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## **Pulsed Electrodeposition of CuInSe<sub>2</sub> Thin Films with Novel Morphology for Solar Cell Applications**

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**Abstract**

Copper indium diselenide ( $\text{CuInSe}_2$ ) films have been prepared by pulse electrodeposition technique on Molybdenum substrate followed by post-deposition annealing at  $550^\circ\text{C}$ . Optimization of pulse parameters by varying the pulse duration (duty cycle) in order to achieve high quality films has been reported. Appropriate manipulation of pulse parameters has resulted in flake like crystallite morphology and better control over the composition of individual elements. The CIS thin films were comprehensively characterized using SEM-EDS, FIB, XRD and UV-DRS to study their morphology, phase constitution, etc. and PEC (photoelectrochemistry) measurements were also carried out to ascertain the photoelectrochemical performance of the CIS absorber layer. The bandgap of the CIS films was determined to be 1.02 eV. The flake like crystallite morphology observed in CIS thin films under the optimized processing conditions was found to yield enhanced cathodic photoresponse under solar simulated light with a photocurrent density of  $20\ \mu\text{A}/\text{cm}^2$  (observed at a potential of  $-0.6\ \text{V}$  vs. SCE). The films exhibited a photoresponse typical of a p-type semiconductor.

## Introduction

Solar energy is expected to play an important role in future energy production as per the current trends. An attractive way to convert solar radiation into electricity is by utilizing the photovoltaic effect. Presently, crystalline silicon plays a dominant role in the production of photovoltaic modules yielding a device efficiency of about 22 % [1]. Although silicon is highly abundant, it requires highly energetic processes to purify and crystallize, thereby making it expensive. Primarily due to this reason, recent interest has shifted to preparation of chalcopyrite thin films like CIGS ( $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ) and CIS ( $\text{CuInSe}_2$ ), highly promising semiconductor materials for the absorber layer in solar cells owing to their suitable bandgap modulation from 1.04 eV to 1.68 eV with the variation of stoichiometry ( $\text{CuInSe}_2$  through  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  to  $\text{CuGaSe}_2$ ) which lies in the optimum bandgap range (1.20 - 1.40 eV) required for the terrestrial solar applications [2, 3]. The favorable optical properties of these materials (direct energy band gap and high absorption coefficient ( $\approx 10^5 \text{ cm}^{-1}$ )) allows the use of thin films (few micrometers,  $\approx 1.5 - 2 \mu\text{m}$ ) instead of thick slices of silicon ( $\approx 150 - 300 \mu\text{m}$ ), thus reducing the consumption of materials [4]. In addition, CIS and CIGS thin-films exhibit highest conversion efficiencies among the thin film solar cells alongwith the long-term stability.

CIS thin films have been extensively used as solar absorber materials for incorporation in high-efficiency photovoltaic devices [5, 6]. Various processing techniques, including co-evaporation [7], sputtering [8] and pulsed laser deposition (PLD) [9] have been reported for preparation of high quality CIS thin films. However, 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 CIS-based solar cells. Therefore, a low cost method amenable for scaling up to industrial level fabrication, such as electrodeposition, is desirable. Electrodeposition has several advantages over vacuum based techniques since it is an economical

method applicable to large area films capable of yielding high quality in addition to efficient material utilization with high deposition rate and minimum wastage [10]. Deposition of CIS films can be done on various substrates like Mo coated soda-lime glass, stainless steel, conducting polymers, etc. with different shapes and sizes. The stoichiometry and thickness of the CIS films can also be conveniently controlled precisely in the electrodeposition route [11].

The synthesis of CIS thin films by electrodeposition is generally performed under potentiostatic and galvanostatic conditions, with either the use of direct current (DC) method wherein a fixed bias of potential or current is applied to the cathode, or a Pulsed current (PC) method. Pulsed electrodeposition (PED) is an advanced form of electrodeposition which offers better control over the deposit properties by controlling the interfacial electrochemical reaction for the formation of thin film [12]. PED technique is usually used to improve the quality of thin films via the application of current or potential with high instantaneous densities in pulses [13]. This process has several advantages over DC electrodeposition since it lends itself to improved process control by virtue of the possibility of manipulating parameters such as deposition potential, duty cycle and period. It can produce a more homogeneous surface with good adhesion to the substrate because the rate-determining step of the electrodeposition process is controlled by a mass-transfer process. It also offers a better control over stoichiometry during the deposition of a ternary or a quaternary system.

