

# Electrodeposition Of CuInSe<sub>2</sub> Thin Films For Renewable Energy Source Applications

Ranjana Sharma, Dixit Prasher, Deepesh Bhardwaj

**Abstract:** In the present work the thin films of CuInSe<sub>2</sub> were grown by electrodeposition technique on highly conducting tin oxide (Fluorine doped) sprayed over glass substrate and stainless steel substrate. CuInSe<sub>2</sub> thin films were deposited on various substrates using an aqueous bath containing Copper chloride, Indium chloride and selenium dioxide in appropriate ratio and pH of the bath was kept at 1.50 using few drops of Hydrochloric acid. To get the structural information, CuInSe<sub>2</sub> thin films were undergo X-ray diffraction (XRD) technique. Morphological and compositional investigations were done using scanning electron microscopy (SEM) attached EDAX. The result obtained revealed that films grown are highly adhesive to respective substrates and are of good quality. SEM micrograph shows that the grown particles are shaped as a nanoflakes when grown on FTO. The surface of the flakes distributed to a length of microns range but the width of a flake has a nano range. However for CuInSe<sub>2</sub> thin films grown on steel substrate, the morphology is drastically changed, the particles in this case are oval shaped with near stoichiometric atomic % ratio. It was found that CuInSe<sub>2</sub> thin films grown on stainless steel were p-type where as those grown on FTO were n-type in nature.

**Index Terms:** CuInSe<sub>2</sub>, Thin films, Cyclic Voltammogram, SEM, XRD.

## 1 INTRODUCTION

Presently, CuInSe<sub>2</sub> is the leading material for the fabrication of solar cells due to its high value of optical absorption coefficient ( $>10^5 \text{ cm}^{-1}$ ) and band gap of around 1.0 eV. It is direct band gap material and belongs to the family of copper based chalcogenide semiconductor. In recent years some members of this family have gained considerable attention because of their potential applications, mainly in opto-electronic devices, non-linear optics and solar cells [1-7]. In particular solar cells fabricated using CuInSe<sub>2</sub> are already reported to reach efficiencies above 18% in laboratory cells [8-9]. The Electrodeposition technique has developed into a competitive process for fabricating low cost thin film photovoltaic cells. Nearly all photovoltaic materials can be electrodeposited; however, no significant effort was devoted to obtaining photovoltaic quality material until a few years ago. Electrodeposition is an easily automated and controlled process that could be expected to produce photovoltaic cells in sufficient quantity to have an impact on solar to electrical energy conversion by the end of this century. There are various factors on which the electrodeposition of the required film depends such as concentration of various chemicals in the bath, suitable deposition potential, current density, bath temperature, and pH of the solution. Electrodeposition is an easily controlled and automated process. All these parameters can be optimized easily for a single metal deposition. The different metals have different Reduction/oxidation potentials, so co-deposition of different metals is quite difficult to form various alloys. Now, It is necessary to bring the reduction potential of different metals at single deposition potential which can be possible by varying deposition parameters (10-14).

Electrodeposition is based on two/three electrodes system and a very economical method. This technique is very easy to operate, requires less wastage of material and frequently used to fabricate low cost thin films and its instrumentation is very attractive [15-17].

## 2 EXPERIMENTAL DETAILS

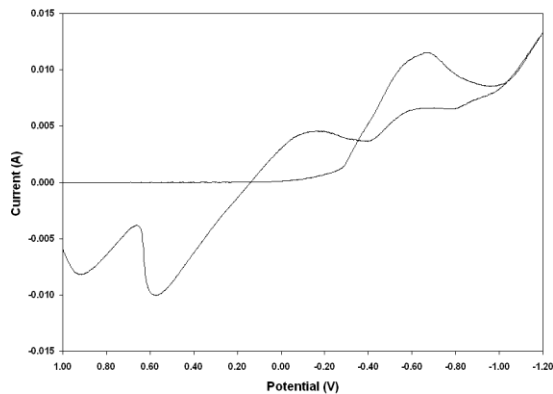
The three electrode system were used for the co-deposition of Copper ions, Indium ions and Selenium content by electrodeposition method. The saturated calomel electrode (SCE) was used to keep the potential of bath constant and named as a reference electrode, to measure the bath potential platinum electrode was used and refer as counter electrode. For the electrodeposition of CuInSe<sub>2</sub> thin films highly conducting tin oxide (Fluorine doped) sprayed over glass substrate and stainless steel substrate were used and refereed as a working electrode. The aqueous bath for CuInSe<sub>2</sub> thin films consisted of .020M CuCl<sub>2</sub>, .005M InCl<sub>3</sub> and 0.020 SeO<sub>2</sub> with 1:3:1 ratio for Cu:In:Se contents and for stainless steel ratio was 1:5:3. To get the suitable potential for the growth of CuInSe<sub>2</sub> thin films cyclic voltammogram was recorded using computer controlled potentiostat and same set up was used for the co-deposition of required ions. The Voltammetry graph shows the plateau region at around -650mV and the same potential was chosen for the deposition versus a saturated Calomel Electrode (SCE). The growth of the films were carried out at room temperature and pH of the bath was kept at 1.50 using few drops of Hydrochloric acid. After electrodeposition, the CuInSe<sub>2</sub> films were vacuum annealed at 300 °C to improve the crystallinity of the film for two hours. X-ray diffractometer was used to get the structural information of the films and model of the XRD instrument used was Bruker D8 advance. Morphological and compositional studies were done on the SEM/EDAX instrument of model Philips SEM/EDAX Model - Quanta 200 FEG.

