Int. J. Electrochem. Sci., 8 **(2013)** 5161 - 5171

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Photocorrosion of $CuInSe_2$ Thin Film by Electrochemical Polarization in Acidic and Alkaline Medium

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Received: 13 November 2012 / *Accepted:* 15 February 2013 / *Published:* 1 April 2013

In this research the effect of varying surface morphology on photocorrosion behavior of $CuInSe_2$ (CIS) was studied in acidic and alkaline electrolytes. Polycrystalline CIS thin films were deposited on to ITO glass by pulse electrochemical deposition method. Duty cycles of 90%, 75%, 50%, and 33% for fifteen minutes (total on-time) were chosen to produce different surface morphologies during electrochemical deposition from aqueous solution. The photocorrosion rates were evaluated from the electrochemical polarization data. Polarization curves were acquired in selected corrosive electrolytes which contained 0.5 M KCl + H_2SO_4 as acidic media and 0.5 M KCl + NaOH as alkaline media. The photocorrosion rates for different morphologies were estimated by current density (i_{corr}) extracted from Tafel plot in all the pH range. Finally activity and passivity behaviors of the thin films were determined by interpreting the polarization curve peaks (E_{corr}) values and the rates of photocorrosions. The results proved photocorrosion behavior of deposited CIS thin film is affected by the surface morphology, and pH of the medium.

Keywords: $CuInSe_2$, Photocorrosion, Electrochemical measurement (Tafel plot), Thin film semiconductor.

1. INTRODUCTION

Photo-electrochemical cells with semiconductor- liquid electrolyte interface have achieved increasing attention due to their practical applications in solar energy conversion [1]. Recently, most interest is in ternary Cu-In-Se semiconductor compounds (which present the maximum photovoltaic efficiency ~18.8% to date) [2, 3]. The physical properties of this ternary compound show n- and p-type semiconductor behaviors. $CuInSe_2$ (CIS) with a ~1.1 eV direct band gap [4], high absorbsion coefficient (~ 10^5 cm^{-1}) and a very suitable photo-electrochemical behavior is one of the most promising chalcopyrite type semiconductors to be studied [5]. Although ternary chalcogenides compounds show high chemical stability [6], the photo-electrochemistry of CIS is greatly affected by its surface morphology, and the composition of the corrosive media [7].

Corrosion measurements by electrochemical techniques such as electrochemical polarization and electrochemical impedance spectroscopy (EIS) are the most popular methods. The rapidity of these methods attracts attention among corrosion engineers. Long term methods, such as weight loss measurement is taken days or weeks while electrochemical methods are done in several minutes or hours. Among electrochemical techniques, electrochemical polarization or Tafel plot is one of the most interesting methods to study corrosion behavior. Although studying photocorrosion rate by electrochemical polarization is a fast method, it provides an estimation of corrosion rate in millimeters per year.

To the best authors' knowledge, no research has been done on photocorrosion of semiconductors thin films by electrochemical polarization. Some studies were done on bulk single or polycrystalline CIS by other methods [7]. These investigations are based on leaching out copper from crystalline structure. The aim of this work is to investigate the optical corrosion behavior of $CuInSe_2$ (photocorrosion) thin film deposited by pulse electrochemical method. The results are discussed base on the relation between different surface morphologies and photocorrosion rate. Selected surface morphologies were studied on various pH values to investigate the effect of acidic and alkaline electrolytes on passive layer creation.

2. EXPERIMENTAL

2.1. Pulse electrochemical deposition of $CuInSe_2$

Thin films of polycrystalline $CuInSe_2$ (CIS) were deposited by pulse electrochemical technique [8]. At potential -0.90 V CIS was deposited from the aqueous solution contained 3 mM $CuSO_4$, 7 mM $In_2(SO_4)_3$ and 11 mM SeO_2. The ITO (Indium-Tin Oxide) glass (3 cm^2) was selected as the substrate thanks to its environmental resistance. 0.1 M H_2SO_4 was used to adjust the pH around 2.1 in aqueous solution during deposition [9]. To fabricate different surface roughness, duty cycles of 33%, 50%, 75% and 90% were applied during pulse electrochemical deposition. Finally as deposited thin films were annealed at 400 ^oC for 20 minutes to improve the crystalline structure and remove Se impurity. In order to achieve suitable depositions, total deposition on-time was selected as 15 min [10].

