

## Pulse Electrochemical Deposition and Photo-electrochemical Characterization of CuInSe<sub>2</sub> Thin Films

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Direct band gap and high absorption coefficient of copper indium diselenide (CIS) make it as one of the most studied ternary chalcogenides for energy conversion. Low cost methods, such as electrochemical deposition are very beneficial because of large scale production possibility, minimum waste of components and no requirement of pure starting materials. The pulse electrodeposition allows independent variation of duty cycle. In this study pulse electrodeposition of polycrystalline thin film of CuInSe<sub>2</sub> (CIS) onto ITO glass substrates from aqueous solution containing CuSO<sub>4</sub>, In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and SeO<sub>2</sub> was carried out. The probable potential for deposition was determined as -0.9 V from cyclic voltammogram. The deposited film was annealed at 400 °C under nitrogen gas flow to provide neutral atmosphere to improve the crystalline quality and remove excess selenium. The film was analyzed using X-ray diffraction which confirmed that CIS deposit has tetragonal structure. The chalcopyrite formation and consistency in terms of stoichiometry in the deposit were proved. The optical property of the thin film was determined base on the measurement by using UV-Vis spectrophotometer. The direct band gap for the thin film is around 1.21 eV. As a result, the deposited CIS thin film is a potential candidate to be used in solar cell devices as an energy convertor. Atomic force microscope was employed to monitor the effect of duty cycles on the morphology of the thin film. It is revealed that with increasing duty cycle the surface morphology shift from smooth to dendrite structure. Photo-electrochemical characterization was performed under chopped white light in acidic redox media. It was showed that CIS film is a photosensitive material and stands as p and n-p type semiconductors by adjusting different duty cycles. The photoactivity of the films was highly affected by their surface morphology.

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**Keywords:** CuInSe<sub>2</sub>, Thin film semiconductor, Material for energy conversion, Pulse electrodeposition, Photoactivity,

## 1. INTRODUCTION

Ternary semiconductor CuInSe<sub>2</sub> (CIS) with a direct band gap of approximate 1.02 eV and high absorption coefficient ( $\alpha$ ) exceeds  $10^5 \text{ cm}^{-1}$  are suitable material for photo electrochemical energy conversions [1]. To utilize CIS for solar energy conversion, single crystal and thin film with high efficiency (~12%) had been synthesized [2]. Polycrystalline CIS thin film can also be synthesized by low cost techniques, such as electrochemical deposition, chemical spray and chemical bath deposition. Electrochemical deposition is very beneficial because of extensive production possibility, smallest waste of components during process and no necessity of pure precursors [3-5]. Pulse electrodeposition allows independent variation of three parameters; potential, period and duty cycle at the same time [6-8]. The advantages of pulse electrochemical deposition in comparison with (the) deposition technique(s) are well dispersed deposition and good deposition-substrate adhesion. [9]. High stability ternary copper chalcogenide and positive flat band of CIS make it an interesting and practical material to be investigated for photo-electrochemical cell. There is a relation between photo-electrochemical characterization (PEC) and surface characteristic [10, 11]. Depend on preparation terms, being n or p type semiconductor and different electrical and optical behavior of CIS can be produce [12]. Heat treatment of the thin film proves the crystalline structure and subsequently the energy conversion quality [13].

This article focuses on electrodeposition of CIS polycrystalline thin film on ITO glass (indium-tin oxide) substrates by pulse electrochemical deposition technique from aqueous solution. The effect of heat treatment on deposited thin film was carried out to obtain high purity CIS phase and improve the crystalline structure. The relationship between surface structure obtained by different duty cycles and photo-electrochemical behavior in acidic media was studied.

## 2. EXPERIMENTAL

### 2.1 Deposition of films

Pulse electrochemical deposition, cyclic voltammogram (CV) and Photo-electrochemical characterization (PEC) were carried out by using three electrode cells; Ag/AgCl as the reference electrode, ITO glass as the working electrode and platinum wire as the counter electrode by hiring  $\mu$ -type III AUTOLAB. Stainless steel crocodile clips were used to attach the electrodes to Autolab.

High transmission and low resistivity ITO coated glass make it as a preference substrate for electrochemical deposition. The ITO glass ( $3 \text{ cm}^2$ ) was washed with detergent to remove the grease and ultrasonicated in 0.1 M NaOH solution, acetone and deionized water for 10 minutes subsequently it was etched in concentrated H<sub>2</sub>SO<sub>4</sub> for two seconds at 80 °C to eliminate the partial indium oxide on the surface of ITO glass[3]. Finally rinsed was done with Millipore water and dried in controlled atmosphere oven at 70 °C.