## 3 RESULTS & DISCUSSION

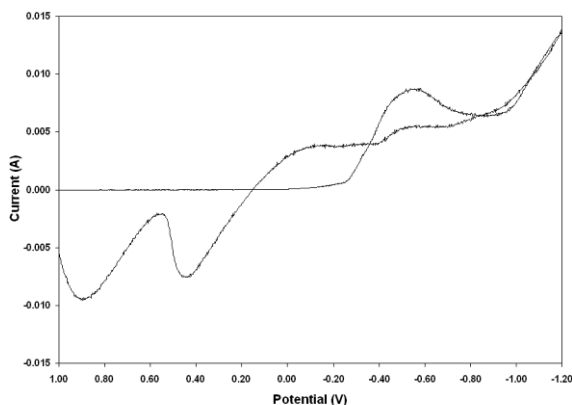
Fig 1 shows the cyclic voltammogram of the copper, indium and selenium ions on FTO substrate when the bath composition was kept at 1:3:1. It can be seen that the reduction of the ions begins from -290 mV and a plateau region is formed. It is also observed that the oxidation peaks are at -790 mV, -390 mV, +590 mV and +930 mV respectively.

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When the  $\text{CuInSe}_2$  films were grown at various potentials from  $-500$  mV to  $-600$  mV with the bath composition kept at 1:3:1, it was found that films grown were not good in stoichiometry. Therefore, the deposition of  $\text{CuInSe}_2$  films for bath composition of 1:3:1 was attempted at  $-650$  mV for 20 minutes. Fig 2 shows the cyclic voltammogram of the copper, indium and selenium ions on stainless steel substrate when the bath composition was kept at 1:3:1. It can be observed from the Fig.2 that as the selenium content increases, the reduction of the ions now begins from  $-260$  mV and again the plateau region is formed. It can be seen that the oxidation peaks are at  $-700$  mV,  $-380$  mV,  $+460$  mV and  $+900$  mV respectively. The voltammogram clearly depicts that as the selenium content increases the reduction region is shifted towards positive potential, whereas the oxidation peaks which were at negative values are shifted towards the positive potential direction and the oxidation peaks which were on the positive side are shifted towards negative side and the grown  $\text{CuInSe}_2$  films are rich in copper content.



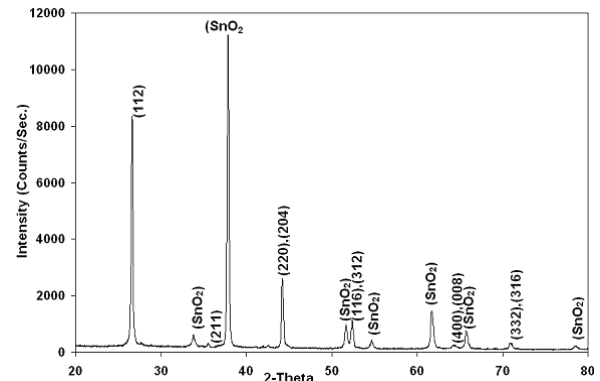
**Fig. 1:** Cyclic voltammogram of the copper, indium and selenium ions on FTO substrate.



