Photoelectrochemistry of Cu(In,Ga)Se2 thin-films fabricated by sequential pulsed electrodeposition

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Abstract

A novel approach for the fabrication of compact stoichiometric copper indium gallium selenium (CIGS) thin-films is reported. It uses a solution of $CuCl_2$, $GaCl_3$ and H_2SeO_3, pH adjusted with HCl with LiCl as additive employing a high purity graphite plate anode and Mo sputtered glass cathode during a simplified sequential pulsed current electrodeposition which avoids impurities from the use of a reference electrode during deposition and a separate selenization step. A Cu-Ga-Se film is optimally deposited by optimizing the deposition voltage, followed by deposition of In from $InCl_3$ solution, and then annealing of the Cu-Ga-Se/In thin-film in an Argon atmosphere at 550 °C. A single phase chalcopyrite CIGS forms with a compact morphology and well-controlled composition of individual elements. The flat-band potential and carrier density of CIGS thin-films are -0.15 V and 2.6×10^{16} cm^{-3}, respectively, as determined by Mott-Schottky studies. The photoelectrochemical performance of CIGS films shows a photocurrent density of -0.8 mA/cm^2 at -0.4 V vs. SCE, an eight fold increment compared our previous reported value. This simplified preparation using pulse plating gives superior quality CIGS films which are promising for application in thin-film solar cells and photoelectrochemical cells.

1.0 Introduction

Cu(In,Ga)Se$_2$ (CIGS) thin-films are one of the most promising absorber layers for solar cell applications due to their direct bandgap ($\approx$ 1.20 eV) and large optical absorption coefficient ($\approx$ 10^5 cm^{-1}) and have yielded highest conversion efficiencies among the thin-film technologies at laboratory scale [1-13]. Efforts to seek an economical and scalable method for the production of stoichiometric CIGS thin-films have been ongoing to realize the commercialization of these devices. Several non-vacuum based methods, including electrochemical [14-19], electroless- [20] and chemical bath depositions [21], have been explored for this purpose. Among these methods, electrodeposition has demonstrated to produce CIGS devices with high efficiency [22]. This method is easily amenable for achieving large area films of high quality with efficient material utilization and high rate deposition [17, 22]. Conventional electrodeposition, with application of direct current (DC) employing a three electrode system, has been explored by several researchers for the production of CIGS thin-films. However, complexing agents such as EDTA, trisodium citrate, sodium sulfamate, etc. are generally used to control the composition and to improve the morphology of CIGS thin-films [22-24]. In addition, multi-step processing (often requiring three to four steps, along with an additional selenization step) has been found to be necessary to achieve the desired stoichiometry in this complex quarternary system by the above route [14-16, 22]. Furthermore, post-treatment of the deposited films using KCN is also practiced to correct for the composition of CIGS by eliminating secondary Cu-Se phases [23, 25]. However, use of complexing agents can lead to presence of impurities in the film and use of KCN etching is found to result in increased surface roughness.

In comparison to DC electrodeposition, pulsed current (PC) electrodeposition is known to offer several advantages since it provides additional variables such as duty cycle and amplitude of pulsed current/potential. Appropriate regulation of these variables can be used for suitable

manipulation of diffusion layer, grain size and nucleation. This, in turn, results in greater deposit homogeneity as well as precise control over stoichiometry and deposition rate. During the deposition of thin films of ternary/quaternary systems like CIS/CIGS, such control over the composition of individual elements is particularly crucial to obtain single-phase by controlling the formation of secondary phases like Cu-Se, In-Se, Ga-Se, etc., thereby making PC electrodeposition an attractive technique [26, 27]. Furthermore, by varying the duty cycle, reduction in porosity can be achieved by avoiding entrapment of hydrogen during deposition and result in a highly dense and compact CIGS films with enhanced photoelectrochemical performance [18, 19].

