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## **Improved Photoelectrochemical Performance of CIGS Thin Films**

### **Prepared by Pulsed Electrodeposition**

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**Abstract:** - Solar cells based on polycrystalline Cu(In,Ga)Se<sub>2</sub> absorber layers have yielded higher conversion efficiency among all the thin-film technologies. CIGS thin-films possess large optical absorption coefficient ( $\approx 10^5 \text{ cm}^{-1}$ ) and a suitable bandgap of  $\approx 1.20 \text{ eV}$  for an ideal stoichiometry of CuIn<sub>0.7</sub>Ga<sub>0.3</sub>Se<sub>2</sub>. In the present study, Direct Current (DC) and Pulsed Current (PC) electrodeposition techniques are employed to obtain the near ideal stoichiometric CIGS thin-films on a Mo foil using a two electrode system at a constant potential. The as-deposited films are annealed at 550 °C under Ar atmosphere. Characterization of the annealed CIGS films is performed using SEM-EDS, XRD, Raman Spectroscopy and Photoelectrochemistry to study the morphology, stoichiometry, phase constitution and the photoelectrochemical response under solar simulated light. PC electrodeposition offered suitable manipulation of various parameters, which has helped in obtaining a better quality stoichiometric single phase chalcopyrite structured CIGS thin films with the elimination of unwanted secondary phases like Cu<sub>2-x</sub>Se. An improved photoelectrochemical performance, characteristic of a p-type semiconductor, is observed for the PC deposited CIGS films.

## **I. INTRODUCTION**

The usage of fossil fuels end up with contaminating the global environment and changing the global climate whereas the recently emerging photovoltaics remains one of the clean energy options for a pollution-free globe and is going to be the major means for future energy-harvesting system. Solar cells directly convert the incident sunlight to electricity based on the principle of photovoltaic effect. The main component of a solar cell is the absorber layer in which the incident light excites the ground state electrons to higher energy levels. An ideal absorber material essentially has to be a direct band gap semiconductor having high absorption

coefficient, long diffusion length and low recombination velocity and should be able to form a good electronic junction with suitably compatible materials. Extensive possibilities are being explored to increase the conversion efficiency and to fabricate low cost solar cells.

Among various absorber materials employed for solar cells, silicon (though an indirect bandgap semiconductor) has yielded highest conversion efficiencies<sup>1</sup>. Although significant fraction of the total solar cell market for terrestrial applications is constituted by Si wafer solar cells, the market for thin film solar cells is booming and is expected to grow significantly in the coming years. Thin films are favored over conventional silicon as the absorber layer due to the cost arguments and the superior energy balance. Thin film solar cells not only have the key advantage of dimensionality but also offer a wide variety of choices in terms of device design and fabrication. Among the thin-film technologies, CuInSe<sub>2</sub> with its direct bandgap, high optical absorption coefficient ( $\approx 10^5 \text{ cm}^{-1}$ ) and electronically rather passive defects is preferable. Substitution of In by Ga such that the ratio of Ga/(Ga + In) is around 25 – 30 %, shifts the bandgap from 1.04 to 1.15 eV, which is nearly ideal for a single junction cell. Presently, Cu(In, Ga)Se<sub>2</sub> thin-film solar cells are the most efficient thin-film based photovoltaics with laboratory efficiencies up to 20%<sup>2-4</sup>. Various processing techniques, including co-evaporation<sup>5</sup>, sputtering<sup>6</sup> and pulsed laser deposition<sup>7</sup> (PLD) have been used for the fabrication of high quality CIGS thin films. However, these conventional vacuum methods have drawbacks such as complexity in processing, high production cost and difficulty in scaling up, which are to be solved prior to the commercialization of the CIGS-based solar cells. Several non-vacuum based methods such as, electrochemical, electroless and chemical bath deposition have been widely investigated to fabricate CIGS thin-films. The above techniques involve electrochemical and chemical reactions