CuInSe<sub>2</sub> was deposited cathodically from aqueous solution which contains 3 mM CuSO<sub>4</sub>, 7 mM In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 11 mM SeO<sub>2</sub> [3]. To let the ions be mature in Millipore water (18 M $\Omega$ -cm), the solutions

were kept for one week in the safe room to be away from light and oxygen. To achieve a homogenized mixture the solution was ultrasonicated 40 KHz was used for 15 minutes.

The electrodeposition was carried out non stirred aqueous solution by using square pulse potential with -0.9 V as on-potential and 0.122 V as off-potential steps voltage . The electrochemical deposition potentials were extracted from the cyclic voltammogram of electrolyte solutions. Pulse period (on-time and off-time) was influenced by different duty cycle values. A proper electrodeposition time was 15 minutes. The effect of pH was studied by adding 0.1 M H<sub>2</sub>SO<sub>4</sub> to the mixed solution.

## 2.2 Films Characterizations

The deposition potential was determined by adjusting various estimated potentials which is done by interpreting the CV graphs. To find the composition of each electrochemical deposited thin films XRD patterns run by Philips PM 1730 with Cu K $\alpha$  radiation (1.54 Å).

Thermal annealing was performed at Carbolite tube furnace to find better stability between deposition and ITO glass, eliminate the excess deposited selenium and improve the crystalline structure. As-deposited sample (dried at 70 °C for 12 hours) was studied in different annealing temperatures from 250 °C to 450 °C for 20 minutes with heating rate of 5 °C/min and the cooling rate of 1 °C/min. To neutralize the atmosphere of furnace, a gentle flow of nitrogen gas was used.

The band gap was calculated by manipulating the absorbance optical behavior raw data measured with UV-visible spectrometer Lambda 35 using Stern equation.

By using Atomic Force Microscope (AFM) with Q-Scop 250 camera in AC mode the effect of different duty cycles on morphology and surface roughness, were visualized.

The photosensitivities of deposited films were examined by Photo-electrochemical characterization (PEC) method. Photo-electrochemical characterization (PEC) was done by illuminating the sample with chopped white light by source of Philips 13096 ELH GY 5.3 120 V halogen lamp with a distance of 12 cm far from the quartz window electrolyte holder , and acidic redox back ground of 0.1 M H<sub>2</sub>SO<sub>4</sub> as electrolyte[3].

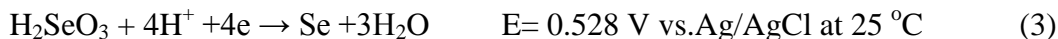
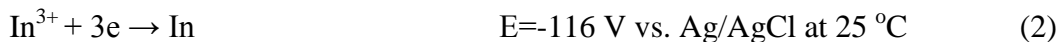
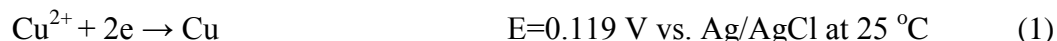
Deaeration of all the solutions and providing the inert atmosphere layer on the surface of electrolyte were done by using nitrogen gas. All the experiments were conducted at the ambient temperature (26.5°C).

## 3. RESULTS AND DISCUSSION

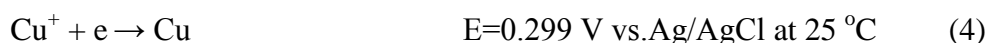
### 3.1. Cyclic voltammogram of aqueous solutions

Cyclic voltammogram (CV) were run between 1.00 - -1.00V with scanning rate of 20 mVs<sup>-1</sup> to determine redox reversible electrolytes behaviors for CuSO<sub>4</sub>, In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, SeO<sub>2</sub>, and their mixture solution in the presence of dilute sulfuric acid. The CVs are shown in Fig 1. The reduction potentials for non mixture solution are around -0.8 V for Cu<sup>2+</sup> to Cu, -0.99 V for In<sup>3+</sup> to In and -0.97 V for Se<sup>4+</sup> to

Se. The nucleation and growth mechanism for electrochemical deposition of CuInSe<sub>2</sub> is most expected caused by the standard half cell reactions as follow[14].

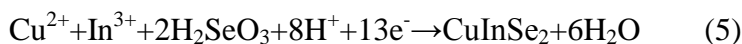


The CV of mixture electrolyte has two peaks in reduction domain, the first peak which is located at -0.37 V belongs to half reaction of Cu in presence of sulfuric acid.



