CuIn1−xGaxSe2 thin-film absorber layers for solar photovoltaics fabricated by two-stage pulsed current electrodeposition

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$CuIn_{1-x}Ga_xSe_2$ thin-film absorber layers for solar photovoltaics fabricated by two-stage pulsed current electrodeposition

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Abstract

Single phase polycrystalline copper indium gallium diselenide (CIGS) thin-films for solar photovoltaic applications were fabricated by an economical two-stage method of Pulsed Current (PC) electrodeposition. Cu, Ga and Se were first co-deposited onto a Mo foil followed by deposition of In. The as-deposited films were annealed in Argon atmosphere at 550 °C for 30 min and were further characterized to study their morphology, phase constitution, and optical absorption. The results revealed that the films have a compact morphology and are comprised of a crystalline chalcopyrite single phase CIGS. The bandgap of the CIGS films was found to be 1.27 eV from absorption studies. The photoelectrochemical studies revealed the p-type nature of CIGS films with improved photocurrent over that obtained for one-stage PC electrodeposited CIGS thin-films.

Keywords: Electrodeposition, Thin Films, Solar Energy Materials, Pulsed Current, Two-stage, CIGS

1. Introduction

$Cu(In, Ga)Se_2$ (CIGS) is one of the most promising semiconductor absorber layer materials among thin-film based solar cells, due to its suitable bandgap, large optical absorption coefficient and high stability [1]. CIGS alloys have been extensively prepared using several techniques [2, 3]. However, an economical and simple method like electrodeposition is preferred for scaling up to industrial level. In this context, the advantages of pulsed current (PC) electrodeposition have been detailed in our previously reported work [4].

Electrodeposition of Cu-In-Ga-Se has been previously reported for fabrication of chalcopyrite CIGS thin-films. However, the film composition has been found to deviate from the ideal stoichiometry, resulting in formation of undesired phases [5]. Easier control over the composition of individual elements has been reported by several researchers using multi-stage DC electrodeposition of CIGS thin-films resulting in higher efficiencies [6-8], but relies on use of additives and an additional selenization step to improve the morphology and stoichiometry of the films.

In the present work, PC electrodeposition with a two-stage approach consisting of a two electrode system is employed for the first time to fabricate stoichiometric chalcopyrite CIGS (CGS/In) thin-films on a Mo foil. This technique is novel in that it overcomes the stoichiometry related problems associated with the single-step method and also obviates the use of complexing agents or an additional selenization step as employed in other previously reported multi-stage methods. The resulting films are found to exhibit a compact morphology devoid of undesirable phases, resulting in superior photoelectrochemical performance compared to the single-stage electrodeposited CIGS films reported previously [9].

2. Materials and Methods

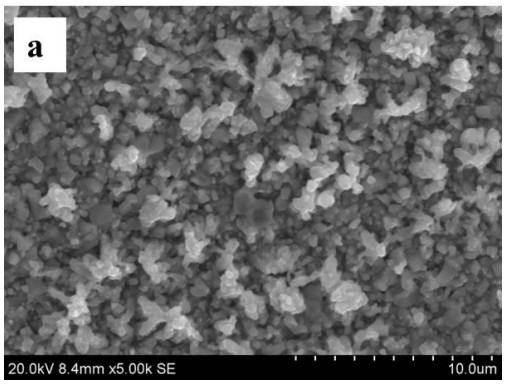
Electrodeposition of Cu-Ga-Se was carried out using a bath containing $CuCl_2$ (3 mM), $GaCl_3$ (8.5 mM), H_2SeO_3 (8.5 mM) and LiCl (250 mM) dissolved in Hydrion buffer (pH 3), followed by In deposition in the second stage using $InCl_3$ (3.2 mM) in Hydrion buffer. Pulse electrodeposition (Dynatronix Pulse Power Supply) was performed in a vertical cell with high purity graphite plate as an anode and Mo foil (25 μm thick) as a cathode. An elaborate procedure was adopted for cleaning the Mo foil prior to deposition [4]. Such a two electrode system is more suitable for larger area thin-films and is commonly practiced by the electroplating industries. A pulse period of 20 ms, duty cycle of 50% and deposition potential of -1.5 V were used in both

stages. The depositions of Cu-Ga-Se and In were carried out for 15 min and 8 min respectively, while maintaining the bath at room temperature without stirring, in the first and second stages for achieving stoichiometric CIGS. In comparison to a classical three electrode system, no significant difference in the features of the electrodeposit was observed with the use of a two electrode system [4, 9-10]. The electrodeposited films were annealed at 550 °C for 30 min under Ar atmosphere. Annealing at a temperature higher than 500 °C is not only expected to improve crystallinity of the CIGS phase but also aids in formation of the crcucial $MoSe_2$ phase at the interface of Mo/CIGS to improve the ohmic contact and adhesion between Mo and CIGS. The annealed CIGS films were characterized using Scanning electron microscopy (SEM), X-ray diffraction, Raman spectroscopy, UV-diffuse reflectance spectroscopy and Photoelectrochemical (PEC) analysis. PEC studies were made in 0.5 M Na_2SO_4 solution with Pt and SCE as counter and reference electrodes, using a solar simulator with AM 1.5G lens as the light source.