leading to the coating on an immersed substrate. Particulate-based processes use solid particles dispersed in a solvent to form an ink, which can be coated onto a substrate. Chemical processes also consist of coating molecular precursor solutions onto a substrate by mechanical means such as spraying or spin coating<sup>8</sup>. Among the non-vacuum-based methods, electrodeposition, a simple and economic method applicable to large area films with high quality in addition to efficient material utilization with minimum waste and high rate deposition process, has already witnessed reasonably higher efficiency CIGS based devices<sup>9</sup>. Electrodeposition of CIGS films can be performed with precise control over the stoichiometry and thickness on various substrates. Bhattacharya et al.<sup>9</sup>, studied electrodeposition of CIGS films by direct current (DC) deposition and have reported an efficiency of 14.1%. Aksu et al.<sup>10</sup>, have employed electroplating using constant current and have reported an efficiency of 15.36 % with the use of additives, complexing agents, etc. Fu et al.<sup>11</sup>, have explored different plating techniques including DC, pulse and pulse reverse electrodeposition for the fabrication of CIGS thin films and reported the elimination of undesired secondary phases like  $\text{Cu}_{2-x}\text{Se}$  to obtain single phase pure chalcopyrite CIGS thin films. Liu et al.<sup>12</sup>, have employed the PC electrodeposition with the variation of duty cycle to remove the excess In and to avoid In-Se compounds during the deposition for the preparation of CIGS thin films. The use of PC electrodeposition offers the manipulation of various parameters like amplitude of the current/potential, duty cycle, and the duration of deposition, thereby enables the control over the composition of individual elements in a ternary/quaternary system like CIS/CIGS to ultimately obtain the single phase CIGS by avoiding secondary phases like Cu-Se, In-Se, and Ga-Se, etc<sup>12</sup>. Also, with the variation of duty cycle, morphology of the thin films would evolve into a highly dense and compact form to yield higher performance of the device. However, very few reports are available on the preparation of CIGS

films by pulse and pulse-reverse electrodeposition, which are expected to result in better control over stoichiometry and morphology.

In the present study, we report the synthesis of stoichiometric CIGS thin films by DC and PC electrodeposition techniques using a two electrode system in an additive-free electrolyte. The additional step of selenization, which is conventionally used, is avoided in the present study. PC electrodeposition has improved the morphology and purity of CIGS which led to an improvement in the photoelectrochemical performance of CIGS thin films.

## **II. EXPERIMENTAL**

Electrodeposition of CIGS films is done from a bath containing  $\text{CuCl}_2$  (3 mM),  $\text{InCl}_3$  (3.2 mM),  $\text{GaCl}_3$  (8.5 mM),  $\text{H}_2\text{SeO}_3$  (8.5 mM) and  $\text{LiCl}$  (250 mM) dissolved in a pH 3 Hydriion buffer solution. The pH of the final solution is adjusted between 2.15 and 2.35 with the use of  $\text{HCl}$  and no additives were used. Electrodeposition of CIGS films by the application of DC and PC (Dynatronix Model DuPR10-3-6 Pulse Power Supply) is performed with an optimized set of pulse parameters (Pulse period – 20 ms and duty cycle – 50 %) in a vertical cell with high purity graphite plate as anode and Mo foil as cathode. Both DC and PC electrodeposition of CIGS are carried out by applying a potential of about -1.5 V for 15 min, at room temperature and without stirring. The electrodeposited films are annealed at 550 °C for 30 min in Ar atmosphere<sup>13</sup>.

X-ray diffraction (XRD) was employed to examine the phase constitution of the annealed CIGS films using a Bruker's D8 advanced X-ray diffractometer (Germany) employing  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). The diffraction patterns were collected in the range of  $2\theta = 10 - 90^\circ$  with

a scan rate of  $1^\circ$  per min. The microstructural and elemental analyses were performed using S3400N Scanning electron microscope (SEM) (Hitachi) with an attached EDAX system (Thermo Electron Corporation). Raman spectra of the samples were investigated using the Horiba Jobin Yvon-Lab Ram HR-800 Raman spectrometer with Ar ion laser as light source (514 nm). Photoelectrochemical (PEC) performance of the CIS thin films was investigated using the CH Instruments electrochemical analyzer (Model 660A). The measurements were carried out potentiostatically in a classical three-electrode electrochemical cell with the CIGS thin film with a surface area of  $1 \text{ cm}^2$  as the working electrode, Pt foil and a Saturated Calomel Electrode (SCE) as the counter and reference electrodes respectively, in  $0.5 \text{ M Na}_2\text{SO}_4$  solution. A Solar simulator (Newport) with AM 1.5 Global ( $80 \text{ mW/cm}^2$ ) lens was used as the light source.

