

Selenization of electrodeposited copper–indium alloy thin films for solar cell applications

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Received: 24 June 2014 / Accepted: 25 July 2014 / Published online: 2 August 2014
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Abstract Copper–Indium (Cu–In) alloys with sulfur and selenium have technological importance in the development of thin film solar cell technology. We have used potentiostatic electrochemical technique with three-electrode geometry for the deposition of Cu–In alloy thin films in an aqueous electrolyte. Cathodic voltammetry (CV) was thoroughly studied to optimize the electrodeposition parameters. The deposition potential for Cu–In alloy was found to be in the range -0.70 to -0.85 V versus Ag/AgCl reference electrode. Polycrystalline Cu_xIn_y thin films were electrodeposited from aqueous bath at room temperature and 45°C . Effect of concentration of citric acid was extensively studied by CV measurements. The as-deposited Cu–In films were characterized with a range of characterization techniques to study the structural, morphological, compositional and electrical properties. Thin layers of Cu–In were selenized in a homemade tubular furnace at 400°C , which reveals the formation of polycrystalline CuInSe_2 (CISE) thin films with tetragonal structure. The band gap of CISE thin film was estimated ~ 1.05 eV by optical absorption spectroscopy. Nearly stoichiometric CISE thin film, Cu = 25.25 %, In = 26.48 % and Se = 48.27 % was obtained after selenization. The linear behavior of current density–voltage (J–V) was observed for Cu–In alloy thin films whereas, the selenized Cu–In alloy films (CISE) possess rectifying properties.

1 Introduction

I-III-VI group semiconductors with chalcopyrite structure have attracted considerable importance in the field of thin film photovoltaic technology. Particularly, Copper indium diselenide (CISE) and copper indium disulphide (CIS) are promising materials as absorber layer in photovoltaic devices because of its direct band gap and high absorption coefficient [1, 2]. The highest efficiency of CuInGaSe_2 based solar cell ~ 20.8 %, has been reported using the co-evaporation of Cu, In, Ga and Se [3]. Various methods have been used for the deposition of CISE and CIS thin films such as, molecular beam epitaxy [4], chemical bath deposition [5], physical vapor deposition [6], spray pyrolysis [7], sputtering [8, 9], electrodeposition [10] etc. Among these techniques an electrodeposition (ED) is one of the low-cost techniques with numerous advantages, become the promising method for preparation of photovoltaic solar cells [10, 11]. Generally, two procedures have been adopted to deposit CISE/CIS thin films; one-step co-deposition of all elements in a single bath and selenization or sulphurization of Cu–In alloy thin films. Bhattacharya et al. [12] have reported 15.4 % power conversion efficiency by electrodeposition in conjunction with the PVD technique. The final stoichiometry was adjusted with depositing In and Ga layers by PVD technique. Often it is difficult to achieve the desired stoichiometry of ternary (CISE) and quaternary (CIGSe) semiconductor thin films suitable for the development of high efficiency solar cells by single-step electrodeposition technique due the wide differences in the redox potentials of Cu, In, Ga and Se. This problem may be defeat by using a complexing agents such as citric acid [13], triethanolamine [14], EDTA [15], etc. to co-deposit Cu, In, Ga and Se. However, the large amount of complexing agent could be the source of

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impurities, which may directly affect on the power conversion efficiency and fill factor of the final solar cell device. Furthermore, the secondary phases of Cu_xSe_y and In_xSe_y may be appeared during the post-deposition heat treatment procedure in the CISE films prepared by single-step electrodeposition technique. To overcome these issues we have deposited Cu–In alloy thin films by electrochemical route in an aqueous bath and selenized at higher temperature. Luo et al. [16] demonstrated the deposition of Cu–In alloy by pulsed laser deposition and reported the formation of $\text{Cu}_{11}\text{In}_9$ phase with metallic In deposition. The deposition of elemental Cu or In is disadvantageous, which could lead to the formation of binary phases of In, Cu and Se.

In this work, we have presented the electrodeposition of Cu–In alloy thin films in presence of various concentrations of citric acid, viz, 0 M, 0.1 M, 0.3 M and 0.5 M. The deposited layers are thoroughly characterized to study the structural, compositional and morphological properties. Subsequently, the alloy films were selenized and characterized with range of characterization techniques.