2.2. Electrolyte

To study the photocorrosion of CIS thin film, the supporting electrolyte for acidic and alkaline media were selected as 0.5 M KCl+ H_2SO_4 and 0.5 M KCl+ NaOH, respectively [7]. The electrolytes were prepared using Millipore water (18 MΩ-cm) and kept for 48 hours to let the ions be hydrated. Aqueous media of all pH contained 0.5 M KCl approached the maximum electrolyte conductivity [1, 11]. The cell contained 75 ml of KCl. To prevent a large change in the volume and molarity of KCl during adjusting the exact pH for acidic and alkaline media different molarities of H_2SO_4 and NaOH were used [12].

2.3. Electrochemical measurements

A three-electrode cell was assembled for electrochemical measurements. An electrochemically deposited thin film of CIS on ITO glass was used as working electrode (WE). The counter electrode was platinum wire and the reference (RE) was Ag/AgCl. The experiments were run at room temperature (26.5 ^{o}C). Nitrogen gas was used to purge the electrolyte to provide the suitable area for running the experiment by removing the dissolved oxygen from the electrolyte. To attach the μ-AUTOLAB type III with electrodes, stainless steel crocodile clips were utilized. Philips 13096 ELH GY 5.3 120 V halogen lamp illuminated the samples as white light source. The lamp positioned 5 cm away from the cell and illumination was done through a quartz window.

2.4. Polarization test

The Tafel plots were performed with respect to 20 mV s^{-1} potential speed scan rate. Experiments were run in the potential range of 1.0 V to -1.0 V. The location of the Tafel plot peak on over-potential axes (ƞ) was known as the value of corrosion potential (E_{corr}) [13]. The intercept of tangents on anodic and chaotic parts of polarization curve was identified as the value of i_{corr} on 10 logarithmic current density axes. The rate of photocorrosion was calculated from the relevant equation by estimating i_{corr}.

3. RESULTS AND DISCUSSIONS

3.1. Effect of duty cycles on the polarization curves

The polarization curves, the anodic and cathodic parts of Tafel plot, of $CuInSe_2$ thin film deposited on ITO glass from both acidic and alkaline media were traced. The images obtained from atomic force microscopy (AFM) revealed that by increasing the value of duty cycles, the surface morphology changes from smooth to dendrite structure [10].

The polarization curves for samples deposited at different duty cycles in figure 1 shows polarization over potential (E_{corr}) at various pH. Each surface morphology which was produced from different duty cycles had its specific E_{corr}.

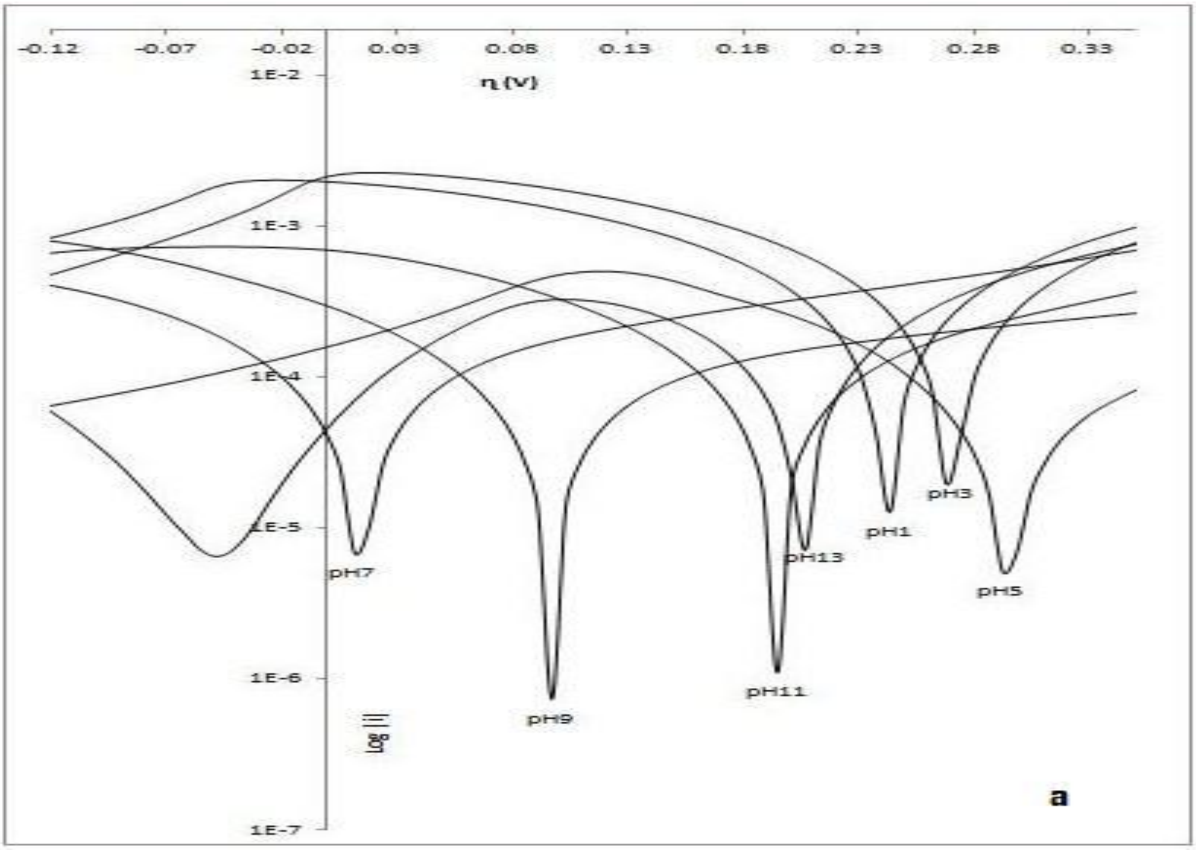
The polarization peaks of the duty cycle 33% (Fig 1-a) in acidic and alkaline media demonstrated that all the peaks occurred at positive over-potential. Higher amounts of H^+ or OH^- ions shifted the location of the peaks to more positive values in comparison with the location of the peak at pH=7. Furthermore the peaks for acidic media located at more positive over-potential than the peaks for alkaline media.