Despite the above advantages, limited reports are available on the use of pulsed electrodeposition for the preparation of CIGS thin-films. Fu et al. have explored different plating techniques including DC, pulse and pulse-reverse electrodeposition for the fabrication of CIGS thin films and reported elimination of secondary phases such as $Cu_{2-x}Se$ to obtain phase pure chalcopyrite CIGS thin-films using pulse-reverse electrodeposition [28]. Liu et al. too have employed PC electrodeposition and showed that use of an appropriate duty cycle can eliminate In-Se phase formation and help in preparation of single phase CIGS thin films [26]. In general, electrodeposition of Ga and In is relatively difficult due to their more negative reduction potentials compared to Cu and Se. Additionally, the required amount of In ($\approx$ 18 at.%) for the formation of stoichiometric CIGS (theoretically, $CuIn_{0.7}Ga_{0.3}Se_2$) is greater than that of Ga ($\approx$ 7 at.%). It has also been observed that the In content decreases with increase in pulse off-time during the PC electrodeposition of CIS/CIGS thin-films [26, 27]. Due to these reasons, often high concentration of In precursor and/or more negative voltage and/or deposition of In-Se on CIGS as a subsequent step have been used to adjust the In content in the films, in order to obtain stoichiometric CIS/CIGS thin-films [14, 15, 27, 29, 30]. However, In is the least abundant

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element among Cu, In, Ga and Se and is frequently used for electronic and optoelectronic applications in the form of materials such as ITO, InP, InGaAs, CIS, CIGS, etc. making it one of most scarce elements in the near future. Hence, it is preferable to use minimal In precursor concentration and to explore the possibility to deposit In/In-Se in the second step. In this context, it is also relevant to mention that the deposition of In-Se on CIGS in the second stage by Bhattacharya et al. not only improved the stoichiometry but also resulted in chalcopyrite CIGS films without any surface dispersed Cu-Se phase [14].

In appreciation of the above, the present work proposes the pulse electrodeposition of CIGS in two steps, with codeposition of Cu-Ga-Se films in the first step being followed by deposition of In in the second step. A two-electrode system, with an additive-free electrolyte, is used and the additional step of selenization is avoided. The sequential approach presented herein minimized the use of In precursor, which is crucial given the scarcity of In, to achieve the desired composition. In addition, optimization of deposition voltage in the first stage resulted in compact phase-pure CIGS thin-films with an eight-fold increment in photoresponse over the study reported previously by our group [18], as discussed herein.

2.0 Experimental

Electrodeposition of Cu-Ga-Se in stage I was carried out using a bath containing $CuCl_2$ (3 mM), $GaCl_3$ (6 mM), H_2SeO_3 (8.5 mM) and LiCl (250 mM) dissolved in Hydrion buffer (pH 3) while In deposition in stage II used $InCl_3$ (2 mM). The pH of the final solution in stage I was adjusted between 2.15 and 2.35 using HCl and no other additives were used. Addition of LiCl as supporting electrolyte is not only known to stabilize the electrodeposition bath solution but also improve the quality of the deposited layer as previously reported [17]. Pulsed electrodeposition of CIGS thin-films was performed by employing a two-electrode system. Conventional

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electrodeposition often employs a three electrode system wherein the reference electrode has been used to maintain the constant potential at cathode. However, the use of reference electrode could possibly increase the impurities in the deposited film. For instance, For e.g. Ag^+ ions from Ag/AgCl electrode have detrimental effects leading to reduced cell efficiencies for electrodeposited CdTe based solar cells [31]. In addition, Dharmadasa et al. reported that the absence of reference electrode does not change the growth voltage appreciably, indicating not much difference in the features (morphology and composition) of the deposit [30]. In addition, the two-electrode system is more suitable for the fabrication of large area thin-films that are to be used in devices and modules compared to a three-electrode system and is commonly practiced by the electroplating industries [27, 30]. Pulsed electrodeposition was performed in a vertical cell with high purity graphite plate as an anode and Mo sputtered glass as a cathode using a Pulse Power Supply (Dynatronix Model DuPR10-3-6). Mo/glass was ultrasonicated for 10 min each in acetone, ethanol and de-ionized water, respectively and was purged with nitrogen gas prior to the deposition. Schematic representations of the electrodeposition set-up, pulsed voltage applied and the corresponding current density are shown in Fig. S1. Schematic representation of the procedure adopted for the deposition of CIGS thin-films is depicted in Fig. S2. The deposition voltage was optimized in stage I while keeping a constant duty cycle of 50 % while a voltage of -1.5 V was used for In deposition. Cu-Ga-Se and In deposition were carried out for 30 min and 10 min, respectively, while maintaining the bath at room temperature without stirring. The electrodeposited films were rinsed thoroughly with DI water and were annealed at 550 °C for 30 min under Ar atmosphere to form the desired CIGS phase by the intermixing of two layers.