The second peak at -0.87 V is a chance to be the prefer potential for electrochemical deposition of CuInSe<sub>2</sub> on ITO glass. In the mixture solution according to Fig.1d, at the potential around 0.112V there is no current. Therefore, the electrolyte has the opportunity to be relaxed and become homogenous. This phenomenon makes this potential to be chosen as off-potential for pulse electrodeposition.

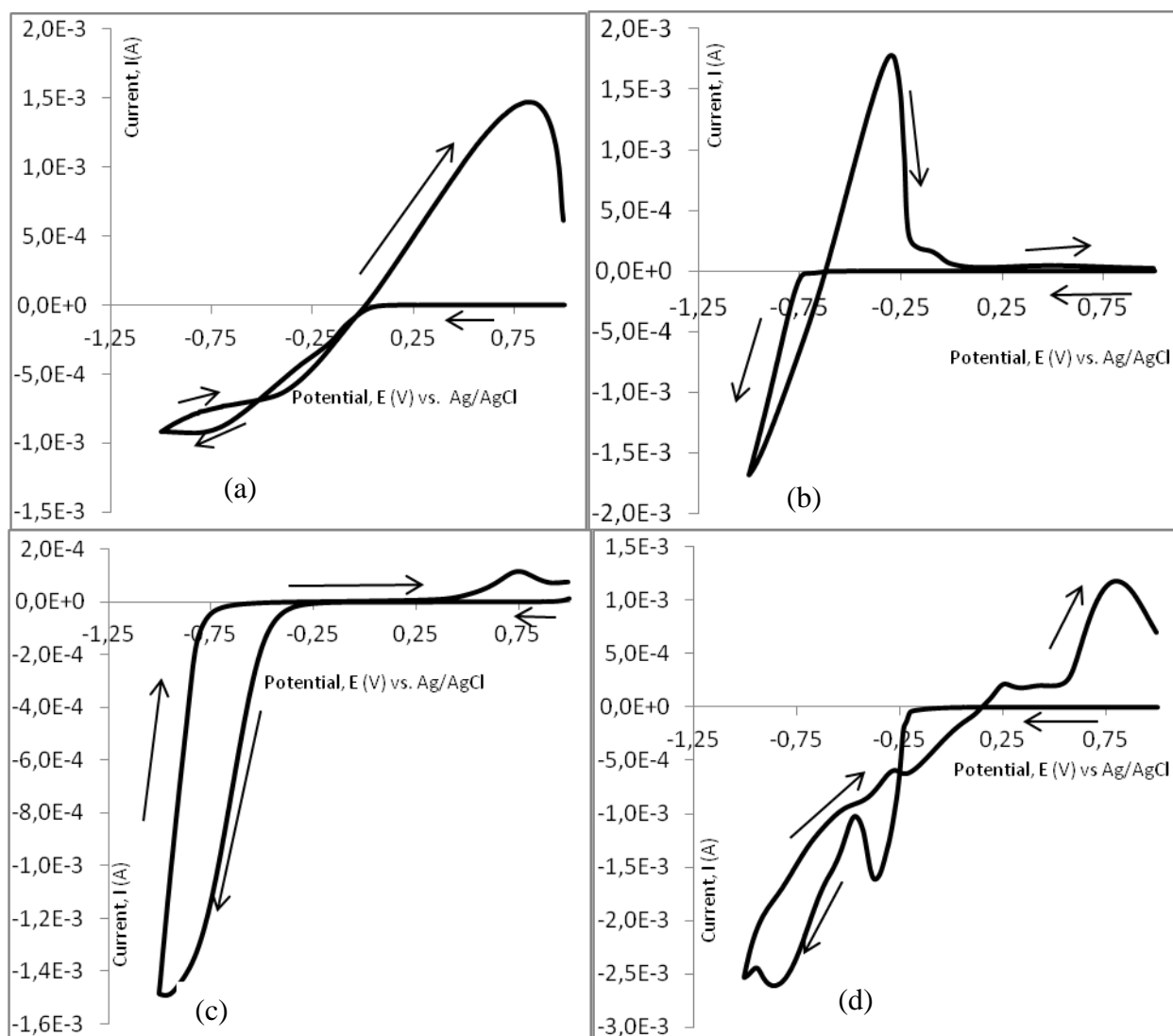
The electrochemical formation process of copper indium diselenide from the electrolyte mixture to ionic solid state reaction can be [6, 15, 16]:



Although the location of reduction peak for Cu is more negative than Se as seen for separate solution, in the mixed solution the deposition potential for Se became more negative in the presence of Cu ions [16]. Because of this in as deposited sample the existence of deposited Se impurity is not negligible.