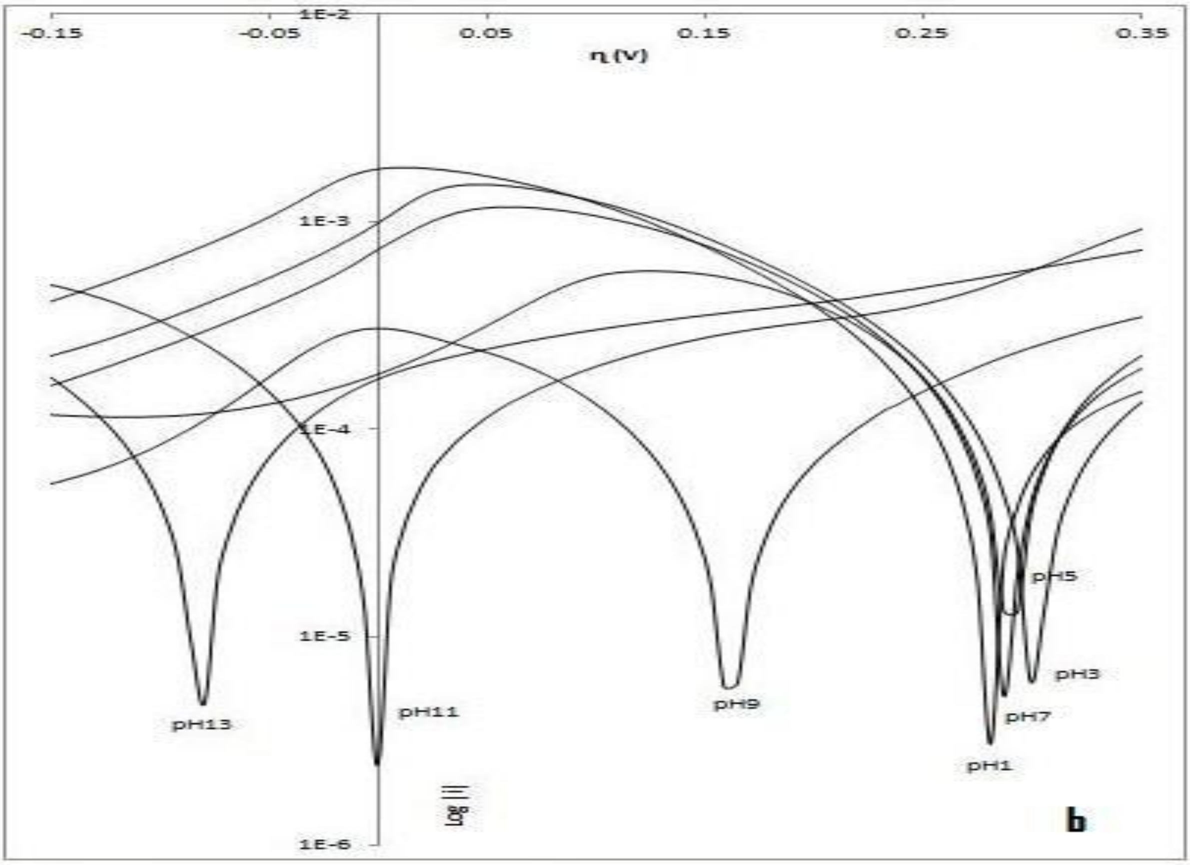
The peaks for the duty cycle 50% show in Figure 1-b. All peaks located at lower than the peak at pH=7, except peaks at pH=5 and pH=3. In acidic media, by reducing the pH to 3 the values of E_{corr} increased, but reducing the pH to 1, the E_{corr} became much lower than pH=7. On the other hand, in alkaline media by reducing the pH value, the peaks shifted to more negative over-potential.