The microstructural and elemental analyses were performed using Scanning electron microscope (SEM) (S3400N Hitachi) with an attached EDAX system (Thermo Electron Corporation). The roughness of the films was measured using profilometry (Mahr Perthometer) and the

measurements were carried out using a traverse length of 5.60 mm at a minimum of 8 locations on the samples. X-ray diffraction (XRD) was employed to examine the phase constitution of the annealed CIGS films using X-ray diffractometer (Bruker's D8 advance) with Cu K$_\alpha$ radiation (λ = 1.54 Å). The diffraction patterns were collected in the range of 2θ = 20 - 70° with a scan rate of 1° per min. Micro-Raman Spectra of CIGS thin-films were recorded using Raman spectrometer (Horiba Jobin Yvon-Lab Ram HR-800) with Ar ion laser of 514 nm as the light source in the scan range of 100 - 600 cm^{-1}. In the present study microscopic focusing was used to detect $Cu_{2-x}Se$ microcrystallites on the surface of CIGS thin-films. In addition, Raman mapping was performed over several sections on the surface of the CIGS films. Typically about 30 μm x 30 μm area was covered in each section with a sesitivity of about 0.9 μm in X and Y directions. An X-Ray Fluorescence spectrometer (Fisherscope, XUV TDD) was used to determine the bulk composition and thickness of the CIGS films. Transmission Electron Microscope (FEI Tecnai G2 200 KV) was used to record the HRTEM images of CIGS thin-films. CIGS thin-films were scraped into powder form which was dispersed in ethanol. Ethanol suspension was dropped onto Cu grid for TEM analysis. Optical absorption spectra were obtained using ultraviolet/visible/near infrared diffuse reflectance spectrometer (VARIAN CARY -5000 UV/VIS/NIR) in the wavelength range of 200-2500 nm.

Mott-Schottky plots were recorded in a 0.5M H_2SO_4 solution using an impedance analyzer (Solartron SI 1260) with an electrochemical interface (SI 1287) wherein Pt, Saturated Calomel Electrode (SCE) and CIGS/Mo/Glass were used as counter, reference and working electrodes, respectively. The photoelectrochemical (PEC) performance of the CIGS thin films was investigated using electrochemical analyzer (CH Instruments 660A). The measurements were carried out potentiostatically in an electrochemical cell. A classical three-electrode cell with Pt foil as the counter electrode, SCE as the reference electrode, and CIGS/Mo/Glass as the working

electrode were used in 0.5 M H_2SO_4 solution. Solar simulator (Newport) with AM 1.5 Global

(100 mW/cm^2) lens was used as the light source for PEC measurements.

3.0 Results and Discussion

3.1 Optimization of deposition voltage for Cu-Ga-Se films

The elemental composition of Cu-Ga-Se films prepared at different deposition voltages, as

determined from energy dispersive X-ray spectroscopy, is shown in Fig. 1. The amount of Ga is

noted to increase from ≈ 3 to 6.8 at.% with the change in deposition voltage from -1.0 to -1.2 V.

An increased negative voltage is expected to increase the Ga content since Ga has more negative

reduction potential, as mentioned earlier. In addition, the use of two-electrode system is known

to require higher deposition voltages than that required for a three-electrode system [27, 30].