3. Results and Discussions

Figure 1a shows the dense and compact morphology of annealed CIGS thin-films. Pulsed current (PC) electrodeposition produces a relatively more homogeneous surface as the rate-determining step is controlled by mass-transfer process [5]. Pulse off-time during deposition allows the diffusion of ad-atoms and facilitates the formation of new nucleation sites, thereby yielding a homogeneous and compact structure [5, 9]. Such a morphology is desirable for the photovoltaic absorber layer since it leads to lower resistance and faster minority carrier diffusion, which ultimately serves to improve cell performance. The elemental composition of individual elements of as-deposited and annealed CIGS thin-films, as obtained from energy dispersive spectrocopy (EDS), are shown in Fig. 1b. The stoichiometry of the annealed CIGS films is determined to be $Cu_{0.96}In_{0.73}Ga_{0.27}Se_{2.04}$. It may be noted that the stoichiometry is close to the preferred near-ideal stoichiometry ($CuIn_{0.7}Ga_{0.3}Se_2$). While development of a single-stage electrodeposition process to fabricate CIGS thin-films with near-ideal stoichiometry can be interesting, prior efforts have led to formation of undesired Cu-Se phases on the surface, which are detrimental to the performance of the device [5]. Use of complexing agents in the electrolyte during deposition and/or etching of the CIGS film using KCN is commonly practiced in order to remove excess Cu and, hence, the secondary Cu-Se phases. However these can lead to presence of impurities in the films and increased film roughness, which adversely influence the performance. Therefore, it is preferable to deposit an In-layer at the surface followed by annealing [7]. In addition, co-deposition of Cu-In-Ga-Se with required stoichiometry is difficult due to the large variation in their deposition potentials, whereas

two-stage deposition makes it relatively easier to achieve the required composition of elements. In a similar attempt, Bhattacharya *et al*. have reported three-stage (CIGS/Cu/In) direct-current (DC) electrodeposition of crack-free dense CIGS thin-films with lower Ga content, attributable to subsequent deposition of Cu and In layers and loss of material during annealing [7]. In the present work, suitable optimization of pulse parameters in the first stage followed by deposition of In in the second stage, aided the formation of stoichiometric CIGS films.



b

Element	Composition (at. %)	
	As-deposited	Annealed
Cu	22.31	24.00
In	17.39	18.25
Ga	5.49	6.75
Se	54.81	51.00

Figure 1

Figure 2a shows the typical XRD pattern of annealed CIGS thin-films prepared by two-stage PC electrodeposition revealing a preferred orientation corresponding to (112) of CIGS, other peaks corresponding to (220), (312) and (424) (JCPDS: 35-1102), confirming the presence of crystalline chalcopyrite CIGS phase [5]. In addition, peaks representing $MoSe_2$ (JCPDS: 29-0914) and Mo substrate (JCPDS: 42-1120) are also observed. Wada *et al*. have reported that formation of a thin layer of $MoSe_2$ at temperatures higher than 500 °C enhances adhesion and improves the ohmic contact between Mo and CIGS [11]. It is also interesting to note that no peaks corresponding to the undesired Cu-Se phases are observed.

Figure 2b shows the Raman spectra of the as-deposited and annealed CIGS films. The spectrum of as-deposited CIGS films reveals peaks corresponding to CIGS and undesired $Cu_{2-x}Se$ situated in the range of 160 – 180 cm^{-1} and 260 cm^{-1}, respectively, with the former peak being broader due to incomplete CIGS phase formation before annealing. In contrast, annealed CIGS thin films have well-defined peaks of CIGS A_1 mode and B_2/E mode at wave numbers of 176 and 215 cm^{-1}. The undesired $Cu_{2-x}Se$ phase is also absent in the annealed samples confirming the formation of single phase chalcopyrite CIGS thin-films, which also corroborates the XRD results. In addition, a mode corresponding to $MoSe_2$ is also observed at 241 cm^{-1} in the

annealed CIGS thin-films. Appropriate optimization of pulse parameters during deposition of Cu-Ga-Se in the first stage and In in the second stage, combined with the annealing conditions chosen, plausibly facilitated control over the overall composition and resulted in stoichiometric CIGS thin-films.