Electrodeposition of  $\text{CuInSe}_2$  thin films was first reported by Bhattacharya *et al.* [14]. Since then, CIS-based solar devices have been widely studied using electrodeposited precursors by several researchers [15-22]. Electrochemical synthesis of CIS films has been studied by Lincot *et al.*, who reported a conversion efficiency of 11.3 %, wherein they have performed one-step electrodeposition of CIS thin films in acidic conditions and have shown that formation of the binary phases precedes the chalcopyrite phase during electrodeposition [15-20]. Bhattacharya *et*

*al.*, have studied the reduction potentials of the individual elements in order to understand the related mechanism and have reported the influence of concentrations of the precursors salts in the bath on the stoichiometry and morphology of thin films using DC electrodeposition [10, 21-22]. Aksu *et al.*, have employed a two step electrodeposition process for the synthesis of chalcopyrite absorber layers which has improved the stoichiometry and hence the performance of these films [23]. However, the films synthesized using DC electrodeposition needed to be annealed in selenium atmosphere to achieve the required concentration of Se [10, 16]. Adhesion of such electrodeposited CIS thin films on a Mo substrate was observed to be poor and use of complexing agents improved adhesion [24]. However, use of additives is undesirable since they contribute to the reduction in efficiency of the cell, in the form of impurities in the absorber layer. PED is expected to make the CIS films more homogeneous and provides a better control over the composition of individual elements in such a ternary system. Kang *et al.*, have reported that preparation of CIS thin-films with pulse reverse electrodeposition results in good adhesion of the film to the substrate and a smooth surface with fine grains [25]. However, a very limited research has been reported on the electrodeposition of CIS thin-films by use of PED. Generally, the performance of the films synthesized by these techniques is investigated by fabricating the complete photovoltaic cell, which involves the deposition of buffer layer (n-CdS) and transparent conducting layers (ZnO) followed by the deposition of a metal top contact, which is a difficult and time-consuming process leading to the longer optimization period to evaluate the suitable thin film. Assessment of the thin films in a PEC cell is faster and it enables one to find the CIS material dependent problems such as interface contact with the full device architecture because the appropriate liquid electrolyte can form a reproducible contact [26]. In addition, CIS thin-films have a long term stability in the whole pH range of the electrolytes and also exhibit good photostability in the visible spectrum [27, 28]. Several groups have performed PEC to ascertain the performance of CIS and CIGS films for similar reasons [26-30].

In the present study, we report the preparation of CIS thin films by pulse electrodeposition technique using a two electrode system. Pulse parameters were optimized in order to achieve high quality CIS thin films and use of additives (complexing agents) and additional step of selenization, which was used invariably by most of the researchers, were avoided. The systematic control over the composition of individual elements with the pulse parameters and a novel morphology are reported, which ultimately improved the photoelectrochemical performance of the CIS absorber layers. Morphology of the pulse electroplated CIS films is used to explain the improvement in photocurrent.

## **Experimental**

Co-deposition of Cu-In-Se by the pulse electrodeposition process was done from a bath containing  $\text{CuCl}_2$  (4.35 mM),  $\text{InCl}_3$  (5.56 mM),  $\text{H}_2\text{SeO}_3$  (8.14 mM) and  $\text{LiCl}$  (0.26 M) dissolved in Hydriion buffer (pH 3) solution consisting of potassium hydrogen phthalate and sulphamic acid. The final pH of the solution was adjusted between 2.15 and 2.25 by addition of HCl. CIS films were deposited in a vertical cell with a two electrode system in which the electrodes (anode and cathode) were suspended vertically from the top of the cell. A high purity graphite plate was used as anode and Mo foil (10mm x 10mm) was used as cathode. Conventionally Pt is used as anode for the electrodeposition of CIS thin-films. However, use of Platinum makes the process expensive, especially for large area deposition, whereas the use of graphite makes the process less expensive and scaling up involves significant reduction in cost compared to the use of Pt anode without compromising over the quality of thin film. In addition, the two electrode system is more suitable for the production of large area electrodes that are to be used in devices and modules compared to a three electrode system for the synthesis of the CIS thin films [31]. Mo foils were mechanically polished using diamond paste prior to electrodeposition. Polished Mo foils were rinsed with