Smaller Gibbs free energy at the edge of ITO coated glass, made by capillary cracks which created there during cutting the glass, makes more opportunity for the embryo(s) to nuclei and grow. As a result, the deposition starts from the edge toward the center.[17].

The existence of ions in the mixture electrolyte makes the solution opaque followed by formation white sediments in the beaker due to reaction between  $\text{In}_2^{+3} + \text{Se}^{+2}$ . Reducing the pH to 2.5 by adding 0.1 M H<sub>2</sub>SO<sub>4</sub> makes the solution clear. However the depositions in to more acidic solution, was not effective due to hydrogen evolution process. The deposited film may not cover the surface of the substrate appropriately. Hereby the pH for electrochemical deposition process was fixed at 2.1.



**Figure 1.** Cyclic voltammogram (a) 3mM  $\text{CuSO}_4$  (b) 7mM  $\text{In}_2(\text{SO}_4)_3$  (c) 11mM  $\text{SeO}_2$  (d) 3mM  $\text{CuSO}_4$ , 7mM  $\text{In}_2(\text{SO}_4)_3$ , 11mM  $\text{SeO}_2$  at pH 2.1 are shown.

### 3.2. XRD patterns for all the possible potential

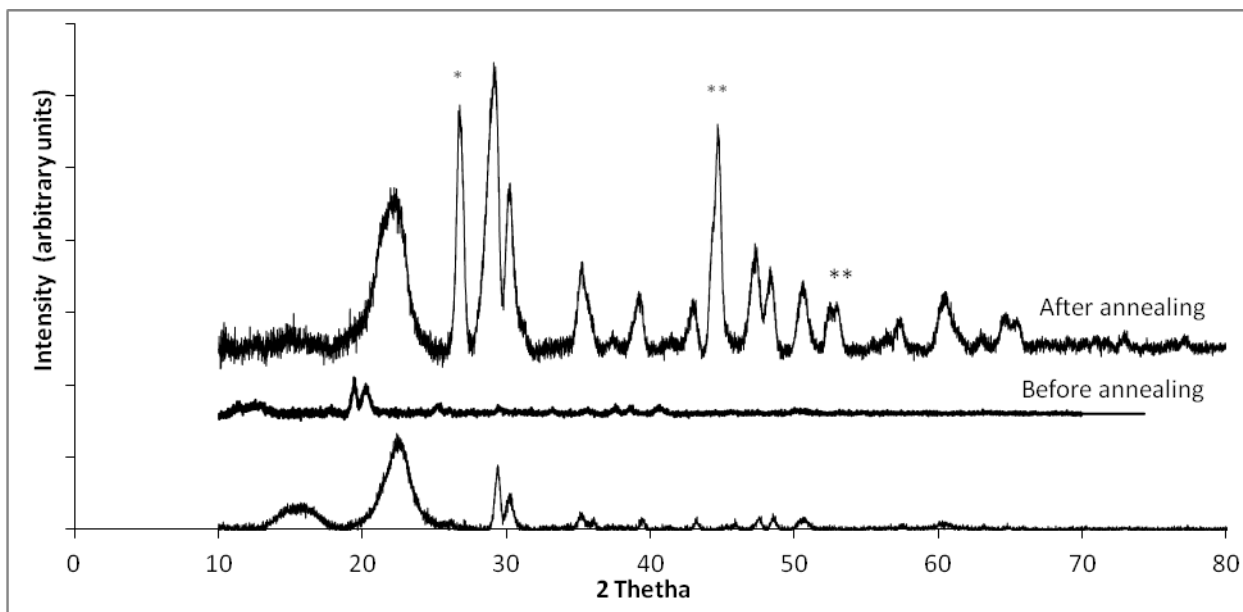
According to CV the probable potential to deposit  $\text{CuInSe}_2$  with less impurities can be in -0.85 to -0.96 V interval. XRD patterns for the entire potentials follow three pattern related to Table 1. Cu, Se,  $\text{Cu}_x\text{Se}$  and  $\text{CuInSe}_2$  can be observed when depositions were performed at potentials -0.85 to -0.89 V. The best potentials to deposit  $\text{CuInSe}_2$  were found to be between -0.90 to -0.94 V at which a little amount of Cu and Se impurities existed. The deposit at -0.96 V composed of mixture of Cu, In, Se and  $\text{CuInSe}_2$ . In these potentials, greater amount of Cu and Se impurities in comparison with the previous potentials and In impurity were observed. These electrochemical deposition reactions were attributed to the relation between pH and the applied potential [16]. The photosensitivities of the deposited samples which had the best PEC belonged to the second style; i.e., from -0.90 to -0.94 V. To get a suitable deposition, it is important to stay away from hydrogen evolution (which affects the deposition surface quality) and find the most appropriate electrochemical deposition; potential -0.90 V was chosen.