Hence, increase in Ga content is attributed to the increased deposition voltage to -1.2 V. Further

change in deposition voltage to -1.5 V, however, leads to a decrease in the amount of Ga to ≈ 4

at.%. The pulsed deposition voltage applied for the deposition and the corresponding current

density during the deposition are shown in Fig S1b and S1c, respectively. It is observed from

Fig. S1b that there is a positive current density during the pulse off-time even without the

application of any voltage. Such an unintended positive current density might oxidize the

elements with least electronegativity from the deposited film leading to the dissolution of

corresponding element into the electrolyte. In the present case, at the deposition voltage of -1.5

V, the magnitude of the positive current density during the pulse off-time might be sufficient to

oxidize Ga, since it has the lowest electronegativity among the three elements. This could

possibly be the reason for the lower Ga content at -1.5 V. A similar phenomenon has also been

reported during pulse electrodeposition of CIS and CIGS thin-films [26, 32]. Considering the

lower Ga content required for obtaining stoichiometric CIGS, it is easier to optimize the Cu-Ga-

Se films at a relatively lower voltage. As can be seen from Fig. 1, a deposition voltage of -1.2 V

yields nearly ideal Ga content required ultimately for the formation of stoichiometric CIGS thin-films.

The surface morphology of Cu-Ga-Se films deposited at different voltages is shown in Fig. 2. Although the films deposited at -1.0 V show a uniform morphology, increasing the voltage to -1.2 V leads to a smoother and denser morphology (Fig. 2b). It is plausible that selective dissolution of surface asperities due to relatively higher electrochemical activity leads to the smooth and compact morphology in films deposited at -1.2 V, which is desirable for uniform deposition of In in the second step. However, the films deposited at a further more negative voltage of -1.5 V are rough and porous compared to the other films. This could be attributed to the rapid deposition rate at more negative deposition voltage, as well as to the previously mentioned dissolution of Ga. Besides the morphological characterization, roughness measurements were also carried out using the profilometry. The average surface roughness (R_a) values are 60, 20 and 90 nm, for samples deposited at -1, -1.2 and -1.5 V, respectively. These values clearly demonstrate the fact that films deposited at -1.2 V (Fig. 2b) are smoothest which further corroborates the morphological studies.

Additionally, the CIGS films were characterized using micro-Raman spectra for phase analysis before annealing to identify the phases formed during the first deposition step. The specific purpose of the high-resolution micro-Raman studies was also to ascertain the vibrational modes of individual phases and detect any surface dispersed microcrystallites of $Cu_{2-x}Se$, as detection of phases like CIS, CGS, CIGS, $Cu_{2-x}Se$ is difficult by XRD due to the negligible variation in 2θ values for the dominant (112) orientation of each phase. Figure 3a shows the micro-Raman spectra of Cu-Ga-Se films deposited at various voltages. Three peaks corresponding to A_1 and E_1 modes of $CuGaSe_2$ (CGS) and A_1 mode of $Cu_{2-x}Se$ noted at approximately 187, 239 and 260 cm⁻

[1], respectively, are of interest [33]. In addition, the broader peak observed at 510 cm^{-1} is attributed to the second harmonic of the A_1 mode of $Cu_{2-x}Se$. As can be seen from the figure, the peak intensities of the E_1 mode of CGS and A_1 mode of $Cu_{2-x}Se$ vary with the deposition voltage. $Cu_{2-x}Se$ is an undesired secondary phase and, being a degenerate semiconductor, it contributes to higher dark current [34]. In addition, $Cu_{2-x}Se$ is a stable phase along with CIGS at the annealing temperature (550 °C) which is used to improve the crystallinity of CIGS phase and is expected to be present in minimal amounts even after annealing [35-37]. The probability of its presence after annealing is higher if the as-deposited films are Cu-rich in composition. Hence, reduction of this undesired secondary phase in as-deposited films is essential to improve the quality of CIGS thin-films which can affect the ultimate device performance. Consequently, presence of higher CGS and lower $Cu_{2-x}Se$ is preferable in the as-deposited film. The ratios of E_1 mode of CGS and A_1 mode of $Cu_{2-x}Se$, as obtained from Raman spectra, are shown in Fig. 3b, for Cu-Ga-Se films deposited at -1.0, -1.2 and -1.5 V, respectively. As the highest ratio of 0.50 corresponding to the maximum amount of CGS phase is obtained at a deposition voltage of -1.2 V, this value was deemed optimum for codeposition of Cu-Ga-Se films in the first stage.