The peaks for duty cycle 75%, illustrated in Figure 1-c, occurred at positive over-potential, except pH=13.The peak for pH=5 occurred at more positive over-potential than pH=7. In acidic media, increasing H^+ ion amounts shifted the E_{corr} to a more positive value. However in alkaline media, by increasing the pH (boosting the number of OH^- ions) the values of E_{corr} shifted to more negative values.

All the peaks belong to the duty cycle 90% (Fig 1-d) located at positive over-potential. Except for pH=13, all the other peaks occurred at positive value related to pH=7. In acidic media, the E_{corr} for pH=1 was larger than the E_{corr} of pH=3 and lower than E_{corr} at pH=5. While in alkaline media, augmenting the pH from 9 to 11, the value of E_{corr} increased but dramatically decreased above pH=11.

The polarization curve for blank ITO glass displayed E_{corr} values in acidic media occurred at negative over-potential and by decreasing the pH these values became more negative. In alkaline media, all peaks found in the positive over-potential values and by increasing the pH, the peaks shifted to more positive values.

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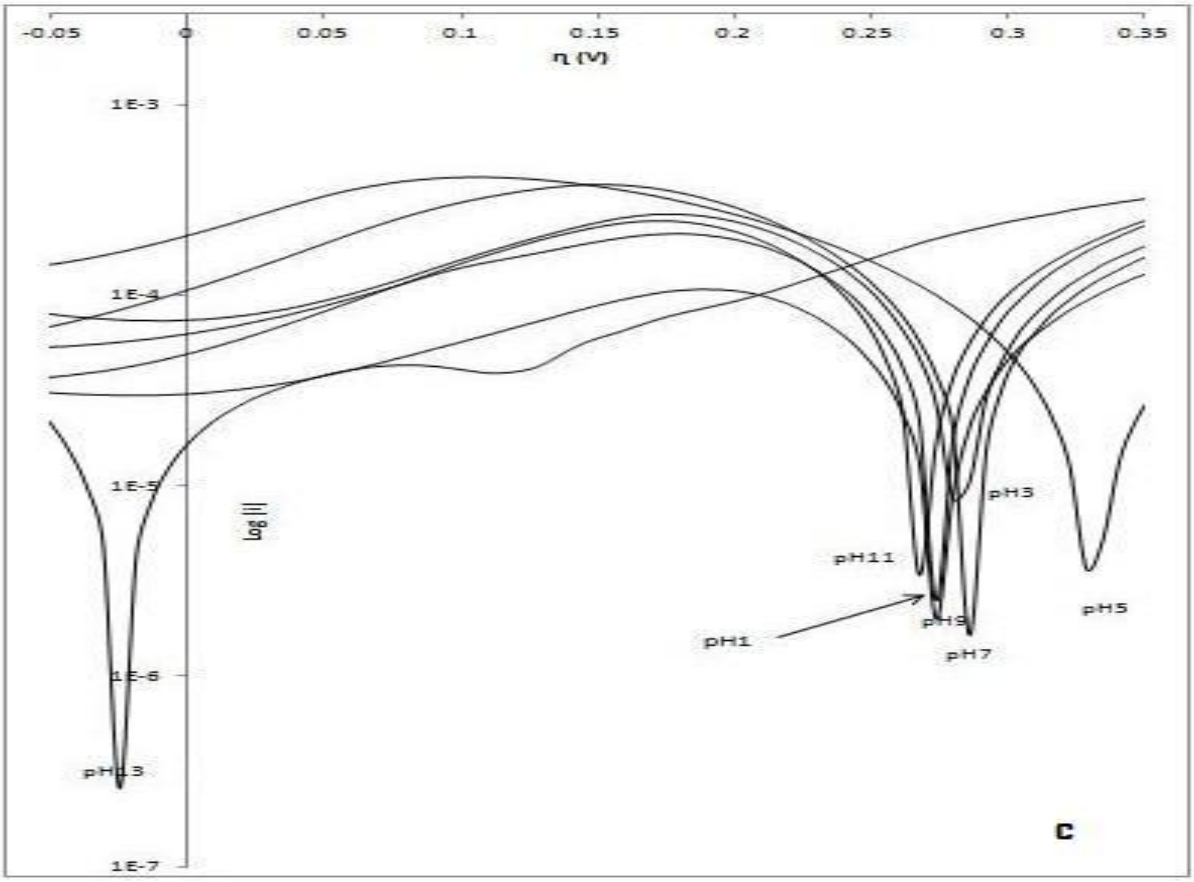
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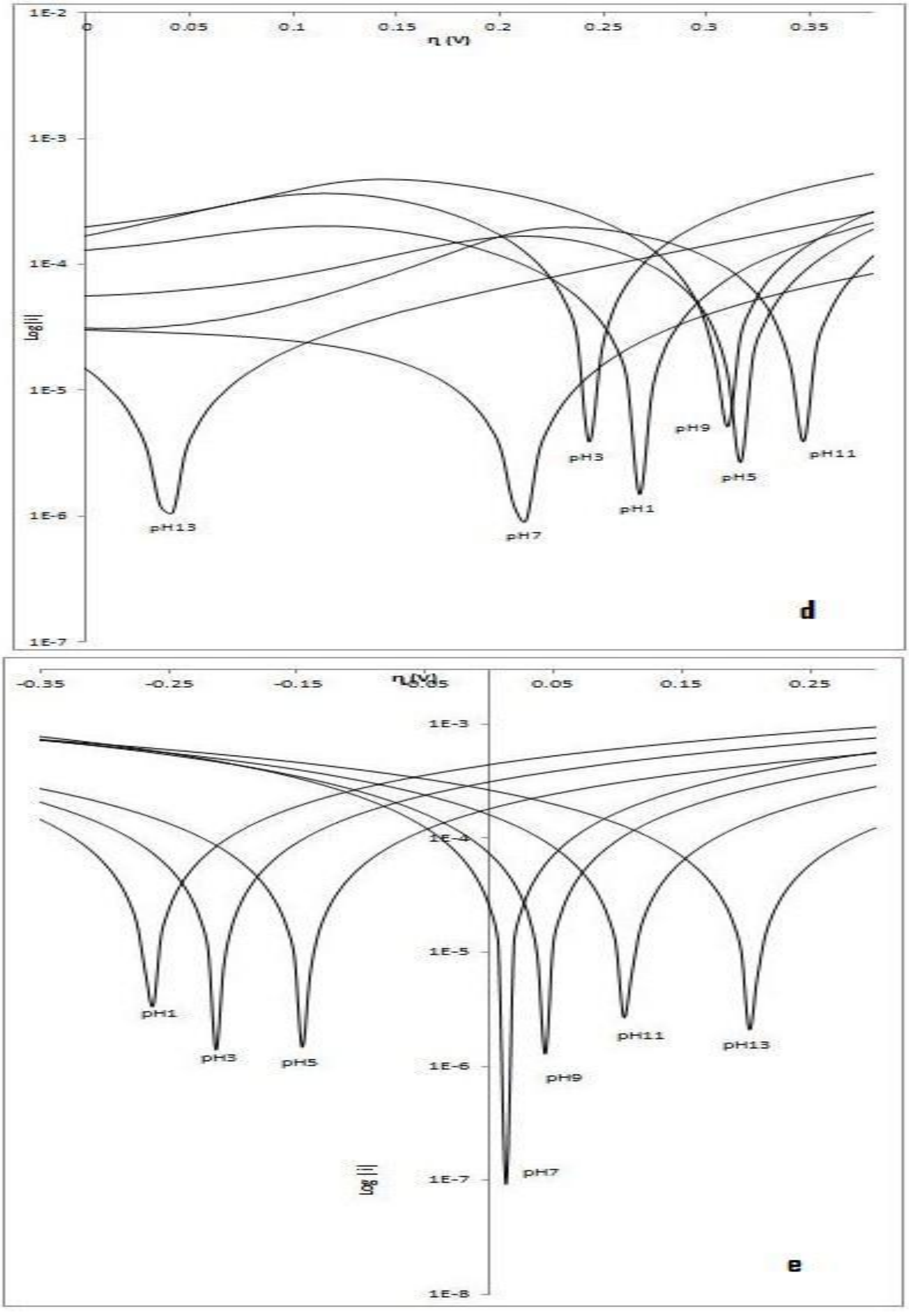


Figure 1. Polarization curves at different pHs for CIS (a)Duty cycle 90% (b)Duty cycle75% (c)Duty cycle 50%(d)Duty cycle33%(e) ITO glass are shown.

This dissimilarity between E_{corr} values of blank ITO and deposited CIS thin film on ITO confirmed that the ITO did not directly involve in the process, even though the substrate indirectly affected the current density and over-potential. Figure 1-e illustrates the polarization curve peaks of blank ITO glass.