Annealing temperatures (between 250 °C- 450 °C) were selected to study the effect of heat treatment in eliminating excess Se and proving the crystalline structure of deposited film by monitoring X-ray diffractometry. The dark color of the sample indicated that the deposit was rich in Cu and Se [1]. The XRD patterns for blank ITO glass and deposited CuInSe<sub>2</sub> on ITO glass before and after heat treatment at 400 °C are shown in Fig.2. The related XRD peaks for CIS were located at 26.7° (112), 44.3° (204), 44.4° (220), 52.3° (116), 52.6° (312).

Results showed that at 350 °C the excessive selenium was completely eliminated. Moreover the best adherence for deposited thin film on ITO glass during PEC belonged to 450 °C, although partial melting happened at this temperature during annealing process. Annealing temperature of 400 °C gave the best film adherence with the elimination of Se impurity [3]. The XRD results proved that heat treatment at 400 °C for 20 min did not decompose CIS or ITO. There were no other phase existed in the thin film after heat treatment. However red amorphous component which was vapor deposited on the wall of the glass tube reactor during annealing. This deposit identified to be red selenium or α-selenium [16].

**Table 1.** Different electrochemical potential and their XRD results observed

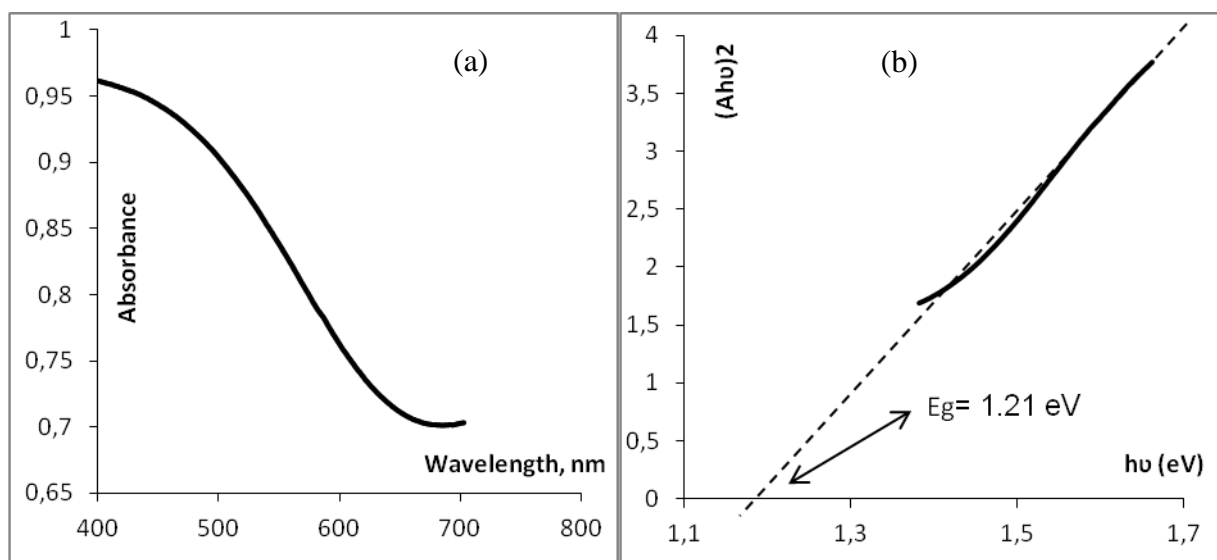
Deposition potential (V)	XRD Observed	notes
-0.85 up to -0.89	Cu, Se and Cu <sub>x</sub> Se	Mostly impurities
-0.90 up to -0.94	CuInSe <sub>2</sub>	Less amounts of Cu and Se impurities were observed. The best photosensitivity was achieved.
-0.95 up to -0.96	Cu, In, Se and CuInSe <sub>2</sub>	More impurities were observed



**Figure 2.** XRD patterns for blank ITO glass, as deposited and annealed sample at 400<sup>0c</sup> for 20 min with -0.90 V applied potential are shown.