2 Experimental

For the electrodeposition of Cu–In alloy thin films, an aqueous bath containing 6 mM InCl_3 and 3 mM CuCl_2 were used. The citric acid (CA) was used as complexing agent. The concentration of CA was varied from 0 to 0.5 M. The cathodic voltammetry (CV) and electrodeposition of Cu–In alloy thin films was performed with the aid of BioLogic potentiostat/galvanostat Model SP-150. A standard three-electrode electrochemical cell consisting a fluorine doped tin oxide (FTO) coated glass substrates, graphite and Ag/AgCl as working, counter and reference electrodes, respectively was used for electrochemical synthesis. The deposition parameters were optimized by CV experiment, which was carried out without stirring at scan rate 5 mV/s. Cu–In alloy thin films were electrodeposited potentiostatically at potential -0.85 V versus Ag/AgCl in an aqueous bath in presence of 0 M, 0.1 M, 0.3 M and 0.5 M citric acid bath at room temperature (RT) and 45°C . The Cu–In alloy thin films electrodeposited at RT were found to be powdery and poor adherent to the substrates; therefore, the results obtained for bath temperature 45°C are reported. Thin films of Cu–In were selenized in a homemade selenization chamber. Films were placed in the quartz holder along with selenium ingots in an air ambient and heated at 400°C for 15–20 min. The as-prepared and selenized films were characterized with the help of X-ray diffractometer (XRD), Model, Bruker D8 advance diffractometer to study the crystal structure. A JASCO UV–Vis–NIR spectrophotometer was employed to study the

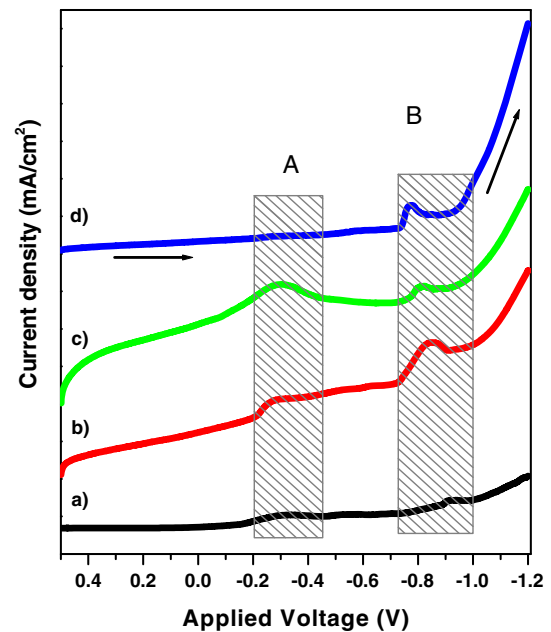
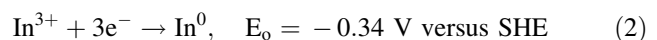
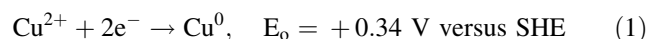


Fig. 1 Cathodic voltammograms recorded for Cu–In alloy in presence of 0 M (a), 0.1 M (b), 0.3 M (c) and 0.5 M (d) citric acid in the electrolyte. The scan rate was 5 mV/s without stirring at temperature 45°C

optical absorption properties. The topographical scanning electron microscopy (SEM) images were recorded using a JEOL JSM-6360A microscope with an operating voltage 20 kV. The same SEM attached with the EDS measurement facility was used to obtain the elemental composition of Cu, In and Se. Two probe measurement setup equipped with potentiostat SP 150 was used for J–V measurements. Prior to the electrical measurements a circular (2 mm diameter) contacts of Au (metal) were made by thermal evaporation. The electrical measurements, J–V characteristics were studied onto a glass/FTO/(Cu–In)/Au and glass/FTO/Selenized (Cu–In)/Au structures.