Thus E_{corr} is affected by surface roughness. For instance, for the same pH at different surface roughness the E_{corr} is different.

3.2. Effect of duty cycles on the rate of photocorrosion

The rate of photocorrosion can be calculated by mathematical treatment by using the approximate i_{corr} value extracted from the intercepting slops of the Tafel plot, at positive and negative parts. According to Faradays law [13]:

$$Q = \frac{nFW}{M} \qquad \text{Equation (1)}$$

Where Q is charge in Coulomb, n is the number of electrons involved in the electrochemical reaction, F is the Faraday constant, W is the weight of electro-active species, and M is the molecular weight of electro active species ,since equivalent weight = M/n and Q = it

$$W = \frac{Q \times E.W.}{F} \qquad \text{Equation (2)}$$

$$W = \frac{i \times t \times E.W.}{F} \qquad \text{Equation (3)}$$

$$\frac{W}{t} = \frac{i \times E.W.}{F} \qquad \text{Equation (4)}$$

W/t is the rate of corrosion in grams versus second. To convert second to year and centimeters to millimeter equation 5 was used:

$$C.R. = \frac{K \times icor \times E.W.}{SA \times \rho} \qquad \text{Equation (5)}$$

Where K is $3.27e^{-3}$ (mmg/μAcm yr), i_{corr} is corrosion current density (μA/cm^2), EW is equivalent weight(g), ρ is density (g/cm^3) and corrosion rate (C.R.) is given in, mm/yr.

X-ray diffractometry revealed that deposited CIS thin film was chalcopyrite and the crystal structure was tetragonal with the calculated density of 5.81g cm^{-3} [14, 15]. The equivalent weight was calculated as 25.8712 g. The convexities located at cathodic part of Tafel plot (Fig 1) is related to Cu^0/Cu^{2+}electrochemical reaction [2]. These convexities made it hard to draw the appropriate slope of the reduction area. To estimate the mean value of i_{corr} and subsequently calculate the photocorrosion rate, the strategy was drawing the slope lines by using a consistent way of drawing in the cathodic and anodic parts of Tafel plot that provided the possibility of finding all the i_{corr} and made the average with the ones located near each other.

Table 1 illustrates the photocorrosion rate values in terms of the duty cycles and pH. It shows that by decreasing the duty cycle values the photocorrosion rates increased except for some pHs of duty cycle 50%. This behavior related to CIS thin films photoactivity (PEC) for duty cycle [10]. The photoactivity of duty cycle 50% was less than duty cycle 33%. The photocorrosion is less active and showed lower photocorrosion rate. At pH=1 and pH=13, the photocorrosion rate and the duty cycles are proportional to each other due to highly corrosive media.

In neutral media, pH=7, because of non corrosive media and no suitable ions for photo-electrochemical reaction of CIS [10]. The photocorrosion rate was controlled only by the surface morphology.

The films in acidic media corroded more in comparison to alkaline media. This feature happened as a result of H_2SO_4 which was more corrosive than KOH at the same concentration. Furthermore the thin films have a better PEC in acidic environment [9].

The photocorrosion rates increased in the pH range of 3 to 7. The maximum of photocorrosion was recorded at pH= 3. Reducing the pH to 1 formed a passive layer. The passive layer lost its photoactivity (Cu became oxide and left the semiconductor crystalline structure); therefore the photocorrosion rate decreased. Similarly in alkaline media, the maximum photocorrosion rate was achieved at pH=11. The rate at pH=13 is low due to passive layer formation.

The discussed result revealed that rate of photocorrosion is relevant and affected by surface morphology, photoactivity and pH of the media.

Table 1. Photocorrosion rate (mm per year) [±0.02] for pulse deposited $CuInSe_2$ at different pH values

Duty Cycle (%) / **pH (± 0.05)**	**90**	**75**	**50**	**33**
1.00	1.65	1.70	3.46	11.59
3.00	4.89	4.73	4.08	11.96
5.00	3.57	3.71	2.78	3.86
7.00	0.37	1.56	1.69	1.92
9.00	1.92	1.93	1.89	2.00
11.00	2.80	2.61	2.58	3.14
13.00	0.12	0.15	0.71	2.48