distilled water and ultrasonicated in acetone for about 10 minutes. Then the foils were pre-treated using 15 % HCl and 1M NaOH solutions in order to remove the oxide layer and impurities on the surface. The pre-treated Mo foils were rinsed again with distilled water thoroughly and sonicated in ethanol for about 10 minutes and were purged with nitrogen gas prior to deposition. PED technique was used for the deposition of CIS films wherein, pulse on-time ( $T_{on}$ ) was maintained at 10 ms while the pulse off-time ( $T_{off}$ ) was varied in the range of 5 ms - 50 ms (Table 1). A Dynatronix Model DuPR10-3-6 Pulse Power Supply was used to electrodeposit the CIS precursor films. Films were deposited with various sets of pulse parameters. The cathodic pulse potential was kept constant at -1.5 V for all the deposition experiments. The deposition was performed for 15 min at room temperature and without stirring. The electrodeposited films were rinsed with deionized water and were annealed at 550° C for 30 min in Ar atmosphere in order to improve the crystallinity of the CIS films and to enhance the ohmic contact.

Grazing Incidence XRD (GIXRD) was employed to examine the X-ray Diffraction patterns of the annealed CIS films using a Bruker's D8 advanced X-ray diffractometer (Germany) employing Cu  $K_{\alpha}$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). An angle of 1° was used for the Grazing incidence XRD. The diffraction patterns were collected in the range of  $2\theta = 25 - 70^{\circ}$  with a scan rate of 1°/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 was investigated using the Horiba Jobin Yvon-Lab Ram HR-800 Raman spectrometer with Ar ion laser as light source (514 nm). UV-Vis-DRS spectra were obtained using CARY VARIAN-5000 UV/VIS/NIR (ultraviolet/visible/near infrared) spectrometer in the wavelength range of 200 – 2500 nm.

Focussed ion beam milling and imaging was performed using a Carl-Zeiss dual beam system



(Neon-40) with Ga as the ion source. A trench was milled over the surface of CIS film to view the cross section using 30kV beam voltage. Rough milling of the trench was done using a 2 nA beam current whereas a 500 pA beam current was used for the final smooth milling of the trench. Cross sectional images were taken by the FIB and SEM at angles of 90° and 54° respectively with respect to the film surface.

The 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 CIS thin film with a surface area of 1 cm<sup>2</sup> as the working electrode, Pt foil as the counter electrode and a Saturated Calomel Electrode (SCE) as the reference, in 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution as the electrolyte [13]. A Solar simulator (Newport) with AM 1.5 Global (80 mW/cm<sup>2</sup>) lens was used as the light source for the PEC measurements.

## **Results and Discussion**

Pulse electrodeposition (PED) of the CIS thin films is performed on Mo substrate using a two electrode system by use of a series of pulse parameters. Use of a three electrode system with SCE or Ag/AgCl as reference electrode is generally in practice for the deposition of CIS thin films since the reference electrode maintains the potential constant at cathode. However, use of reference electrode is shown to increase the impurities in the film causing reduction in the photovoltaic response [31]. Dharmadasa *et al.*, 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 [32]. Therefore, a two electrode system with a higher deposition potential of -1.5 V are used in the present work for the deposition of CIS films. Electrodeposition potentials lower than -1.5 V with the two electrode system resulted in In poor films for all the pulse parameters.