3 Results and discussion

Figure 1a–d shows the cathodic voltammograms recorded at scan rate 5 mV/s in an electrolyte consisting CuCl_2 and InCl_3 dissolved in double distilled deionized water in presence of 0 M, 0.1 M, 0.3 M and 0.5 M concentration of citric acid. The bath was unstirred at temperature 45°C . Two shoulders about -0.25 and -0.80 V marked as ‘A’ and ‘B’ were attributed in CV measurements assigned to the reduction of Cu and In, respectively with following corresponding charge transfer reactions;



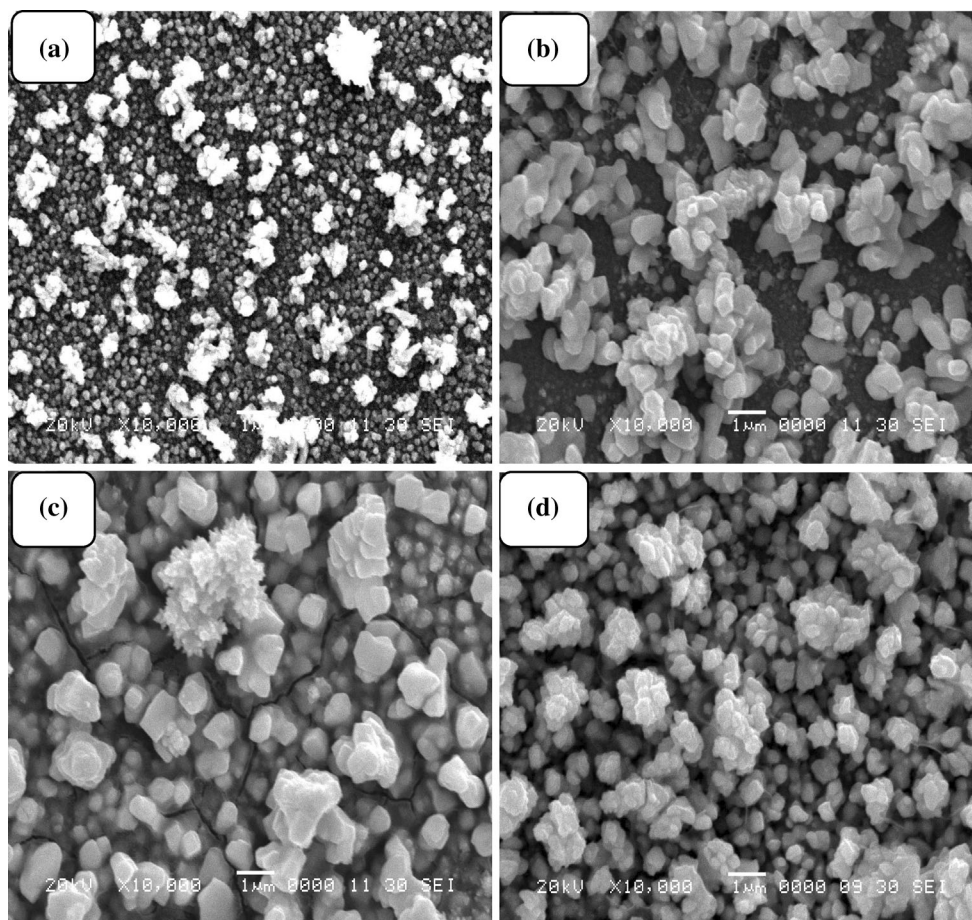


Fig. 2 SEM images of Cu–In alloy thin films electrodeposited at -0.85 V versus Ag/AgCl reference with 0 M (a), 0.1 M (b), 0.3 M (c) and 0.5 M (d) concentration of citric acid. The scale bar represents 1 micron scale

Beyond -1.0 V the sharp rise in the cathodic current was observed due to the hydrogen evolution. The plateau region observed in the range -0.6 to -0.85 V is proposed for the deposition of Cu–In alloy thin films. The CA used in the bath can reduce the deposition rate of copper by forming the complex which supports to bring the deposition potentials of Cu and In closer to electrodeposits the desired stoichiometry of Cu–In thin films with an appropriate deposition potential. It was found that the CA also helped to improve the adhesion of Cu–In alloy films to the substrate. Note that with increasing the concentration of CA in the bath the peak/shoulder associated to indium reduction has been shifted systematically towards lower cathodic potentials (closer to Cu reduction potential). A broad hump of Cu reduction revealed in cathodic voltammogram indicates that the Cu can be electrodeposited in a broad region.