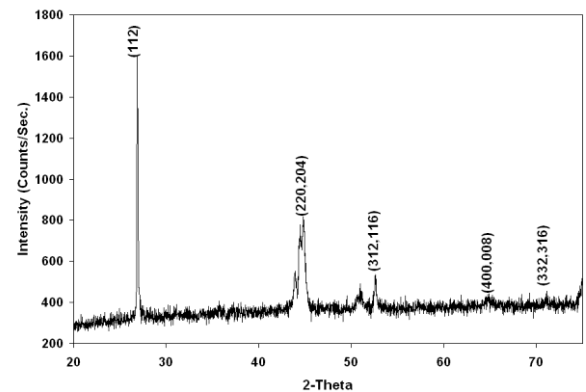
**Fig. 2:** cyclic voltammogram of the Cu, In and Se ions on stainless steel substrate.

Fig. 3 depicts the XRD peaks of a annealed  $\text{CuInSe}_2$  films deposited on FTO glass substrate at a cathodic potential of  $-650$  mV [12]. The XRD pattern shows very sharp  $\text{CuInSe}_2$  peaks and some of the substrate ( $\text{SnO}_2$ ) indicating the good quality and formation of single phase  $\text{CuInSe}_2$  having the (112) orientation. The films possess good crystallinity and have crystallized in the chalcopyrite phase, which is observed from

the presence of (211) peak. Fig. 4 shows the XRD peaks of an annealed  $\text{CuInSe}_2$  films grown on stainless steel substrate at a deposition potential of  $-650$  mV. It can be seen that XRD pattern consists of sharp and broad  $\text{CuInSe}_2$  peaks, revealing that  $\text{CuInSe}_2$  films can also be grown on stainless steel substrate reducing the cost of material as its low cost, easily available material and it also has good conductivity, which is required for Electrodeposition.

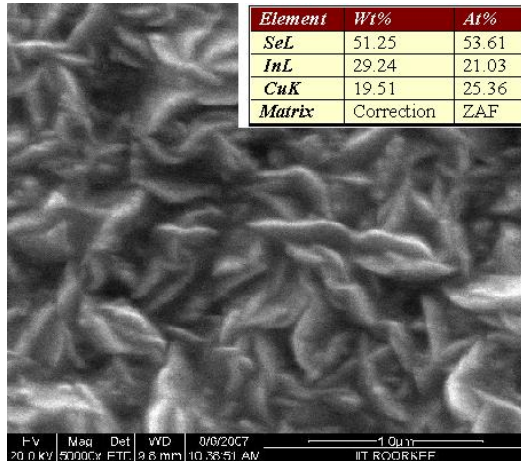


**Fig 3.** XRD graph of annealed  $\text{CuInSe}_2$  film on FTO coated glass substrate at the deposition potential of  $-650$  mV.

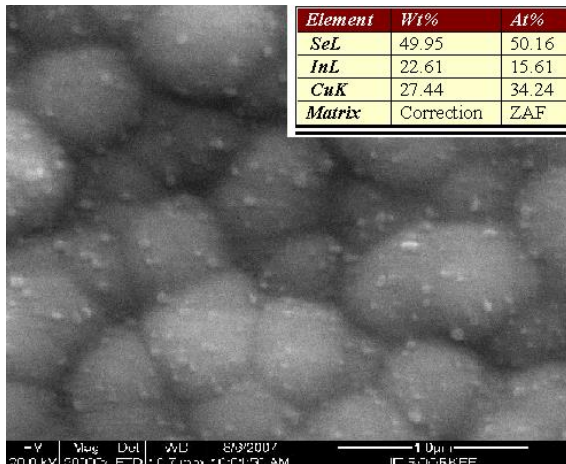


**Fig 4.** XRD of annealed  $\text{CuInSe}_2$  film on Stainless Steel Substrate at the cathodic potential of  $-650$  mV.

Fig. 5 and Fig. 6 shows the SEM pictures along with the EDAX table of electrodeposited  $\text{CuInSe}_2$  at  $-650$  mV on FTO glass [18] and on stainless steel substrates respectively. It can be seen that films on both the substrates uniformly covered with grains of size 0.1 to 0.5 microns. SEM micrographs shows that the particles are appearing in the form of nanoflakes when grown on FTO. The surface of the flakes distributed to a length of microns range but the width of a flake has a nano range. However for  $\text{CuInSe}_2$  thin films grown on steel substrate, the morphology is completely different, the particles in this case are oval shaped for near stoichiometric compositions. The ratio of Cu:In:Se is very near to the stoichiometric standard ratio of 1:1:2, revealing the formation of good quality  $\text{CuInSe}_2$  compound. Hot Probe technique was used to study the conductivity type of  $\text{CuInSe}_2$  thin films. It was found that  $\text{CuInSe}_2$  films electrodeposited on FTO glass shows n-type and on glass substrate shows p-type conductivity. Overall we can say that a good quality p-type  $\text{CuInSe}_2$  thin films can be deposited on stainless steel substrates and these films are suitable for photovoltaic applications



