

Electrodeposition of near stoichiometric CuInSe₂ thin films for photovoltaic applications

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Abstract: This work investigates on the single step electrodeposition of quality CuInSe₂ (CIS) thin film absorber layer for photovoltaics applications. The electrodeposition was carried using an aqueous acidic solution with a *pH* of 2.25. The deposition was carried using a three electrode system in potentiostatic conditions for 50 minutes. The as-deposited and nitrogen (N₂) annealed films were characterized using XRD, FE-SEM and Raman spectroscopy. It has been observed that the SDS has the tendency to suppress the copper selenide (Cu_xSe) secondary phase which is detrimental to the device performance.

Keywords: *Semiconductor, Electrodeposition, Thin films, Solar cells*

1. Introduction

The ternary CuInSe₂ is an excellent photovoltaic material due to its high optical absorption coefficient ($\alpha=10^5 \text{ cm}^{-1}$) [1]. When compared to first and third generation solar cells such as organic solar cells [2], Si-based solar cells [3] etc., photovoltaic devices (PV) based on CIS thin films are efficient as they can be easily fabricated over flexible substrates. CIS thin films are deposited by various techniques such as sputtering [4], spray coating [5], chemical synthesis [6–8] etc. Though most of the reported CISE/CIGSe high efficiency devices are fabricated by vacuum techniques, bottle necks such as high capital and material wastage is a major hurdle for industrialization. However, when compared to vacuum based techniques, electrodeposition is cheaper as it requires less equipment capital with minimized material wastage and is industrially scalable [9,10]. Several schemes in electrodeposition such as Cu/In binary stack deposition, CuInGa alloy deposition, Cu/In/Ga alloy deposition and further complicated schemes were also reported [11]. These layers can be either electroplated in conventional direct current mode (DC) or by using pulsed current mode (PC). These steps require selenization using Se powder or H₂Se to obtain the photovoltaic quality CuInSe₂ or CuInGaSe₂ thin films [12]. Most often, the compositional deviation is dependent on the thickness of the layers deposited in the stack. Also deposition of each layer followed by post-processing annealing and compositional optimizations are often time consuming. Hence, when compared to other deposition schemes and techniques, electrodeposition of CISE or CIGSe using single-step deposition techniques is highly advantageous where co-deposition of all the elements takes place by applying one constant potential. The stoichiometry of the CISE films can be tuned by varying the electrolyte composition. Till date most of the high efficiency CISE or CIGSe devices are often of Cu-poor composition. Even a slightest deviation [$\text{Cu/In} \geq 1$] from the stoichiometry leads to the formation of detrimental Cu₂Se secondary phase. These highly conductive Cu₂Se phase contribute to the leakage current and affects the open circuit voltage (Voc) of the devices. Due to this reason, the [Cu/In] < 1 ratio is always preferable [13].

In the present work, we report the electrodeposition of CuInSe₂ thin films by single step electrodeposition technique. For improving the film adhesion, we have used sodium dodecyl sulfate (SDS) as surfactant. The advantage of using SDS is that they can limit the undesirable copper selenide binaries (Cu₂Se) phase and thus improves the film quality. The as-deposited and N₂ annealed CISE films were subjected to XRD, FE-SEM and Raman spectroscopy analysis.

2. Materials and methods

The deposition bath electrolyte was prepared by using chloride salts of copper chloride (CuCl₂) - 2 mM and indium chloride (InCl₃) - 9.375 mM along with Selenious acid (H₂SeO₃) - 5 mM for the



Selenium ions. The final *pH* of the bath was maintained at 2.25 using H_2SO_4 . A well cleaned Fluorine doped tin oxide (FTO) coated glass substrates ($2 \times 3 \text{ cm}^2$) was used as the substrates and platinum foil as the counter electrode. All the electrochemical studies and deposition were performed in Biologics SP-150 and the deposition was carried out for 50 minutes at -0.70 V/SCE . The as-deposited films were then annealed in N_2 atmosphere at 450°C for 40 min. The phase, structure and morphology was analyzed by using XRD (Pan analytical with Cu source $\lambda\text{K}\alpha 1=1.54 \text{ \AA}$), FESEM imaging/compositional studies (Nova NanoSEM 650) and Micro-Raman spectroscopy (HORIBA Jobin Yvon LabRamHR800L with high resolution) with Ar^+ polarized laser green line ($\lambda=514.53 \text{ nm}$). To avoid crystallization effects, 2-5% of the laser beam intensity was used on the films with the acquisition time of 400 s.