Therefore, -1.5 V was chosen as deposition potential. Dharmadasa et al. [32], have used higher potentials (around 2.20 – 2.40 V) to increase the content of In to desired value using DC electrodeposition with the electrolyte pH around 1.70. Also it is reported that, at potentials less than 2.0 V and greater than 2.5 V (in the range of 2.53 – 2.56 V), the films grown are disrupted and dissolved in the electrolyte which indicates the composition of the electrodeposited layers at these particular voltages is not helpful in growing stable layers for fabrication of solar cells. The particular compositions seem to create weak bonding between atoms and hence produce cracking, disruption and dissolution of the film into the electrolyte [32]. Although higher potential is employed for deposition but the corresponding effective current density was around 7 – 8 mA/cm<sup>2</sup> [31, 32]. In addition, current efficiency was calculated to be  $\approx 95\%$ , by use of Faraday's law. This fact affirms that there is no considerable hydrogen evolution during the deposition. In the present case PED is employed, which provides a better control over the compositions of the elements by varying the pulse parameters, has helped in obtaining high quality CIS thin films at lower potentials without any disruption and dissolution of the film into the electrolyte. During PED, deposition of CIS films occurs on the cathode during the pulse on-time, while during pulse off-time, formation of new nucleation sites and selective dissolution of the deposited material take place. Also faster deposition rate is observed with the application of potential in pulses and ultimately reduced the time of deposition to 15 min. Deposited CIS films were annealed at 550° C for 30 min under Ar atmosphere. Wada *et al.*, have reported that, at the Mo/CIGS interface, formation of a thin layer of MoSe<sub>2</sub> takes place at temperatures higher than 500° C and this not only promotes the adhesion between Mo and CIS but also improves the ohmic contact [33]. Effect of pulse parameters on the composition of individual elements and morphology of the electrodeposited CIS films was studied in detail. It has been observed that content of Indium in the films increased drastically and the amount of Copper and Selenium reduced with the variation of T<sub>off</sub>. In order to further investigate, a detailed study on the optimization of In content with the variation of pulse off-time is employed.

Table 1 shows the variation of atomic percentages of individual elements (obtained from elemental analysis using EDS) and, hence, the composition of annealed CIS films deposited using different values of  $T_{\text{off}}$ . The ideal stoichiometry of copper indium diselenide is  $\text{CuInSe}_2$  corresponding to a composition (in atom %) of Cu-25%, In-25% and Se-50%. It is clearly observed from Table 1, that the film composition exhibited a stoichiometry close to ideal value for a film deposited with  $T_{\text{off}}$  values of 8 ms and 10 ms for a fixed  $T_{\text{on}}$  value of 10 ms i. e. samples 2 and 3. It is also observed that the concentration of In decreased with increase in  $T_{\text{off}}$  value. For sample 6, very small amounts of In was found in the film. The morphology of CIS films for different  $T_{\text{off}}$  values, while  $T_{\text{on}}$  was kept constant at 10 ms, is shown in Fig. 1. The morphologies of CIS films 2 and 3 are shown in Fig. 1a and 1b. The morphology, in both the cases, exhibits a flake like crystallite structure. This structure is novel and to the best of author's knowledge, is being reported for the first time for CIS thin films. Such a structure is expected to be advantageous in increasing the photoelectrochemical response of the film. With optimization of  $T_{\text{off}}$ , the desired morphology can be achieved. Flake like crystallites formed during PED are expected to increase the area of the film which is exposed to light, thereby causing improvement in photoelectrochemical response. This is expected to be particularly advantageous at the device stage since it facilitates increase in the p-n junction area of the solar cell which directly influences its performance. The morphology of CIS film, sample 5, shown in Fig. 1c, contains the crystallites, but is deviated from the morphology of sample 3 probably due to the insufficient In content in the film. As previously mentioned, very small amounts of In was found in the film for sample 6. The morphology for the same pulse condition is shown in Fig. 1d. The surface morphology for such high values of  $T_{\text{off}}$  deviated from the flake like crystallite structure and the In content too, was not sufficient to form the desired phase of  $\text{CuInSe}_2$ . Kang *et al.*, have reported the faceted growth of CIS films (annealed under selenium atmosphere) by pulse electrodeposition technique and reported an efficiency of 1.43% [25]. The present optimized CIS films contain flake like crystallite structure which is expected to improve the

photovoltaic performance of CIS films.

Focussed ion beam analysis was employed for the first time to study the cross section of the Mo-CIS thin film interface. A FIB cross sectional image of the CIS film (sample 3) is shown in Fig. 2. It can be clearly observed that there is a well defined interface with a continuous layer between the Mo foil (substrate) and the deposited CIS layer. The thickness of the CIS layer around this Mo-CIS interface is of the order of 100 nm. The presence of this interface confirms the fact that Mo is not exposed to light during the measurement of photoelectrochemical response of the CIS thin films. The lower dark current during the photoelectrochemical performance confirms the same, as shown later in Fig. 6, because being a metal Mo is expected give very high dark currents upon exposure to the electrolyte.