### **III. RESULTS AND DISCUSSION**

Stoichiometric chalcopyrite CIGS thin films with good adhesion to the Mo foil using a two electrode system by optimizing the precursor concentrations, pH of the electrolyte deposition potential and pulse parameters. In a conventional three electrode system, although the reference electrode maintains a constant potential at cathode, it could possibly increase the impurities in the deposited film. Dharmadasa et al.<sup>14</sup>, reported that the absence of reference electrode changes the potential of the cathode only by a few mV indicating not much difference in the features of the deposit. In addition, a two electrode system is suitable for scaling up the process. During the process of optimization PC electrodeposition method, several parameters are varied for the deposition of CIGS thin films, however, the films are observed to have stoichiometry away from the ideal value, which resulted in presence of several other phases in addition to chalcopyrite CIGS. Hence in the present context, optimized CIGS thin films are being

discussed. Electrodeposition of the CIGS films is also done by use of DC electrodeposition at a potential of -1.5 V for comparison. Figures 1a and 1b show the SEM micrographs of the annealed DC and pulse electrodeposited CIGS films respectively. It can be observed from Fig. 1a that the morphology of the DC electrodeposited CIGS film exhibits a porous structure with finer spherical particles and the film appeared to be rough. The porosity of the film could be due to the building-up of the material at existing nucleation sites and/or due to the entrapment of hydrogen, generally evolved during the direct current deposition. Unlike the DC electrodeposited CIGS films, highly dense and smooth films with slightly coarser spherical particles exhibiting good uniformity are observed for PC electrodeposited CIGS films (Fig. 1b). PC method can produce relatively more homogeneous surface with good adhesion to the substrate because the rate-determining step of the deposition process is controlled by a mass-transfer process. Relaxation time in the PC electrodeposition not only allows the diffusion of ad-atoms but also facilitates the formation of new nucleation sites thereby leading to the homogeneous and compact structure unlike the DC deposition. Compositional analysis of CIGS thin films is performed by energy dispersive X-ray spectroscopy (EDS). The stoichiometry of the annealed DC and pulse electrodeposited CIGS films is obtained to be  $\text{Cu}_{1.10}\text{In}_{0.54}\text{Ga}_{0.23}\text{Se}_{2.13}$  and  $\text{Cu}_{0.98}\text{In}_{0.73}\text{Ga}_{0.25}\text{Se}_{2.03}$  respectively. The stoichiometry of DC deposited CIGS films is slightly away from the ideal value whereas near ideal stoichiometry is observed for the PC electrodeposited CIGS film.

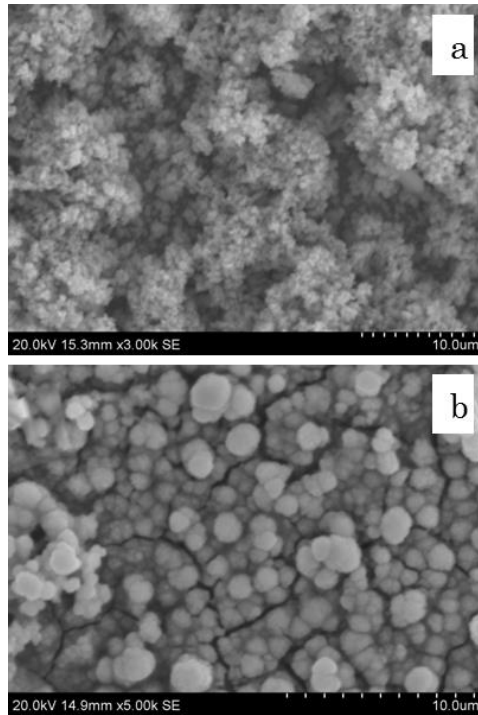


Figure 1: SEM Micrographs of annealed CIGS films prepared using a) DC and b) PC Electrodeposition