Figure 2 depict the SEM images of Cu–In alloy thin films deposited at -0.85 V versus Ag/AgCl reference electrode at temperature 45 °C in presence of 0 M (a),

0.1 M (b), 0.3 M (c), and 0.5 M (d) concentration of CA. Tiny grains with some irregular shaped clusters were deposited for the film grown without citric acid. It was also observed that the films deposited without CA were powdery and not adherent to the substrate. On the other hand, the films deposited in the presence of CA were compact and well adherent to the substrate with grayish metallic appearance. The clusters of size about 1–2 micron were deposited on the uniformly deposited film (surface), probably due to the formation of highly conducting (metallic) cathode which support the higher mass transport. The similar morphology was observed by Cummings et al. [17] for Cu–In alloy thin films electrodeposited using rotating disc electrode at -0.85 V versus SCE in presence of sodium tartrate as complexing agent. The compositional analysis of all the films was studied by energy dispersive spectroscopy and the results are summarized in Table 1. We found that without CA only metallic Cu was deposited at -0.85 V conversely nearly stoichiometric Cu–In alloy thin films, (Cu/In ratio = 1) were electrodeposited in

Table 1 Compositional analysis of Cu–In thin films electrodeposited at -0.85 V with different citric acid concentration obtained by EDS technique

Citric acid concentration in (M)	Elemental composition (at.%)		Cu/In
	Cu	In	
0	100	0	–
0.1	49.17	50.83	0.97
0.3	45.38	54.62	0.83
0.5	18.16	81.84	0.22

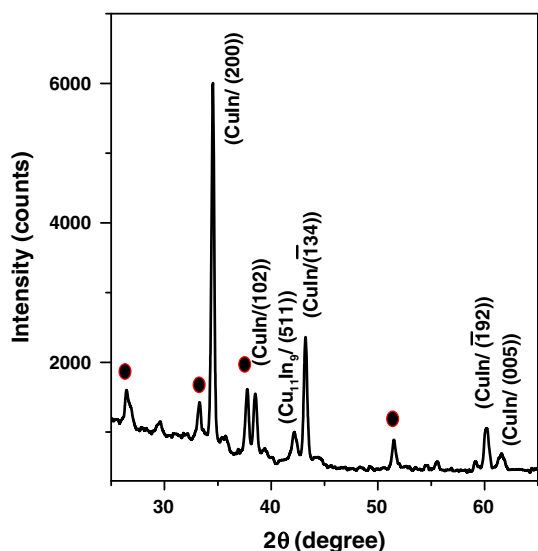


Fig. 3 XRD pattern of Cu–In alloy thin film electrodeposited at -0.85 V in presence of 0.1 M citric acid

presence of 0.1 M CA in the electrolytic bath. For higher concentrations of CA 0.3 and 0.5 M, the Cu–In alloy films were Cu deficient with Cu/In ratio, 0.80 and 0.22, respectively could be due to the complex formation of Cu with hydroxide ions.

Figure 3 shows the XRD pattern of Cu–In thin film electrodeposited at -0.85 V in presence of 0.1 M CA in an electrolytic bath. The XRD results are compared with the standard JCPDF database (file no. 35-1150 and 41-0883) of CuIn and $\text{Cu}_{11}\text{In}_9$. The results are in good agreement to the standard JCPDF data with monoclinic structure of both $\text{Cu}_{11}\text{In}_9$ and CuIn. The metallic Cu and/or In peaks were not observed in the XRD pattern. The peaks attributed from the FTO substrate are marked as solid circle (●). Calixto et al. [18] have employed electroless technique to deposit the Cu–In alloy films. They have reported the deposition of $\text{Cu}_{11}\text{In}_9$ and elemental Cu and In with average atomic percentages of Cu and In are 30.79 % and In = 69.21 %, respectively.

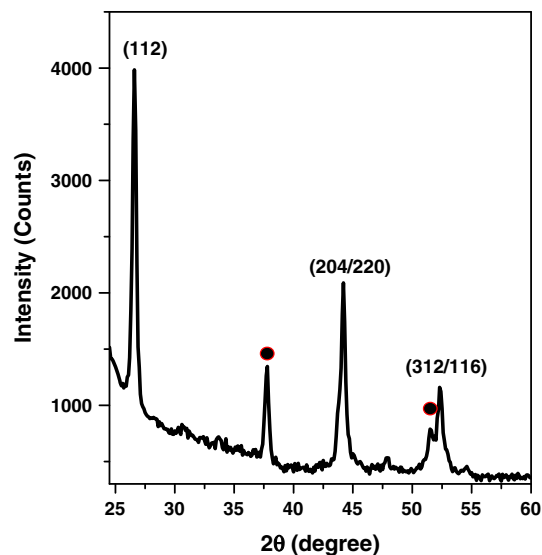


Fig. 4 XRD pattern of the selenized Cu–In alloy thin films (CISE) electrodeposited at -0.85 V in presence of 0.1 M concentration of citric acid. The peaks associated to FTO substrate are marked as solid circle (●)

respectively. However, we have obtained nearly stoichiometric Cu–In alloy thin films with 0.1 M CA in an electrolyte at -0.85 V. Furthermore, we have not observed any elemental peaks of Cu and In.