3.2 Preparation of CIGS by deposition of In and annealing

As mentioned earlier, deposition of In was subsequently carried out at -1.5 V for 10 min in stage II on Cu-Ga-Se films deposited at different voltages in stage I. A low concentration of In precursor was used to achieve the desired amount of In since the deposition was performed in a separate step.. The CGS/In films were annealed at 550 °C under Ar atmosphere to form the CIGS by intermixing of the two layers. The elemental composition of annealed films, as well as the relevant compositional ratios Cu/(In+Ga) and Ga/(In+Ga) in the films are depicted in Fig. 4. It was deemed informative to plot the above as a function of the deposition voltage applied during stage I because, although In was deposited in a subsequent step, the composition of the

Cu-Ga-Se films achieved after stage I plays a key role in determining the eventual stoichiometry of the annealed CIGS films. This is primarily because, in the tetragonal chalcopyrite structure of CIGS, the Ga and In atoms compete for identical lattice sites [33, 38]. Consequently, the uptake of In during stage II is influenced by the Ga content in Cu-Ga-Se films after stage I as clearly revealed in Fig. 4. The composition of Cu and Se in the annealed sequentially deposited CIGS films does not vary substantially with change in deposition voltage during stage I. The Cu and Se contents are also found to be close to the ideal values required for formation of stoichiometric CIGS films. In contrast, considerable variation is observed in the Ga and In content in the annealed CIGS thin-films depending on the deposition voltage applied during Cu-Ga-Se deposition in stage I. When the amount of Ga is relatively lower at stage I deposition voltages of -1.0 V and -1.5 V, the In content correspondingly increases. However, at -1.2 V, the Ga and In are present in near-ideal quantities to form stoichiometric CIGS. At the stage I deposition voltage of -1.2 V, the Cu/(In+Ga) and Ga/(In+Ga) ratios are observed to be 0.97 and 0.27, respectively, for annealed CIGS films, which are close to the desirable values for high efficient CIGS thin-films [2, 39, 40]. The stoichiometries of the films, as obtained from EDS, were $Cu_{0.97}In_{0.90}Ga_{0.10}Se_{2.03}$, $Cu_{0.97}In_{0.73}Ga_{0.27}Se_{2.03}$ and $Cu_{1.02}In_{0.81}Ga_{0.19}Se_{1.98}$ at -1.0 V, -1.2 V and -1.5V, respectively, indicating the near-ideal stoichiometry in the films deposited at -1.2 V.

Figure 5 shows the morphology of sequential deposited and annealed CIGS thin-films for various deposition voltages employed during stage I. As can be seen, a rough surface morphology is observed for films deposited at -1.0 and -1.5 V. The films deposited at -1.2 V were noted to have a smooth and compact morphology (Fig. 5b). Such a dense morphology is well-suited for application as solar absorber layers, since it facilitates easier diffusion of minority charge carriers and reduces recombination, which ultimately yields improved cell performance [18, 26]. The roughness measurements by profilometry yielded the R_a values as 90, 30 and 130

nm, for the films deposited at -1.0, -1.2 and -1.5 V, respectively, also support the observed SEM results.