Figure 2 shows the XRD patterns of annealed DC and PC electrodeposited CIGS thin films. These patterns show preferred orientation corresponding to (112) and other orientations to (211), (220), (312) and (424) for CIGS (JCPDS diffraction file no. 35-1102) are observed in the film<sup>11</sup>. This confirms the presence of crystalline chalcopyrite CIGS phase in the film. In addition peaks representing MoSe<sub>2</sub> (JCPDS diffraction file no. 29-0914) and Mo (substrate, JCPDS diffraction file no. 42-1120) are also observed for both DC and PC electrodeposited films. Wada et al.<sup>13</sup>, have reported that at the Mo/CIGS interface, a thin layer ( $\approx$  100-150 nm) of MoSe<sub>2</sub> forms at temperatures higher than 500 °C, which not only improves the adhesion between Mo and CIGS but also enhances the ohmic contact. Except for the diffraction peaks from Mo substrate, MoSe<sub>2</sub> and CIGS films, the Cu<sub>2-x</sub>Se secondary phase (JCPDS diffraction file no. 53-0523) is also observed in specimen fabricated with the DC electrodeposition technique. However, the



secondary phase was absent in the specimens prepared by the pulse electrodeposition technique. This indicates that the pure phase of CIGS is successfully fabricated by the pulse electrodeposition technique ( $V = -1.5$  V vs. SCE with  $T_{on} = 10$  ms and  $T_{off} = 10$  ms and total time of deposition is 15 min).

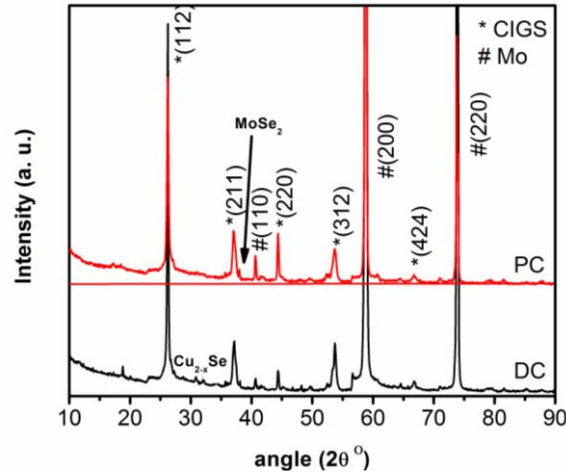


Figure 1: X-Ray Diffraction Patterns of annealed DC and Pulse electrodeposited CIGS thin films

Figure 3 shows the Raman spectra of the annealed DC and PC electrodeposited CIGS thin films.  $A_1$ ,  $B_2$  and  $E$  modes of the CIGS film are found at  $176$ ,  $205$  and  $232$   $\text{cm}^{-1}$  respectively for both CIGS thin films<sup>11</sup>. In addition to these peaks, a less intense peak corresponding to  $A_1$  mode of  $\text{Cu}_{2-x}\text{Se}$  is found at  $260$   $\text{cm}^{-1}$  in case of DC electrodeposited CIGS thin film. This  $\text{Cu}_{2-x}\text{Se}$  secondary phase is generally dispersed on the surface (Is it the dendritic part) of CIGS thin films. However, the  $A_1$  mode of the  $\text{Cu}_{2-x}\text{Se}$  secondary phase is not found in the thin film fabricated by the PC electrodeposition technique. It is suggested that the CIGS thin film fabricated by the PC electrodeposition technique with a pulse period of 20 ms and duty cycle of 50 % can effectively remove the  $\text{Cu}_{2-x}\text{Se}$  secondary phase and produce a single phase of CIGS chalcopyrite structure. As it can be seen from the stoichiometry of the DC and PC electrodeposited CIGS films ( $\text{Cu}_{1.10}\text{In}_{0.54}\text{Ga}_{0.23}\text{Se}_{2.13}$  and  $\text{Cu}_{0.98}\text{In}_{0.73}\text{Ga}_{0.25}\text{Se}_{2.03}$ ), excess Cu is

being deposited in case of DC deposited CIGS led the film to be away from the near ideal stoichiometry and hence facilitated the formation of the undesired  $\text{Cu}_{2-x}\text{Se}$  secondary phase. Use of complexing agents in the electrolyte during deposition and/or etching of the deposited CIGS film using KCN are in practice for the removal of excess Cu and hence the secondary  $\text{Cu}_{2-x}\text{Se}$  phase<sup>15</sup>. However, use of complexing agents might lead to the impurities in the film and KCN etching is found to make the film rough. Hence, in the present study, PC electrodeposition is employed with suitable optimization of parameters to control the composition of individual elements and aided the elimination of undesired  $\text{Cu}_{2-x}\text{Se}$  secondary phase.