Subsequently, the part of the Cu–In film electrodeposited at -0.85 V in presence of 0.1 M CA was selenized in the tubular furnace at rotary vacuum ~ 0.005 torr in selenium atmosphere. The crystal structural of the selenized Cu–In alloy was studied using X-ray diffractometer and the resulted XRD pattern is depicted in Fig. 4. Three most prominent peaks, (112), (204/220) and (312/116) of tetragonal structure of CISE are attributed in the XRD results [19, 10]. Peaks related to FTO are marked as solid circle (●). Secondary phases like In_xSe_y , Cu_xSe_y or any other elemental related diffraction peaks were not attributed in the selenized XRD pattern of Cu–In alloy films. However, Calixto et al. [18, 20] have reported the presence of elemental Cu and In peaks separately along with CISE reflections in selenized Cu–In thin films prepared by two-step electrodeposition technique.

The optical absorption spectra $(\alpha h\nu)^2$ versus $(h\nu)$ recorded for selenized Cu–In thin film is shown in Fig. 5. The value of energy band gap was estimated to be ~ 1.05 eV which is close to the reported value of CISE [10]. SEM images of as-prepared and selenized Cu–In thin film are shown in Fig. 6a, b, respectively. Both films were compact and very well adherent to the substrates. The small grain covered with the clusters of size approximately 200 nm of CuIn alloy were imaged by SEM. The large

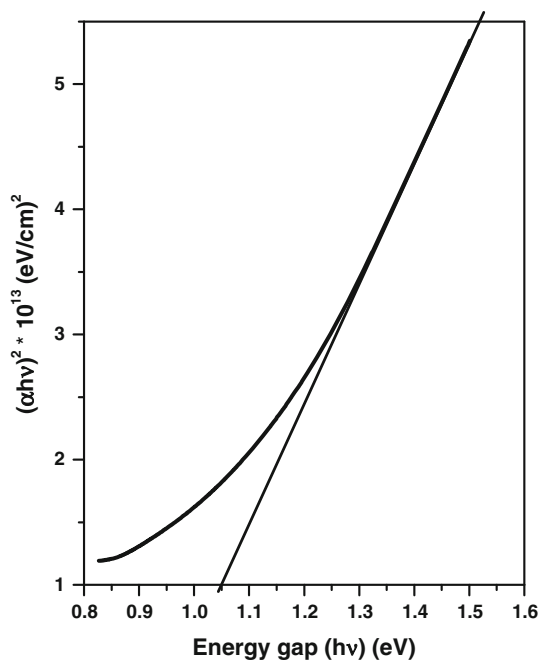


Fig. 5 Plot of $(\alpha hv)^2$ versus (hv) of selenized Cu–In thin films (CISE) electrodeposited at -0.85 V in presence of 0.1 M citric acid

grains of size about 1 to 1.5 micron can be clearly seen after selenization at 400°C for 15–20 min. The growth of non-uniform grains observed in the SEM micrograph of selenized Cu–In thin films could be due to the selenization conditions, such as vapor pressure of selenium, annealing temperature and duration, temperature gradient, etc. [17].

The compositional analysis of as-prepared and selenized Cu–In alloy thin film obtained by EDS analysis is

Table 2 A summary of the compositional analysis of as-prepared and selenized Cu–In alloy thin films electrodeposited at -0.85 V in presence of 0.1 M CA obtained by EDS

0.1 M Citric acid	Elemental composition (at.%)		
	Cu	In	Se
As-deposited Cu–In	49.17	50.83	00.00
Selenized Cu–In	25.25	26.48	48.27

summarized in Table 2. The stoichiometric composition of CuInSe_2 (25:25:50) was obtained for the selenized Cu–In alloy sample. This result supports the structural and optical data obtained from selenised Cu–In thin films.