XRD patterns of annealed CIS films deposited with the variation of off-time are shown in Fig. 3. All these spectra show that the strongest peak corresponds to the (110) preferred orientation of the molybdenum substrate (JCPDS diffraction file no. 42-1120). In addition, the chalcopyrite structure of CIS thin film (JCPDS diffraction file no. 35-1102) is also confirmed by the XRD patterns with preferred diffraction orientation to (112). It has already been explored by several researchers that CIS thin film has preferred diffraction orientation to (112), however, it varies with the orientation of the substrate [15-20]. Also orientations of CIS film, corresponding to (220), and (312) are seen in the patterns [24]. XRD patterns show higher intensity for the desired  $\text{CuInSe}_2$  (112) orientation for samples 2 and 3. A very less intense peak corresponding to  $\text{CuInSe}_2$  (112) phase was observed for the sample 6 since the content of In present in the films was minimum. Undesired copper selenide phases, which are generally observed in the DC electrodeposited CIS films, are not observed from the XRD patterns in the present PED deposited CIS films.

Fig. 4 shows the Raman spectra of electrodeposited and annealed CIS films for samples 3 and 5, respectively. Presence of different phases for CIS films are being explored. For sample 3, well-defined peaks of  $A_1$ ,  $B_2$  and E modes of CIS were observed at wave numbers of 176, 215 and 234  $\text{cm}^{-1}$ , respectively while for sample 5 only  $A_1$  mode was noted. In addition, the  $A_1$  mode of  $\text{Cu}_{2-x}\text{Se}$  is also found at 260  $\text{cm}^{-1}$  in both the spectra [13], however, it can be seen that the  $\text{Cu}_{2-x}\text{Se}$  Raman mode has a stronger peak for sample 5 compared to sample 3. This can be attributed to the lower content of In at higher values of  $T_{\text{off}}$ , resulting in the formation of the undesired  $\text{Cu}_{2-x}\text{Se}$  phase. The presence of such copper selenide phases is detrimental to the performance of the CIS film upon exposure to sunlight, as being a degenerate semiconductor,  $\text{Cu}_{2-x}\text{Se}$  is highly conductive and results in high dark currents [34]. These results from Raman spectra also indicate that the PED technique allows good control over phase formation by suitably manipulating the pulse parameters to obtain the required phases. Fig. 5 shows the  $(\alpha h\nu)^2$  vs  $h\nu$  plot of annealed CIS thin film (sample 3). Extrapolation of the linear section of this plot yields a bandgap of 1.02 eV, which is close to the reported value of 1.04 eV for  $\text{CuInSe}_2$  [35].

The photoelectrochemical performance of the electrodeposited  $\text{CuInSe}_2$  thin films was studied in a 0.1 M  $\text{Na}_2\text{SO}_4$  solution at pH 4.0 [13]. Current vs. potential curves were obtained in the range of 0 to -1.0 V vs SCE with a potential sweep rate of 10 mV/s. Fig. 6 shows the current-potential curves under dark and AM 1.5 G solar simulated light for the sample 3. The I-V curve is similar to the one reported [29]. An increase in cathodic photocurrent, a characteristic of a p-type semiconductor, is observed with increase in cathodic potential. This behavior is attributed to an incomplete photonic conversion, which causes a recombination of charge carriers at the grain boundary of the semiconductor [30]. Photocurrent density obtained at a potential of -0.6 V vs. SCE is  $\approx 20 \mu\text{A}/\text{cm}^2$ . Ugarte *et al.*, observed multinuclear, spherical particle like growth in morphology and reported a photocurrent density of  $10 \mu\text{A}/\text{cm}^2$  at -0.6 V for the CIS film, however glycine acid