### 3.3 Optical absorption and band gap

The absorbance of polycrystalline copper indium diselenide film in the light spectrum of 400-700 nm, Fig. 3-a. The band gap energy  $E_g$  estimated by Stern equation as 1.21eV (Fig. 3-b). The divergence of experimental band gap belongs to numerous factors such as grain size and impurities [18]. The tangent in Fig. 3b indicate that CIS has a direct band gap ( $n=1$ ). This optical behavior makes CIS to be used as a promising material for energy conversion.



**Figure 3.** Optical behaviors (a) optical absorbance (b) band gap energy are shown.

### 3.4. Effect of different duty cycles on the surface roughness

The surface roughness was affected by varying duty cycles,  $\theta$ , by changing the on-times and off-times of the square wave shape. Potential cycles produced different surface morphologies [7]. The deposition time to get the acceptable thin film was found as 15 min total on-time. Equation 1 was used to calculate the duty cycles based on the percent of on and off-time.

$$\% \theta = \frac{T_{ON}}{T_{OFF} + T_{ON}} \times 100$$

Eq.1

By varying  $\theta$ , it was found that the lowest surface roughness was obtained at  $\theta=10\%$ . With increasing duty cycle the roughness increases and dendrite structure was observed at  $\theta=90\%$  (Fig. 5) [7]. Double layer and electrodeposition occurred during on-time. At off-time (relaxation time) the aqueous solution became homogenous by ion immigration [17].

By adjusting the potential in the electrolyte, the electron flow direction tends to AB direction. Due to this fact, a peak was appeared in the time-current diagram. This peak was an indication of the double layer. Then as soon as the capacitor was charged, the current became stable; the electron flow direction tends to CD direction. At this moment, the resistance in the electrolyte belonged to the electrodeposition process (Fig 4).

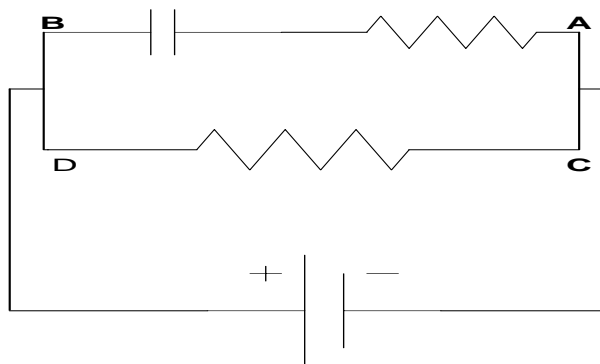
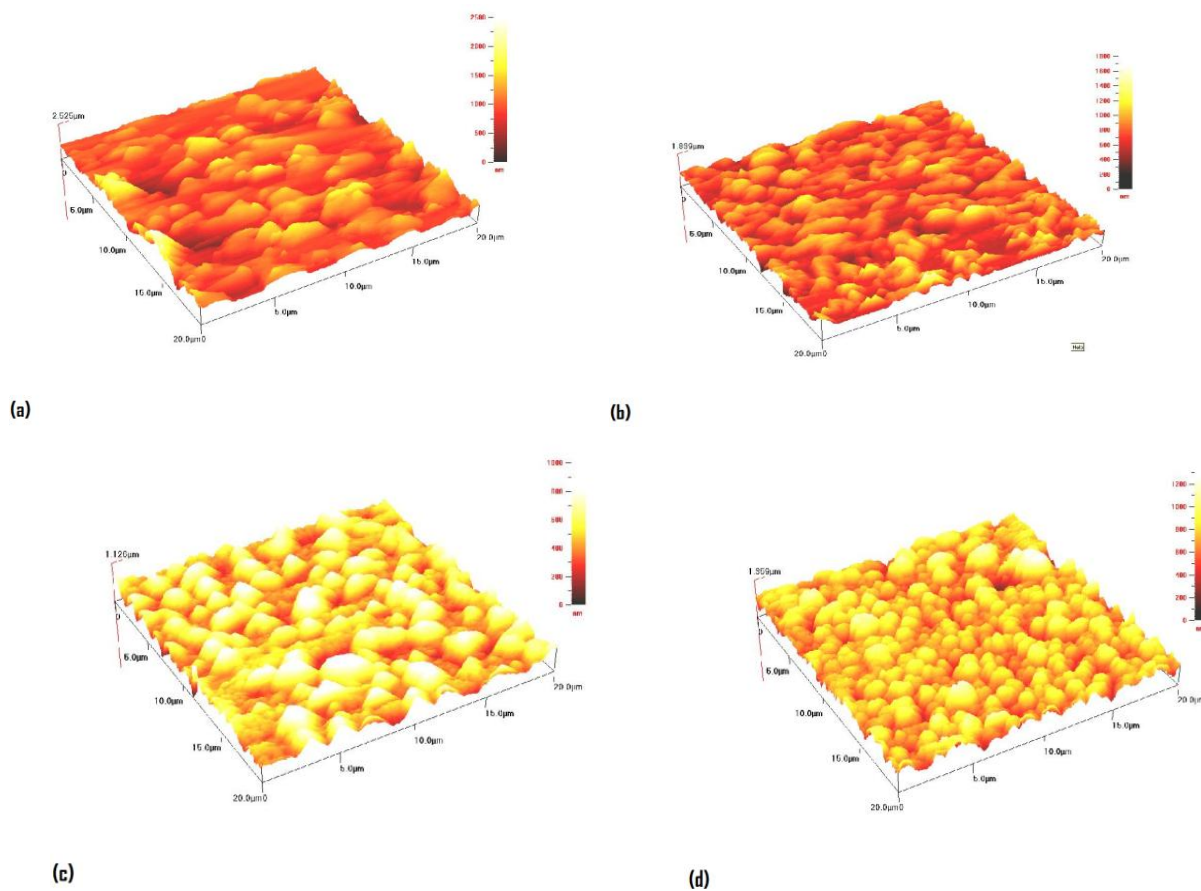
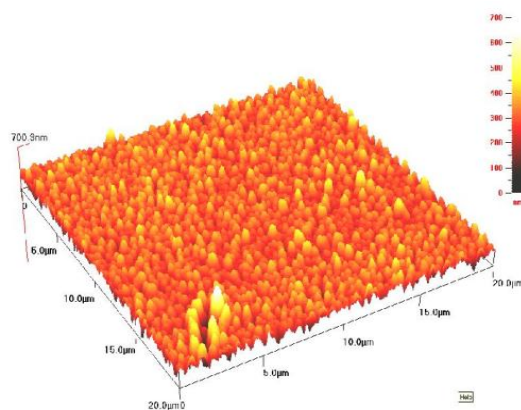