Figure 6 shows the X-ray diffraction patterns of sequential deposited and annealed CIGS thin-films at various deposition voltages used in stage I. The XRD patterns in each case are observed to have a preferred orientation corresponding to (112) of CIGS, with the presence of other peaks corresponding to (220), (312) and (424) (JCPDS: 35-1102) confirming the presence of crystalline chalcopyrite CIGS phase [41]. In addition, a peak corresponding to Mo from the substrate (JCPDS: 42-1120) is also observed. However, a closer inspection reveals a shift in the (112) orientation of CIGS to a lower 2θ value for the CIGS films deposited at -1.0 V (inset of Fig. 6). It is well known that with decrease in the amount of Ga the (112) peak shifts to lower 2θ values as incorporation of Ga leads to a decrease in lattice parameter [42, 43]. As evident from the EDS analysis, the film deposited at -1.0 V has a relatively lower Ga content and is expected to have a CIGS phase with larger lattice parameter. Also, the higher In content results in a secondary indium selenide (In_2Se_3) phase in the films deposited at -1.0 V. The XRD patterns of films deposited at -1.2 V and -1.5 V are, however, found to have well defined peaks corresponding to only ideal stoichiometric chalcopyrite CIGS. No considerable shift was observed for (112) orientation in the films deposited at -1.2 V and -1.5 V owing to a very minor variation in the Ga content. However, such a negligible difference is clearly observed in Raman spectra as discussed later. It can also be seen that the maximum peak height is observed in the case of CIGS deposited at -1.2 V in stage I, affirming -1.2 V to be the optimized voltage. It is also interesting to note that no peaks corresponding to the undesired Cu-Se and In-Se phases are observed for the optimized case.

Figure 7a shows the Raman spectra of the sequential deposited and annealed CIGS films for

various deposition voltages employed during stage I. The spectra reveal peaks corresponding to A_1 and B_2/E modes of CIGS at wave numbers of 176, 215 and 232 cm^{-1}, respectively [33]. In addition, a small peak observed at the wavenumber of 480 cm^{-1} can attributed to the presence of secondary In_2Se_3 phase for the films deposited at -1.0 V. Figure 7b shows the shift of A_1 mode of CIGS with deposition voltage. The A_1 mode for CIGS films deposited at -1.0 V in stage I is observed at a lower Raman shift of 172 cm^{-1}. This could be attributed to the lower Ga content observed in these films at -1.0 V. It is well reported that the A_1 mode is observed at lower wavenumbers in the range of 171-173 cm^{-1} for CIGS films with very low Ga content, with the peak shifting to higher wavenumbers of 176-178 cm^{-1} for stoichiometric CIGS thin-films and to 187 cm^{-1} for CuGaSe$_2$ [33, 44, 45]. The CIGS films deposited at -1.5 V, are also observed to have A_1 mode at a lower Raman shift of 173 cm^{-1}. As it is evident from EDS, the Ga content is higher compared to films deposited at -1.0 V and lower compared to films deposited at -1.2 V. The relatively lower Ga content is accountable for the shift of A_1 mode to lower wavenumbers. However, the films deposited at -1.2 V exhibit a sharp peak at 176 cm^{-1} which corresponds to the stoichiometric CIGS A_1 mode and does not contain any CGS and $Cu_{2-x}Se$ phases which were observed prior to the second step of deposition, thereby confirming formation of a phase-pure chalcopyrite CIGS thin-film. As previously mentioned, elimination of the undesired $Cu_{2-x}Se$ secondary phase in the annealed films is extremely crucial, and is successfully achieved in the present case by the optimization of deposition voltage in the first stage followed by the deposition of In in the second stage.

3.3 Characterization of optimized CIGS thin-films

The optimized stoichiometric annealed CIGS thin-films (CGS deposited at -1.2 V in stage I) were further characterized using XRF, HRTEM, FESEM, UV-Vis-NIR diffuse reflectance spectroscopy, electrochemical impedance spectroscopy and photoelectrochemical analysis. XRF

is used to infer the bulk composition and thickness of the CIGS thin-films, which are presented in Table 1. As it can be seen, the optimized CIGS films possess desired composition and exhibit the near-ideal stoichiometry as required for ideal CIGS absorber layer. The ratios of Cu/(In+Ga) and Ga/(In+Ga) are calculated to be 0.94 and 0.27. The composition of the elements and the relevant ratios are not only in the desirable range but also in agreement with the results obtained from EDS analysis, confirming the uniform composition of the elements in the bulk of the films. The thickness of the CIGS films is determined to be ≈ 1.76 µm, which is desirable for high efficient CIGS devices [46].