We have studied the electrical properties, current density–voltage (J–V) characteristics of as-deposited and selenized Cu–In films deposited at -0.85 V in presence of 0.1 M CA in the bath. Figure 7a, b shows the J–V curve of as-prepared and selenized Cu–In films. The device structure geometry, FTO/Cu–In/Au and FTO/selenized Cu–In/Au used for the electrical measurement is given in inset of Fig. 7a, b. Ohmic behavior was observed for as-deposited Cu–In alloy thin film, while selenized sample (CISE) showed rectifying behavior, usually observed for semi-conductors. The semi logarithmic graph of $\ln(I)$ against the applied voltage for selenized Cu–In sample (CISE) is depicted in Fig. 8. The value of the ideality factor (η) is calculated from the slope of linear region of the forward bias J–V curve using the following equation [21],

$$\eta = \frac{q}{kT} \frac{dV}{d(\ln I)} \tag{3}$$

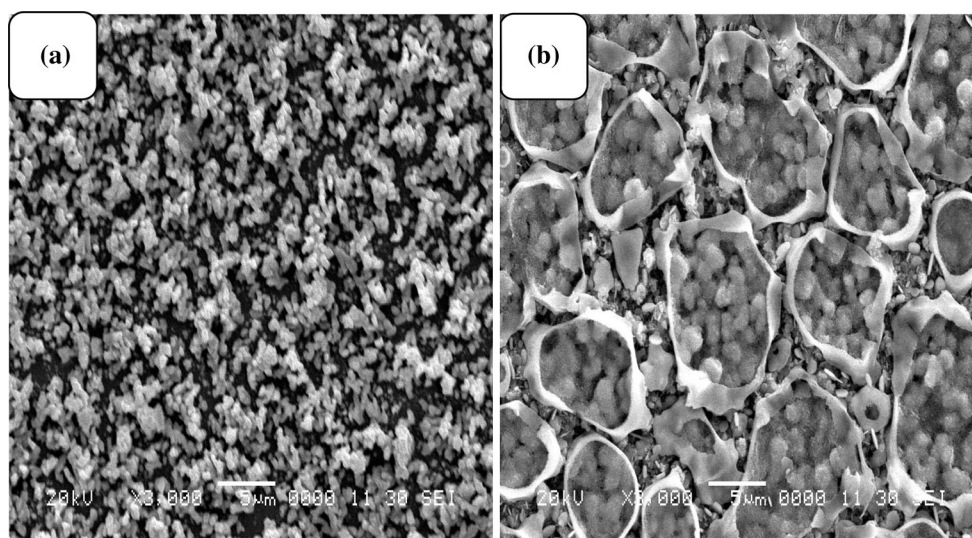


Fig. 6 SEM images of Cu–In (a) and selenized Cu–In (b) thin film (CISE) electrodeposited at -0.85 V in presence of 0.1 M citric acid. The scale bar represents 5 micron size

