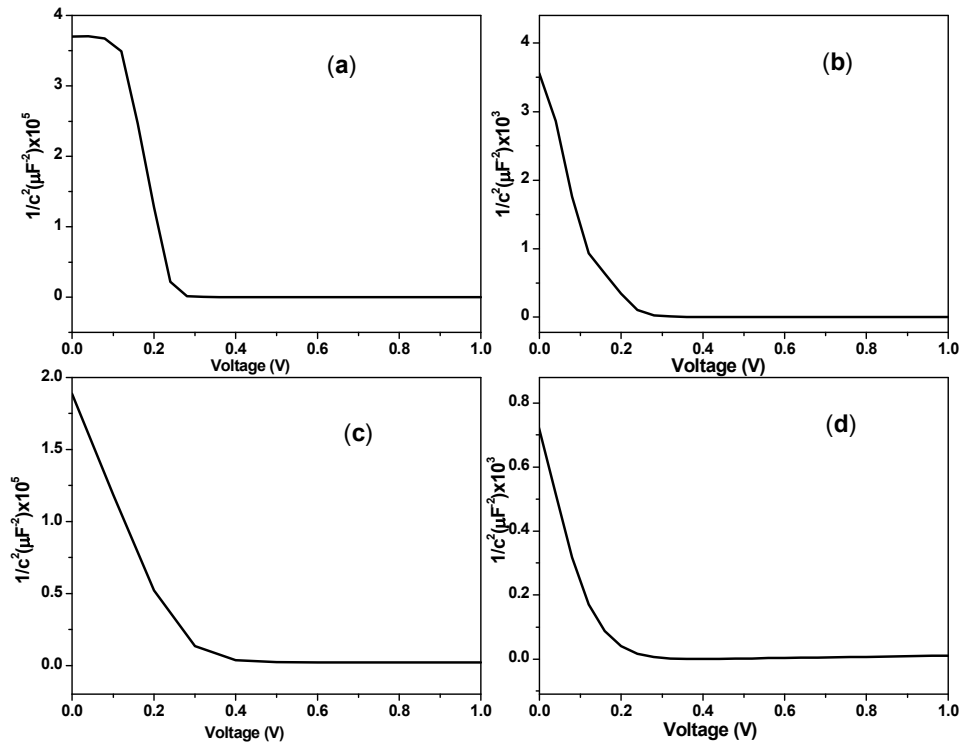


Fig. 4. Plot of CV measurements of CIS thin films a) -0.6 V, as-deposited , b) -0.6 V, annealed, c) -0.8 V, as-deposited and d) -0.8 V, annealed at 400 °C for 15 minutes

$$n = \frac{q}{nkT} \left(\frac{1}{\text{slope}} \right) \text{----- (1)}$$

n is ideality factor, q is Charge on electron, k is Boltzmann constant and T is the absolute temperature. Slope is by plotting the graph ln(I) versus V (Dhanwate *et al.*, 2015). The calculated values of barrier height and Ideality factor for the CIS is summarized in Table 1. Schottky barrier diode characteristics can be expressed as;

$$I = I_0 e^{\frac{qV}{nkT}} \text{----- (2)}$$

I₀ is reverse saturation current which is y-intercept of graph ln(I) versus V from Figure 3. Barrier potential can be calculated by the equation;

$$\phi_B = \frac{kT}{q} \ln \left(\frac{A^* T^2}{I_0} \right) \text{----- (3)}$$

ϕ_B is barrier potential, A* is Effective Richardson constant which is calculated by

$$A^* = \frac{4\pi q k^2 m^*}{I_0} \text{----- (4)}$$

h is Planck’s constant , m* is effective mass. m*/m₀ = 0.73 for CIS (Rincon *et. al*, 1999). m₀ is rest mass. Richardson constant for CIS is 8.732 x 10⁵ A/cm²/K²

The capacitance-voltage measurement is usually carried out in order to estimate doping concentration of the semiconductor. Flat band potential is used as characteristics potential of individual semiconductor electrodes in the same way as the potential of zero charge is used for metal electrodes and the flat band voltage of the Schottky diode. The C-V characteristics of all the CIS thin films involved three distinct region inversion, depletion, and accumulation, Semiconductor doping concentration can be calculated by the equation (Sze, 2009).

$$N_A = \frac{2}{q \epsilon A^2 \left(\frac{d(1/C^2)}{dV} \right)} \text{----- (5)}$$

NA is doping concentration of semiconducting material, q is charge on electron, ε is permittivity of the material and slope is obtained from graph 1/C² versus V in Figure 4. After the heat treatment C-V plot shows decrease in flat band potential and increase in carrier concentration of CIS thin films (Giulio *at et al.*, 1987). Flat band potential is determined by extrapolation to C = 0 which are in Table 2. Anodic flat band potential indicates that material is P-type material, as the concentration of acceptors increases).

Conclusion

CuInSe₂ thin films have been deposited on FTO coated glass substrates by cathodic electrodeposition technique at temperature 400 °C. The films deposited at cathodic potential -

0.6 V and -0.8 V. Both as-deposited and thermally treated films were highly compact with uniform and very well adherent to the substrates. The Schottky behavior with high cathodic current density observed in both samples indicates the deposition of high mobility semiconductor thin. Anodic flat band potential indicates that material is P-type material, as the concentration of acceptors increase. After the heat treatment C-V plot shows increase in carrier concentration of CIS thin films

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