In addition to the micro-Raman analysis of CIGS films shown in Fig. 7, Raman mapping of the optimized CIGS films is performed to further verify their phase-purity. Figure 8 shows the Raman mapping of optimized CIGS films wherein red portion of the mapped image refers to the dominant CIGS, green refers to secondary $Cu_{2-x}Se$ and blue refers to the In_2Se_3 phase. The Raman map of the as-deposited single-step electrodeposited CIGS films is shown in Fig. S3 for comparison. It can be clearly observed that the as-deposited CIGS films contain the mixture of phases such as CIGS and $Cu_{2-x}Se$. However, the map of optimized sequentially deposited and annealed CIGS films contains only CIGS hase, thereby indicating the absence of any possible secondary phases. In addition, it also affirms the fact that the elements undergo interdiffusion during the annealing and form the desired chalcopyrite CIGS phase. Furthermore, glass/Mo/interface has been characterized using Raman spectroscopy to analyze the presence of different phases over the film's cross-section. The image recorded while analyzing the films with Raman and the corresponding the Raman spectra are shown in Fig. S4. Except for CIGS, no secondary phases are observed across the cross-section affirming the formation of phase-pure chalcopyrite CIGS in the bulk of the films.

TEM analysis has been carried out to further confirm the inter-diffusion of In and to infer the CIGS phase formation. The transmission electron micrograph, the high resolution TEM image and TEM-EDS spectrum of CIGS particles are shown in Figure 9. The selected area diffraction (SAD) pattern is included as an inset in Fig. 9a. The SAD pattern shows the orientations corresponding to (112), (220), (312) and (400) of CIGS, which are in agreement with the previously discussed observation from XRD. Figure 9b shows the high resolution TEM image of CIGS thin-films, which reveals planes with an interplanar spacing of approximately 3.32 Å and 2.03 Å. These values are in good agreement with the theoretical values for the (112) and (220) orientations of CIGS [41], which corroborates the presence of polycrystalline chalcopyrite CIGS observed from XRD analysis. TEM-EDS analysis was also performed as indicated in Fig. 9a and is shown in Fig. 9c. The presence of Cu, In Ga and Se affirms the interdiffusion of In (deposited in stage II) during annealing leading to the formation of CIGS films.

The bandgap of optimized CIGS films is determined to be 1.27 eV, by using *(αhv)²* vs. *hv* as shown in Fig. S6, is close to the value for stoichiometric CIGS thin-films [35]. Mott-Schottky (MS) analysis was used to ascertain the flat-band potential, V_{FB}, of the CIGS thin-films using the following relation:

$$\frac{1}{C^2} = \frac{2}{q\varepsilon\varepsilon_0 N_a} \left(V - V_{FB} - \frac{k_B T}{q} \right)$$

where C is the capacitance, N_a is the acceptor concentration, ε is the dielectric constant, ε_0 is the permitivity of free space, q is the electronic charge, k_B is the Boltzmann's constant, T is the temperature, V is the applied potential and V_{FB} is the flat-band potential.

Figure 10 shows the Mott-Schottky ($1/C^2$ vs. V) plot of CIGS thin-films in 0.5M H_2SO_4 at a frequency of 10 kHz in the dark. The slope of the MS plots is negative, thereby confirming that the CIGS film is p-type. The flat band potential was found to be -0.15 V (vs SCE) by extrapolating the linear section to x-axis. In addition, $N_a \approx 2.6 \times 10^{16}$ cm^{-3}, calculated using the

slope of the curve. The flat-band potential and acceptor density determined herein are close to the desirable values for stoichiometric CIGS films that have been reported previously [47].