and EDTA were used during deposition to improve the photocurrent of CIS thin films [29]. In the present study, the reason for the increment in the photocurrent can be attributed to the flake like crystallite structure of the CIS films achieved through appropriate control of pulse parameters. Zhou et al., have achieved similar morphology and reported that the CZTS flower like particles increased the performance of the device and also observed the reduction in electrical resistivity [36]. In the present case flake like crystallite structure is favorable to increase current carrier concentration, electron transmission and thus induce the generation of photocurrent [36]. In addition to the flake like crystallite structure, considerable reduction of undesired  $\text{Cu}_{2-x}\text{Se}$  secondary phases, achieved with suitable variation of pulse parameters, is one of the significant factors in the improvement of photocurrent. Kemell *et al.*, observed that the photoactivity of CIS films was completely lost and have attributed that it might be due to the segregation of the detrimental  $\text{Cu}_{2-x}\text{Se}$  phase to the surface or at the grain boundaries [34]. Also, the interfacial adhesion between the CIS thin film and the Mo substrate becomes very poor, resulting in an adverse effect on the interface resistance which deteriorates the performance of the solar absorber layer [13]. Hence in the present context, with suitable manipulation of pulse parameters  $\text{Cu}_{2-x}\text{Se}$  phases were reduced which resulted in improved photoelectrochemical performance of the CIS thin films.

## Conclusions

Optimized CIS thin films with controlled Cu, In and Se content have been successfully deposited by pulse electrodeposition technique at a cathodic potential of about -1.5 V with the optimized pulse condition of  $T_{on} = 10$  ms and  $T_{off} = 10$  ms. A two electrode system is considered over a three electrode system as mentioned earlier which is economical for scaling up. The optimized CIS thin films contained flake like crystallite structure which is advantageous because of the high surface area that improves the photoresponse of the film. Flake like crystallite structure is also expected to be advantageous at device stage due to the possible increment in the junction area which further improves the performance of the solar cell. The chalcopyrite structure of the CIS films is confirmed from the XRD and Raman spectroscopic measurements. From the Raman spectra it is also concluded that the undesired secondary phase of  $Cu_{2-x}Se$  can be reduced by varying the pulse parameters and is observed to be minimum for the electrodeposited CIS with optimized pulse condition. Optical absorption studies confirmed the bandgap of CIS films as 1.02 eV which is similar to the value reported earlier. Photoelectrochemical response of the CIS films is studied and a photocurrent density of  $\approx 20 \mu A/cm^2$  is obtained for the CIS film which is deposited at the optimized pulse condition. Further, the studies are under progress including the growth mechanism of CIS film by PED, the device fabrication and testing with the optimized pulse electrodeposited CIS thin-film.

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**Figure Captions:**

Figure 1: Morphology of annealed CIS films deposited with the variation of pulse off-time: (a) 8 ms, (b) 10 ms, (c) 18 ms and (d) 50 ms. ( $T_{on} = 10$  ms, deposition potential = -1.5 V, deposition time = 15 min ).

Figure 2: Cross-sectional FIB image of an annealed CIS film deposited at  $T_{on} = 10$  ms and  $T_{off} = 10$  ms.

Figure 3: XRD spectra of electrodeposited and annealed CIS films with the variation of pulse parameters.

Figure 4: Raman spectra of electrodeposited and annealed CIS films for different pulse off-times of 10 ms and 18 ms.

Figure 5: Plot of  $(\alpha h\nu)^2$  against  $h\nu$  for the CIS film deposited at the optimized pulse condition ( $T_{on} = 10$  ms and  $T_{off} = 10$  ms).

Figure 6: PEC measurements: I-V characteristics of the annealed CIS film deposited at the optimized pulse condition ( $T_{on} = 10$  ms and  $T_{off} = 10$  ms) under AM 1.5 G solar simulated light.

**Table Captions:**

Table 1: Variation of In content and film composition with pulse off-time. (At constant  $T_{on} = 10$  ms)

## Tables

Table 1

Sample No.	Off-time (ms)	Cu Content (at. %)	In Content (at. %)	Se Content (at. %)	Film Composition
1	5	24.75	40.20	35.00	$\text{Cu}_{0.99}\text{In}_{1.61}\text{Se}_{1.40}$
2	8	26.00	24.78	49.25	$\text{Cu}_{1.04}\text{In}_{0.99}\text{Se}_{1.97}$
3	10	24.25	24.69	51.25	$\text{Cu}_{0.97}\text{In}_{0.98}\text{Se}_{2.05}$
4	15	32.50	18.75	48.75	$\text{Cu}_{1.30}\text{In}_{0.75}\text{Se}_{1.95}$
5	18	37.25	15.35	47.75	$\text{Cu}_{1.49}\text{In}_{0.61}\text{Se}_{1.91}$
6	50	53.75	1.99	40.50	$\text{Cu}_{2.15}\text{In}_{0.23}\text{Se}_{1.62}$