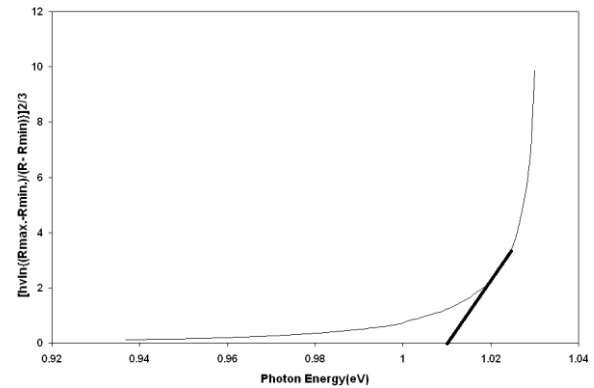
**Fig 5.** SEM alongwith EDAX table of annealed  $\text{CuInSe}_2$  on FTO glass substrate



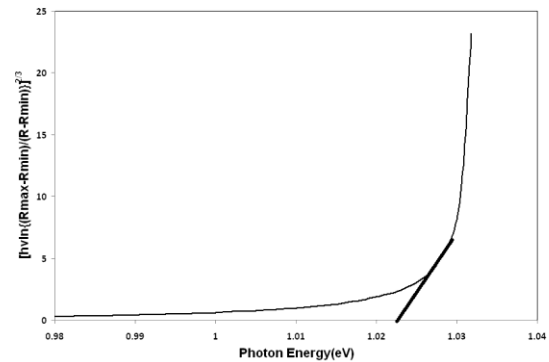
**Fig. 6.** SEM alongwith EDAX table of annealed  $\text{CuInSe}_2$  film on stainless steel substrate

It was observed from the optical studies that reflection reduced with the decrease in the wavelength. There is a sharp decrease in the reflection at or around the wavelength of 1200 nm near the absorption edge which reveals the presence of the optical direct band gap in the  $\text{CuInSe}_2$  films grown at different potential. A sharp peak occurs in the reflection spectrum at or around 1200 nm. Below this wavelength the reflection decreases and goes to minima at about 1000 nm. The energy optical gap (band gap) of the  $\text{CuInSe}_2$  films grown at  $-650\text{mV}$  on various substrates was determined using the reflection graph. The absorption coefficient,  $\alpha$ , is given by  $\alpha h\nu = A (h\nu - E_g)^{1/2}$  for direct band gap material, where  $E_g$  the energy band gap, constant A, is different for different allowed transitions, ( $h\nu$ ) is photons energy[19]. Also the absorption coefficient,  $\alpha$  is directly proportional to  $\ln \{(R_{\text{max}} - R_{\text{min}})/(R - R_{\text{min}})\}$  and is given by  $\alpha = \ln [(R_{\text{max}} - R_{\text{min}})/(R - R_{\text{min}})]/t$ , where t is the thickness of the film, R, Reflection is the the reflectance at a given photon energy,  $h\nu$ . The plot between  $(\alpha h\nu)^2$  or  $[h\nu \ln \{(R_{\text{max}} - R_{\text{min}})/(R - R_{\text{min}})\}]^2$  and  $h\nu$  (which gives the energy band gap) for the  $\text{CuInSe}_2$  films grown at

$650\text{mV}$  on various substrates are shown in Figs.7 and Fig. 8 The band gap values which are the intercepts on the  $h\nu$  axes are in the range  $1.01\text{ eV}$ - $1.04\text{ eV}$  which are near to the earlier reported band gap values of single crystal and vacuum evaporated  $\text{CuInSe}_2$  [20-23].



**Fig.7:**  $(\alpha h\nu)^2$  Vs  $h\nu$  plot for the band gap determination at the deposition potential of  $-650\text{mV}$  on FTO substrate



**Fig. 8:**  $(\alpha h\nu)^2$  Vs  $h\nu$   $\text{CuInSe}_2$  film grown at the deposition potential of  $-650\text{mV}$  on stainless steel substrate.

#### 4 ACKNOWLEDGMENT

The authors are grateful to IIC, IIT Roorkee for the XRD, SEM and EDAX studies.

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