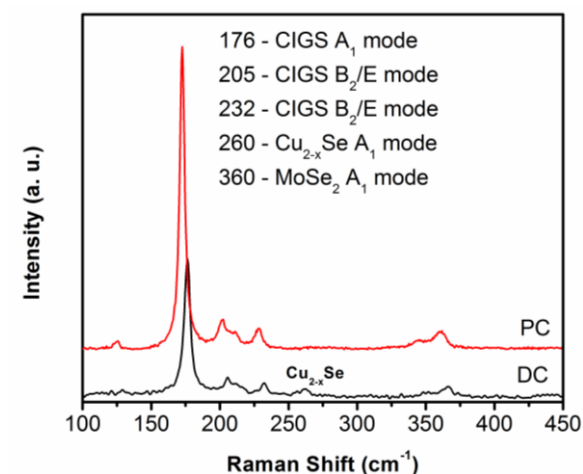


Figure 2: Raman Spectra of annealed DC and pulse electrodeposited CIGS thin films

The photoelectrochemical performance of annealed DC and PC electrodeposited CIGS thin films is studied in 0.5 M  $\text{Na}_2\text{SO}_4$ . Current vs. potential curves are obtained in the potential range of -0.1 to -0.7 V vs. SCE with a sweep rate of 10 mV/s. Figure 4 shows the I-V curve in dark and under AM 1.5 G solar simulated light for the CIGS thin films. An increase in cathodic photocurrent in the third quadrant, a characteristic of a p-type semiconductor, is observed with increase in cathodic potential in both the cases. This behavior is attributed to an incomplete

photonic conversion, which causes a recombination of charge carriers at the grain boundary of the semiconductor<sup>12, 16</sup>. Photocurrent densities of 49 and 85  $\mu\text{A}/\text{cm}^2$  at a potential of -0.6 V vs. SCE are observed for DC and PC electrodeposited CIGS thin films respectively. Relatively higher dark current is observed for the DC deposited CIGS over PC electrodeposited CIGS, which could be attributed to the presence of  $\text{Cu}_{2-x}\text{Se}$  secondary phase.  $\text{Cu}_{2-x}\text{Se}$ , being a degenerate semiconductor; is highly conductive and results in high dark currents<sup>17</sup>, is generally present in the CIGS films deposited by direct current (DC) deposition<sup>11</sup>. Near ideal stoichiometry and highly dense uniform morphology of the CIGS film and the reduction in quantity of  $\text{Cu}_{2-x}\text{Se}$ , the undesired secondary phase by PC electrodeposition have resulted in the improved photocurrent densities.

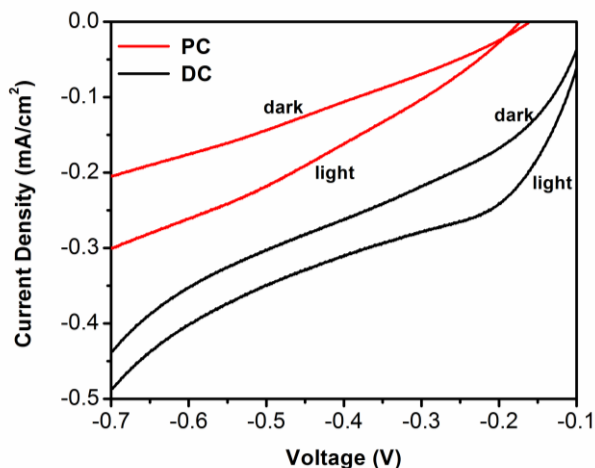


Figure 3: Photoelectrochemical response of annealed DC and pulse electrodeposited CIGS films

#### IV. CONCLUSIONS

CIGS thin films are deposited using DC and PC electrodeposition techniques in an additive free electrolyte by avoiding the additional step of selenization. DC electrodeposited CIGS films are slightly away from the near ideal stoichiometry and observed to have porous morphology with high surface roughness. However, parameters are successfully optimized for PC electrodeposition to produce near-ideal stoichiometric single phase chalcopyrite structured CIGS films with the elimination of undesired secondary phases. In addition, a highly dense uniform morphology is observed for PC deposited CIGS films which ultimately resulted in the improved photoelectrochemical performance of CIGS thin films. The characteristic of p-type semiconductor is observed in the both the DC and PC deposited CIGS thin films.

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