Figure 4. Electrolyte schematic circuit







(e)

**Figure 5.** The effects of duty cycle on surface morphology (a) duty cycle 10% (b) duty cycle 33% (c) duty cycle 50% (d) duty cycle 75% (e) duty cycle 90% are shown.

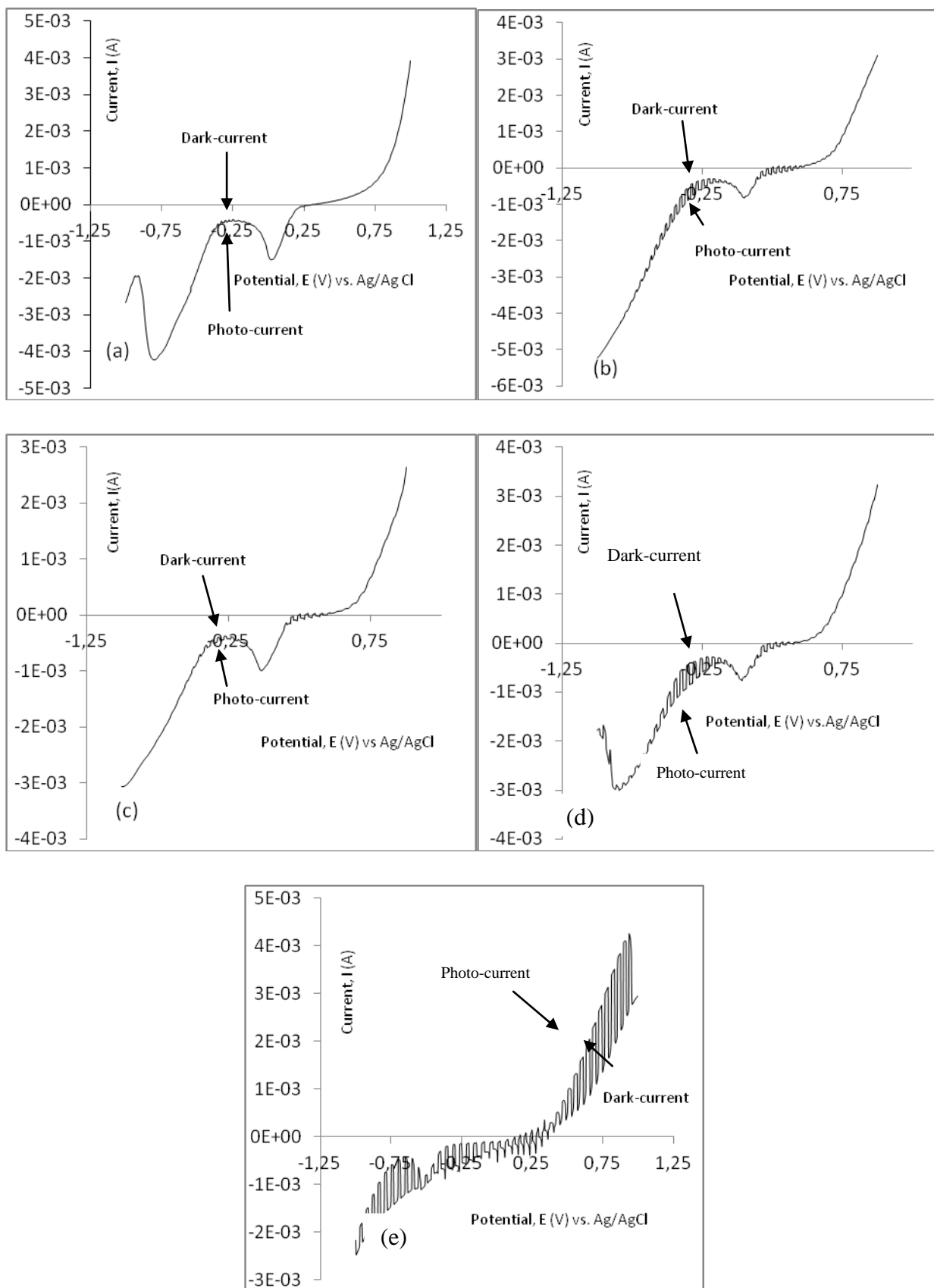
### 3.5. Effect of different surface roughness (morphology) on PEC