3.3. Behavior of Active –Passive layer

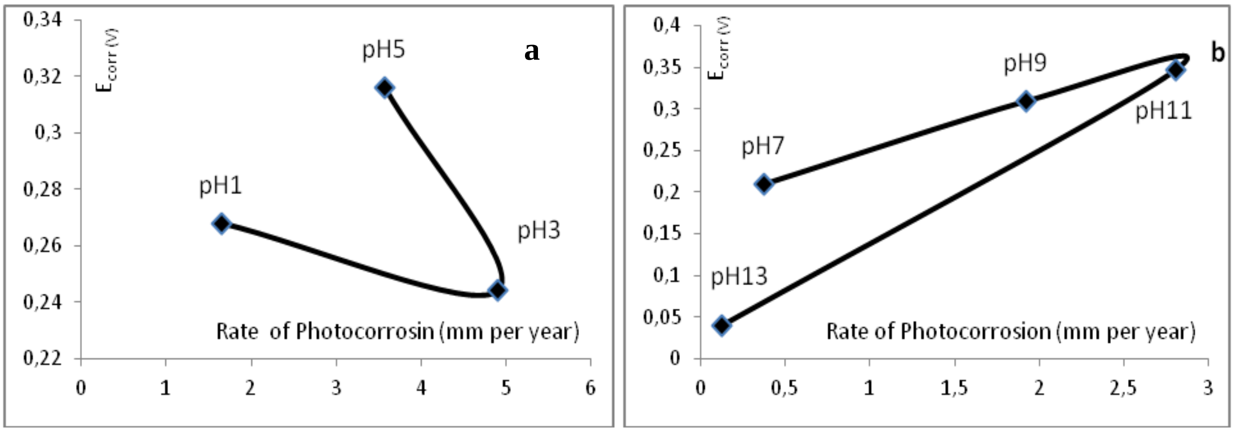
The product of the reaction between the environment (electrolyte) and $CuInSe_2$ thin film was a passive layer [16,17]. Cu and In in CIS reacted with the acidic or alkaline environments. CIS thin film lost its photoactivity because the Cu and In atoms left the CIS atomic structure [3].

Anodic dissolution behavior of active-passive for surface morphologies which were affected by duty cycles 90% and 75% followed the same manner. Figure 2-a,b,c and d illustrate the behavior of active–passive layer for surface morphologies affected by duty cycles 90% and duty cycle 75% in acidic media and alkaline media. In acidic media, at pH=3-5 the thin film remained active. The passive layer was formed in the pH range of 1-3. In this pH range, since the passive layer didn’t have photoactivity (PEC), the E_{corr} for pH=1 was smaller than E_{corr} for pH=5. In alkaline, media pH=7 - 11 belong to active region and at pH=13 passive layer was formed.

Sample deposited at duty cycle 50%, has a similar passivity behavior as duty cycles 90% and 75%, but in the acidic media the rate of photocorrosion for pH=5 is smaller than pH=1. This phenomenon is consistent with the result of photoactivity of CIS thin film [10]. The passivity was not good enough to keep the corrosive electrolyte away but the thin film lost its PEC characteristic. In alkaline high concentration of OH^- ions made the thin film loss its photoactivity. By increasing the pH to more than 11, the thin film passivation occurred. Figure 2-e and f shows the behavior of active–passive layer for surface morphologies affected by duty cycle 50% in acidic and alkaline media.

Figure 2-g and h illustrate the behavior of active–passive layer for surface morphologies affected by duty cycle 33% in acidic media and alkaline media. The deposited thin film on ITO glass for duty cycle 33% was not as stable as the thin film deposited for 90%. This stability is affected by the activation and passivation behavior of the thin film. In acidic media, the film remained active in the pH range of 3-5. Although the thin film showed passive behavior in pH 1-3, the photocorrosion rate increased. The surface features of the film made the passive layer unstable. It provided a chance for the corrosive electrolyte to reach the active layer under the passive layer. The photoactivity of thin film continued to reduce during the process by increasing the hydronium ions conduction.

Due to that the photocorrosion rate increased but the corrosion potential became smaller. In alkaline media, the semiconductor thin film showed similar behavior as active-passive metals. The primary passive potential (E_{pp}) and the critical anodic current density for passivity (i_{crit}) were found to be as 0.194 V and ~2.16 E^{-4}A, respectively.