3. Results and Discussion

The linear sweep voltammetry (LSV) behavior of Cu-In-Se ternary system is shown in fig.1. The potential was swept between OCP to -1.2 V/SCE at a scan rate of 10 mV/Sec . The reduction peak appearing at C1 can be assigned to the single step reduction of Cu^{2+} to Cu^+ followed by the reduction of Cu^+ to $\text{Cu}(0)$ and subsequent formation of Cu-Se (Cu_3Se_2 or Cu_2Se) secondary phase at C2. As in scan #2, the reduction peak C2 is considered to be the formation of CuInSe_2 phase through the surface induced reactions which is indicated by the reduced intensity of the reduction peak. The Cu_3Se_2 phase further reduces to form H_2Se and Cu_2Se phase which initiates at the reduction peaks C3 and C4. The chemical reaction between the evolved H_2Se and In^{3+} ions takes place at C4 to form a In_2Se_3 phase which can chemically reacts with the CuSe phase to form CuInSe_2 phase [14–18]. The direct reduction of In^{3+} to $\text{In}(0)$ at C5 and C6 along with hydrogen evolution reaction (HER) due to the protonation of H^+ ions. From the LSV studies, the suitable deposition potential for co-deposition of CuInSe_2 as a single phase can take place between C3 to C5. Hence, the potential was chosen to be -0.70 V/SCE and the deposition were carried for 50 min using chronoamperometry (CA) technique. The as-deposited CIS films were metallic bright in color indicating the presence of In-rich layer over the surface. The as-deposited and N_2 annealed (400°C for 30 min) CuInSe_2 thin films were used for XRD, FE-SEM and Raman spectra characterization.

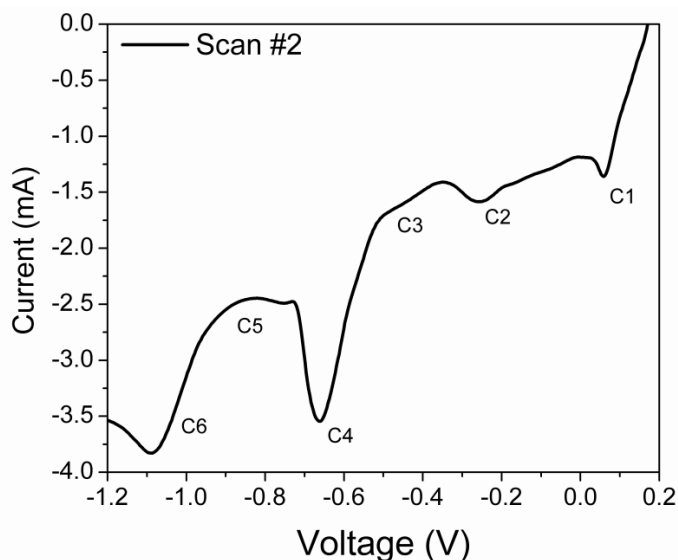


Figure 1. 1 LSV behavior of Cu-In-Se ternary system (Cu- 2mM, In-9.375 mM, Se-5 mM, SDS-1 mM, LiCl- 150 mM)

Table 1: Compositional studies of CIS thin films

Elements	Cu (at.wt %)	In (at.wt %)	Se (at.wt %)
As-deposited	25	20	55
Annealed	23	25	52

Fig.2 (a,b) shows the FE-SEM of as-deposited and annealed CIS thin films. After 50 min deposition, the CIS films with spherical particle morphology were homogenous and smooth. Such smooth films is a required during annealing as it can eliminate the formation of pinholes and porosity issues which are detrimental to the solar cell device performance. Moreover, the as-deposited CIS thin films exhibited good adherence to the FTO substrates. After annealing, the crystallization of the CIS thin films was improved as shown in fig.2b. In Fig.2c, the XRD of as-deposited and annealed CIS thin films were given. For the as-deposited CIS, the broad diffraction pattern corresponding to (220)/(204) planes indicates the presence of poor crystalline CIS precursor film. However, upon annealing, the improved crystallinity of the peaks indicates the formation of a single phase CuInSe_2 thin films. Well defined characteristic peaks at 17° , 26.6° , 35.5° , 44.1° and 52.4° , 70.9° , correspond to the diffraction of the (101), (112), (211) (204) ,(312) and (332) planes respectively. The diffraction peaks corresponding to annealed CuInSe_2 films were in good agreement with the JCPDS card No: 40-1487. Using the Scherrer's formula, the average crystallite size for as-deposited and annealed CIS films were 32 nm and 60 nm respectively, indicating the improvement in the crystallinity after annealing.