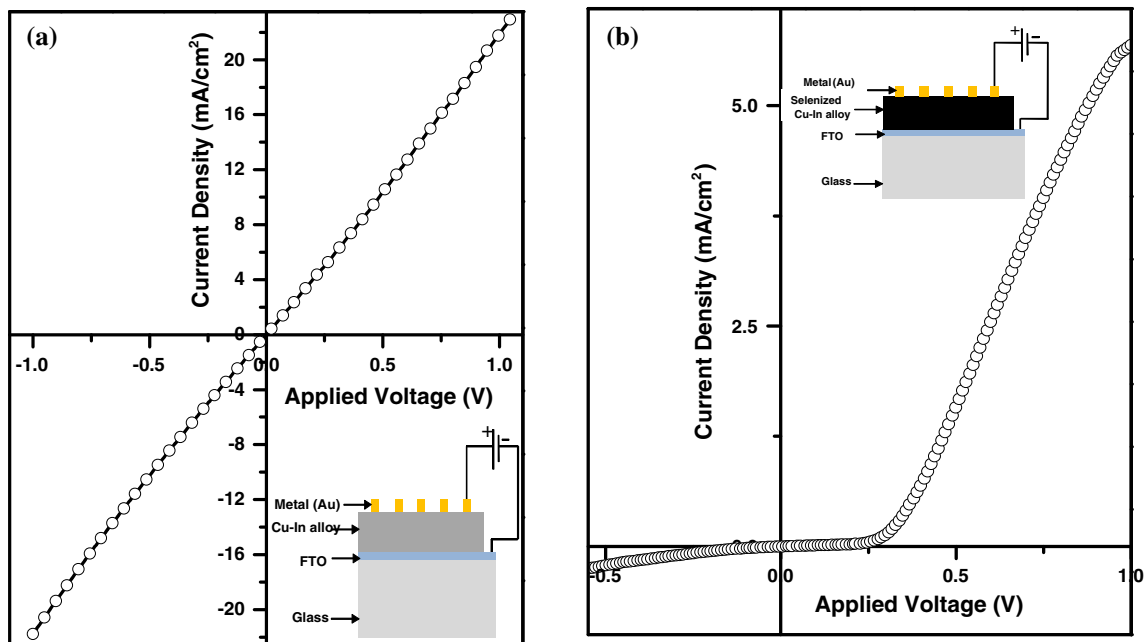


Fig. 7 Current density–Voltage (J – V) characteristics of (a) Cu–In and (b) selenized Cu–In thin film (CISe) electrodeposited at -0.85 V in presence of 0.1 M citric acid. *Inset* shows the structural geometry used to study electrical measurements

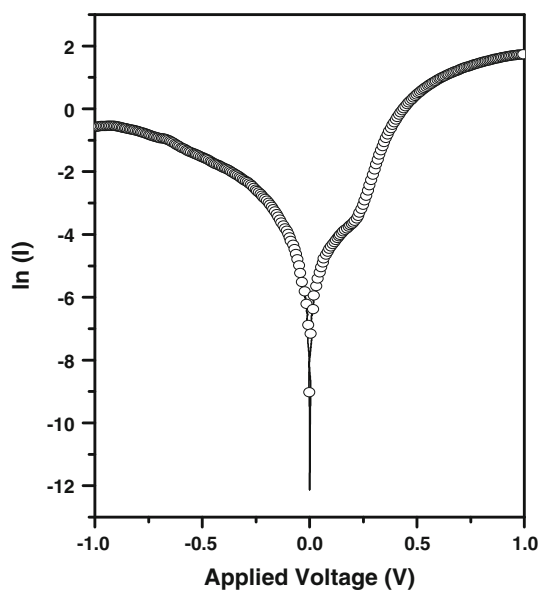


Fig. 8 Semi logarithmic graphs of $\ln(I)$ versus applied voltage Selenized Cu–In thin film (CISe) electrodeposited at -0.85 V in presence of 0.1 M citric acid

where ‘ q ’ is the charge of electron, ‘ V ’ is the applied voltage, ‘ η ’ is the ideality factor, ‘ k ’ is the Boltzmann constant, ‘ T ’ is the temperature and ‘ I ’ the is diode current. The ideality factor, $\eta = 1.93$ was calculated for the selenized Cu–In thin film electrodeposited at -0.85 V. The calculated value of ideality factor is higher, could be due to the leakage current in the diode. This value can be obtained

close to the ideal one with optimizing the post-deposition annealing and selenization conditions. Thin film solar cell development using the selenized Cu–In alloy film (CISe) is under progress.

4 Conclusions

In summary, the polycrystalline, stoichiometric and well adherent thin films of Cu–In alloy thin films are electrodeposited in an aqueous bath in presence of 0.1 M citric acid at -0.85 V. The selenization of Cu–In alloy thin films in the controlled selenium atmosphere result the polycrystalline chalcopyrite CISe thin films with tetragonal structure. The EDS analysis confirmed the formation of stoichiometric CISe thin film after selenization. The particle size of CISe was found to be improved significantly up to 1 to 1.5 micron which could be suitable for the preparation of high efficiency solar cells. Electrical measurement showed ohmic behavior for as-deposited Cu–In thin film whereas rectifying behavior is observed for selenized Cu–In (CISe) thin film. The ideality factor, 1.93 was calculated for the selenized Cu–In thin film electrodeposited at -0.85 V in presence of 0.1 M citric acid, which is higher could be due to the leakage current in the diode.

Acknowledgments The financial support received from DRDO, New Delhi, Project No. ERIP/ER/10003866/M/01/1388 and ISRO-UOP, Space Technology Cell are gratefully acknowledged.

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