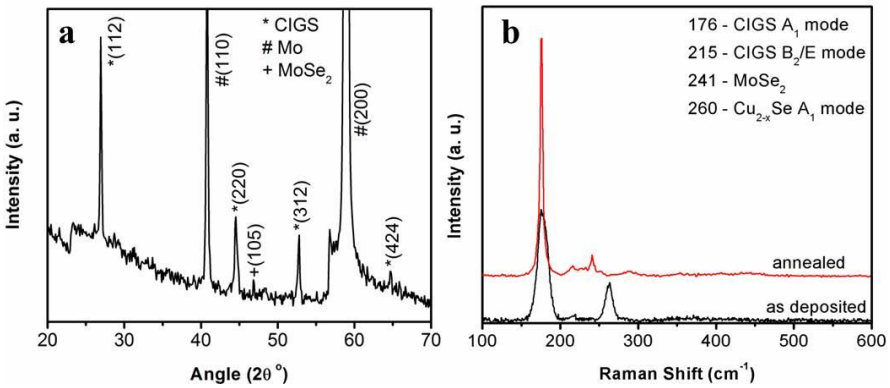


Figure 2

Figure 3a shows the $(\alpha h\nu)^2$ vs. $h\nu$ plot of annealed CIGS thin-films. Extrapolation of the linear section of the plot yields a bandgap of 1.27 eV, which compares well with the desired value. The photoelectrochemical performance of CIGS thin-films was investigated in 0.5 M Na_2SO_4. Current vs. potential curves were obtained in the potential range of 0 to -0.7 V vs. SCE at a sweep rate of 10 mV/s. Figure 3b shows the I-V curves in dark and under AM 1.5G solar simulated light for the CIGS films. I-V curve of one-stage PC electrodeposited CIGS films are also shown in Fig. 3b for comparison. An increase in cathodic photocurrent, characteristic of a p-type semiconductor, is observed with increase in cathodic potential. This behavior can be attributed to incomplete photonic conversion, which causes a recombination of charge carriers at the grain boundary of the semiconductor [12]. A photocurrent density of ≈ 0.2 mA/cm^2 at a potential of -0.6 V vs. SCE is observed. It is pertinent to note that significant reduction in the dark current and a considerable improvement in the photocurrent are observed compared to single-stage electrodeposited CIGS films previously reported, which yielded a photocurrent of ≈ 0.089 mA/cm^2 at a potential of -0.6 V vs. SCE [9]. The near-ideal stoichiometry and dense morphology achieved by the two-stage electrodeposition process, combined with complete elimination of the undesirable Cu-Se phase, could have resulted in the reduction of dark current and improved photocurrent. It is important to note that Cu-Se is present in the CIGS films deposited by DC deposition [5] and, being a degenerate semiconductor, is highly conductive. Consequently, its ability to sit at grain boundaries and/or at the surface of the film facilitates electron flow without any resistance even in the absence of light thereby contributing to high dark currents [13].

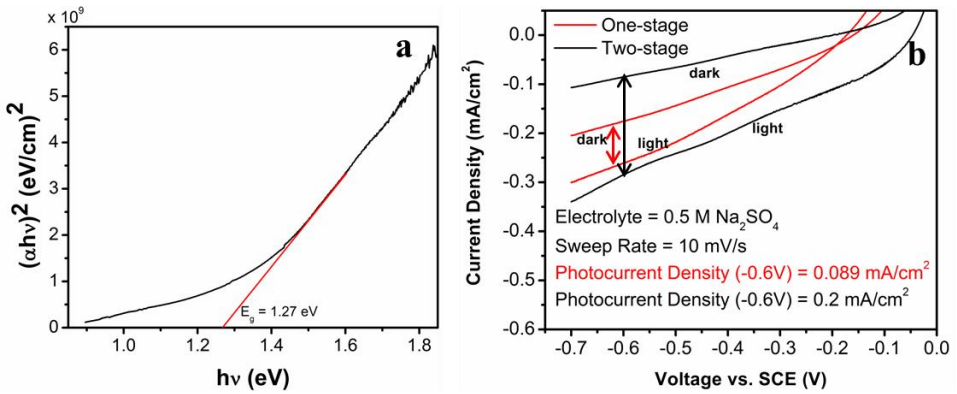


Figure 3

4. Conclusions

Near-ideal stoichiometric single phase chalcopyrite CIGS ($Cu_{0.96}In_{0.73}Ga_{0.27}Se_{2.04}$) thin-films have been deposited using two-stage (Cu-Ga-Se/In) PC electrodeposition. Second stage incorporation of In was found to successfully avoid formation of undesirable phases like Cu-Se. Deposition of phase pure CIGS films with dense morphology by this scalable process resulted in improved photoelectrochemical performance.

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Figure Captions

Figure 1: a) SEM image of an annealed two-stage PC electrodeposited CIGS thin-film and b) Elemental composition of CIGS thin-film before and after annealing

Figure 2: a) XRD pattern of annealed and b) Raman spectrum of as-deposited and annealed two-stage PC electrodeposited CIGS thin-films

Figure 3: a) $(\alpha h\nu)^2$ vs. $h\nu$ plot of two-stage PC electrodeposited CIGS thin-films and b) Photoelectrochemical response of annealed one-stage and two-stage PC electrodeposited CIGS thin-films