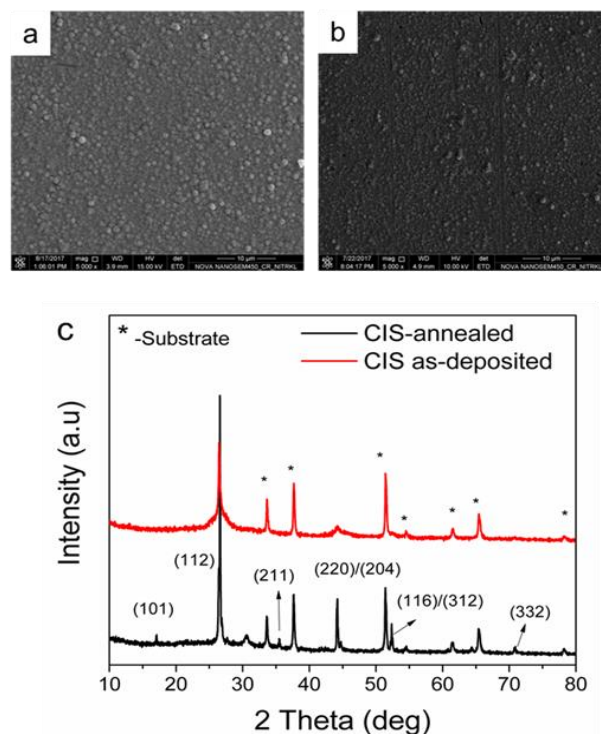


Figure.2 FE-SEM of as-deposited (a) and annealed (b) CIS thin films, c) XRD of as-deposited and annealed CIS films (*-FTO substrate peaks)

The compositional studies were carried by FE-SEM EDAX studies (table.1). From the compositional studies, it was found that the as-deposited CIS were initially rich in Cu and Se. In the as-deposited films, the nanocrystalline In_2Se_3 phase might be dispersed in the precursor film. Due to their nanocrystalline nature; it is difficult to confirm their presence through XRD and Raman studies. The increase in indium content after annealing have been observed as the indium selenide binaries involves in alloy formation with Cu-Se to form a single CuInSe_2 chalcopyrite phase.

The deposits and annealed CIS films were subjected to micro-Raman studies to understand the phase formation and is shown in Fig.3. The Raman analysis was carried between the spectral regions of 100-600 cm^{-1} . The peak at 177 cm^{-1} is assigned to the characteristic A1 mode of the chalcopyrite CuInSe_2 phase. The presence of elemental selenium is confirmed by the peak at 240 cm^{-1} due to trigonal selenium. An appearance of a shoulder peak around 160 cm^{-1} indicates the Cu-poor CuIn_3Se_5 compounds known as ordered vacancy compounds (OVC). The presence of OVC indicates the Cu-poor composition of the as-deposited CuInSe_2 films [19]. The Raman peaks corresponding to the copper selenide binaries (260 cm^{-1}) were not observed due to the selection of high $[\text{Se}^{4+}/\text{Cu}^{2+}]$ ions ratio used for electrodeposition. After annealing, the blue shift of the A1 mode from 177 to 176 cm^{-1} is probably due to a nanocrystalline structure or to residual stress.

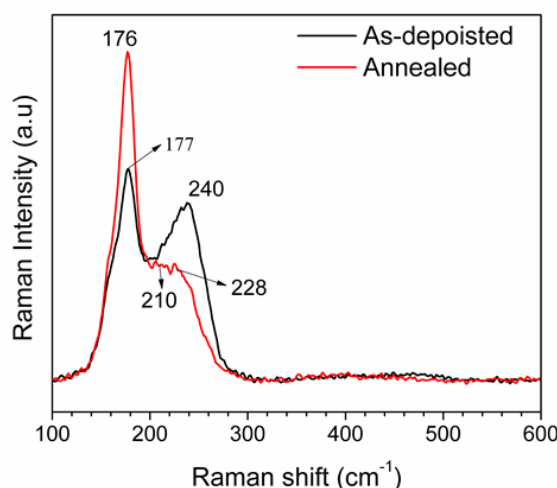


Figure.3 Raman spectra of as-deposited and annealed CuInSe_2 films

The disappearance of Se (0) peak after annealing confirms that they have involved in the chalcopyrite phase formation followed by the appearance of peaks at 210 and 228 cm^{-1} which can be assigned to the B2, E mode of the chalcopyrite CIS films. The decrease in full width half maxima (FWHM) of A1 mode indicates the improved crystallinity of the annealed CIS films.

4. Conclusions

In the present study we have successfully electrodeposited CIS thin films. The as-deposited and annealed CIS films were stoichiometric with minimized CuSe secondary phase. The absence of copper selenide binaries are due to the high $[\text{Se}^{4+}/\text{Cu}^{2+}]$ ion ratio bath used for the electrodeposition. Moreover, the use of SDS surfactant helps in inhibiting the copper selenide formation and improves the film compactness. The mentioned properties are confirmed by XRD, FE-SEM and Raman studies.

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