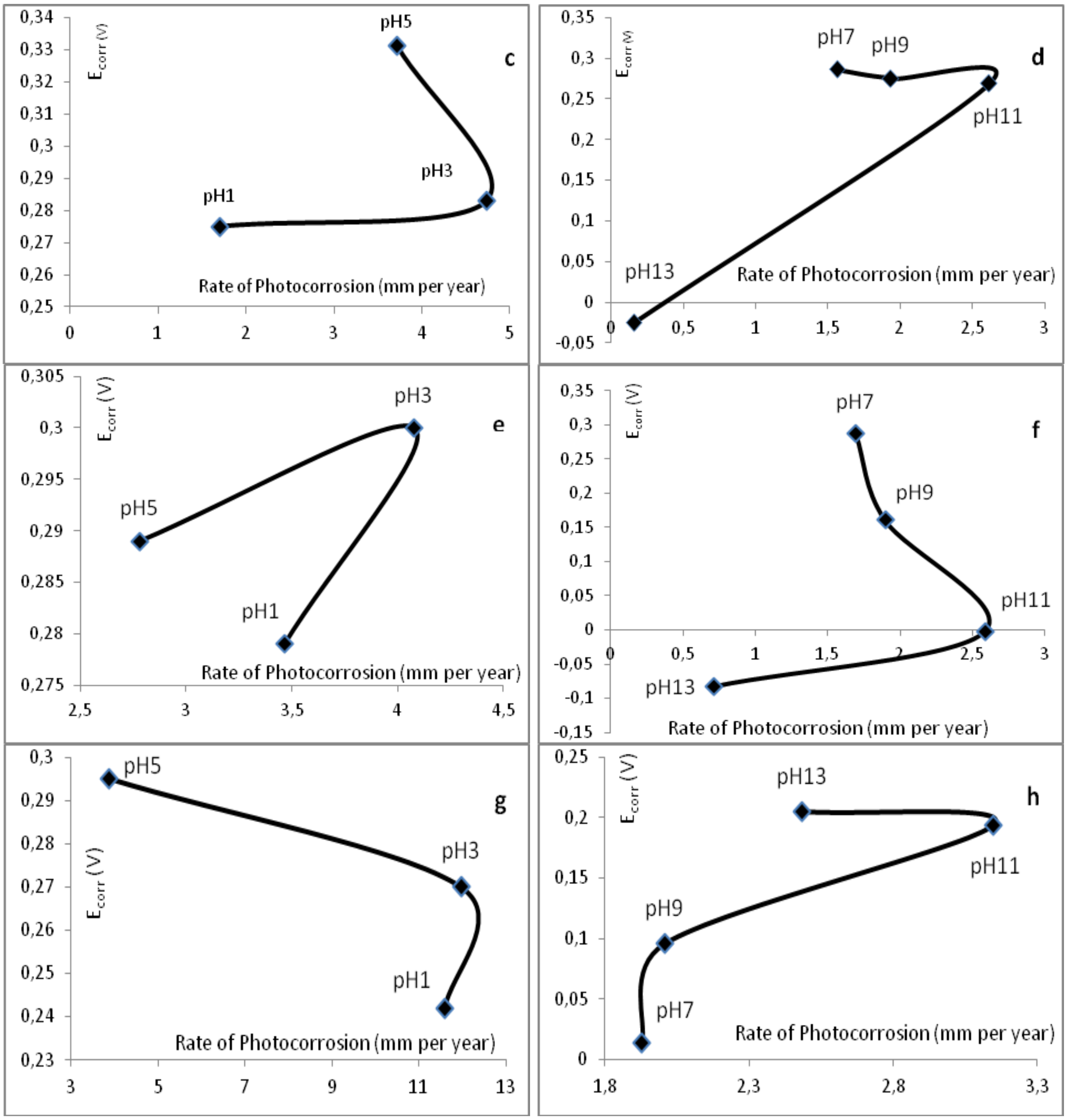


Figure 2. Behavior of Active –Passive layer for surface morphology affected by (a) duty cycle 90%(c)duty cycle 75%(e) duty cycle 50%(g)duty cycle 33% in acidic media(b) duty cycle 90%(d)duty cycle 75%(f) duty cycle 50%(h)duty cycle 33% in alkaline media

4. CONCLUSION

In this research, the photocorrosion behavior of CuInSe2 was investigated by electrochemical method. Small band gap value, positive flat band potential and good chemical stability of CIS made it as a promising energy conversion component to be used in photo-electrochemical cell devices. The study was done on the deposited polycrystalline thin film samples which were prepared by pulse electrochemical deposition at varying duty cycles form 33% to 90% which affected the surface morphology. The results from electrochemical measurements (Tafel plot) which were run in acidic and alkaline media, showed that by changing the surface morphology from dendrite to smooth, the photocorrosion rate increased expect for duty cycle 50%. Result of this study confirmed that first; photocorrosion behavior was a function of surface morphology, photoactivity and pH of the media. The affect of these factors make photocorrosion rate be 0.122 mm per year in alkaline media for duty cycle 90% (The least corroded morphology) and 11.96 mm per year in acidic media for duty cycle 33% (The most corroded morphology). Second; the occurrence of passive layer is affected by the amount of hydronium and OH^- ions in the solution.

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