Figure 11a shows dark and illuminated current density – voltage characteristics of the annealed CIGS thin-films deposited by sequential PC electrodeposition, measured using a photoelectrochemical analyzer in 0.5 M H_2SO_4 with a sweep rate of 10 mV/s. The nature of the J-V curve confirms the photo-activity of CIGS thin-films. In addition, it shows the increase in cathodic photocurrent with increased cathode potential, which is a characteristic of a semiconductor with p-type conductivity. A photocurrent density of $\approx$ 800 $\mu A/cm^2$ at a potential of -0.4 V vs. SCE is observed. This represents a considerable improvement in photocurrent density compared to the previously reported value of $\approx$ 100 $\mu A/cm^2$ for single-step electrodeposited CIGS films by our group [19]. The crack-free dense morphology observed in the present optimized CIGS thin-films supports the easier diffusion of minority carriers and is responsible for the improved photoelectrochemical performance. It is also to be noted that the photocurrent increases gradually without attaining a saturated value. This behavior can be attributed to incomplete photonic conversion, which causes a recombination of charge carriers at the grain boundaries of the semiconductor [26]. Figure 11b shows the amperometric current-time (I-t) curve of annealed sequential PC electrodeposited CIGS films obtained at -0.4 V by chopped light. It clearly demonstrates the nature of photoactivity of CIGS films with a photocurrent density of $\approx$ 0.8 mA/cm^2. The improved photoresponse of sequentially deposited and annealed CIGS films indicate their potential for application in thin-film solar cells. In addition, the photoelectrochemical performance of these films demonstrates their potential application for photoelectrochemical hydrogen generation.

Conclusions

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A novel sequential pulsed current approach has been employed for the fabrication of CIGS thin-films. Deposition voltage has been optimized for the co-deposition of Cu-Ga-Se films in stage I followed by deposition of In in the second stage. A convenient control over the composition of individual elements has been achieved by the suitable manipulation of process parameters. Characterization of annealed films using XRD and Raman analyses has confirmed the formation of phase-pure stoichiometric chalcopyrite CIGS phase. Raman mapping indicated the phase-pure CIGS phase formation over the entire surface. CIGS films exhibited p-type conductivity as demonstrated from Mott-Schottky as well as PEC studies. Furthermore, a significantly improved photoelectrochemical performance has been observed. This technique presents a simplified, economic and scalable method for fabrication of CIGS thin-films for solar cell applications.

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Figure Captions

Figure 1: Variation in composition of individual elements obtained from EDS analysis for as-deposited Cu-Ga-Se films with varied deposition voltage.

Figure 2: SEM images of as deposited Cu-Ga-Se films at a voltage of a) -1.0, b) -1.2, and c) -1.5 V.

Figure 3: a) Raman spectra of as deposited Cu-Ga-Se films at various voltages and b) ratio of CGS to $Cu_{2-x}Se$ intensities from Raman spectra.

Figure 4: a) Elemental composition and b) Cu/(In+Ga) and Ga/(In+Ga) ratios in sequentially deposited and annealed CIGS thin-films with variation in deposition voltage applied during stage I. In was deposited at -1.5 V in stage II.

Figure 5: Morphology of annealed CIGS thin-films deposited at a voltage of a) -1.0 V, b) -1.2 V and c) -1.5 V in stage I.

Figure 6: XRD pattern of annealed sequentially deposited CIGS thin-films at various voltages in stage I. Inset: Closer inspection of (112) orientation of CIGS thin-films.

Figure 7: a) Raman spectra of annealed sequentially deposited CIGS thin-films at various voltages in stage I and b) a closer inspection of A_1 mode.

Figure 8: Raman mapping of optimized sequentially deposited and annealed CIGS thin-films

Figure 9: a) TEM image (Inset: SAED), b) HRTEM image and c) TEM-EDS of optimized sequentially deposited CIGS. Red circle in image (a) indicates the position where EDS, SAED and HRTEM are performed.

Figure 10: Mott-Schottky ($1/C^2$ vs. V) plot (recorded at 10 kHz in the dark) for the optimized sequentially deposited and annealed CIGS thin-films.

Figure 11: a) Photoelectrochemical I-V characteristics (under AM1.5G solar simulated light) and b) Amperometric I-t curve at -0.4 V of optimized sequentially deposited and annealed CIGS thin-films.

Table Captions

Table 1: Bulk composition and thickness of optimized sequentially deposited annealed CIGS

films obtained from X-Ray Fluorescence spectroscopy

Table 1

Composition (at. %)				Stoichiometry	Cu/(In+Ga)	Ga/(In+Ga)	Thickness (μm)
Cu	In	Ga	Se				
24.01	18.52	6.96	50.51	$Cu_{0.96}In_{0.74}Ga_{0.28}Se_{2.02}$	0.94	0.27	1.7