Photosensitization of film was studied the photo-electrochemical semiconductor-liquid junction by PEC in alternative dark and illuminate medium. Fig.6 illustrate the maximum and minimum of current versus potential which was extracted. By illuminating the sample with energy larger than band gap the electrons are promoted from valence band (VB) to conduction band (CB) and make the electrons flow in the circuit. At illumination media the absolute value of photo-current is bigger than dark-current value. At the minimum or dark-current because of there is no light to promote the electrons to CB the value of dark-current is supposed to be zero.

Normally, at minimum or dark-current, there is no electrical current; however, in this case, all the PEC graphs in Fig. 6 conceal even in the dark field there is current. The conductivity is due to the redox system overlapping with valence band or conduction band associated with n or p type manner of semiconductor.

The peak occurred around potential zero (Fig. 6) belongs to copper electrochemical reaction in pH-potential diagram [1]. The potential of  $\sim 0.35$  V, where the current is zero for all PEC graphs is the flat band potential for CIS. The tracing of CIS surface charge manner during PEC by interpreting photo-current revealed that accumulation of electrons occur when the photo-current value is located in more negative than flat band for the p-type. While depletion of electrons happens, for p-type when its photo-current is more negative than flat band and for n-type when its photo-current is bigger than flat band.

The effect of duty cycles (the surface morphology) on PEC revealed that at duty cycle 10% the deposited thin film have p-type feature (Fig. 6a) whereas for the rest of the duty cycles thin films produced are of n-p type behavior. These occur as a result of surface morphology. The impurity of Cu or Se penetrate during heat treatment into the crystalline structure of intrinsic semiconductor (CIS) and converts it to n-p type semiconductor [2, 19].



**Figure 6.** The effect of duty cycle on PEC (a) duty cycle 10% (b) duty cycle 33% (c) duty cycle 50% (d) duty cycle 75% (e) duty cycle 90%

Fig. 6 shows by increasing the duty cycles value, a better PEC was observed except at duty cycle 50% (Fig. 6c). The reason was attributed to amount of impurity in deposited thin film and morphology of structure.

#### 4. CONCLUSION

Polycrystalline thin film of copper indium diselenide (CIS) was successfully deposited onto ITO glass by pulse electrochemical deposition technique at -0.9 V which was estimated from cyclic voltammogram in aqueous solutions. Heat treatment at 400 °C for 20 minutes was conducted to prove the crystalline structure and eliminate excess deposited selenium. XRD revealed the film has tetragonal crystalline structure. The band gap energy for this sample (15 min deposited) is 1.21 eV. By increasing the value of duty cycle, the surface morphology shifted from smooth to dendrite structure. This change affected the semiconducting behavior and the photoactivity behavior of thin film. . The PEC results revealed that the deposited CIS is p-type and n-p type semiconductors.

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