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Studies on the electrochemical stability of CIGS in H_2SO_4

R.C. Valderrama[a], P.J. Sebastián[a,b,*], M. Miranda-Hernandez[a],
J. Pantoja Enriquez[a], S.A. Gamboa[c]

[a] Solar-Hydrogen-Fuel Cell, Privada Xochicalco SN, CIE-UNAM, 62580 Temixco, Morelos, Mexico
[b] Instituto Mexicano del Petróleo, Eje Central Lazaro Cardenas 152, 07730 Mexico, Mexico
[c] División de Ciencia e Ingenieria Ambiental, CIMAV, Miguel de Cervantes 120, Complejo Ind. Chihuahua, 31109, Chihuahua, Chih. Mexico

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Abstract

In this work, we investigated the performance of $Cu(In,Ga)Se_2$ (CIGS) based photo-electrodes in a solid–liquid electrochemical system. The stability studies related to photocorrosion and dissolution of the photo-electrode in 0.5 M sulfuric acid medium were carried out using electrochemical methods based on linear and cyclic voltammetry. The stability of the CIGS-PVD/H_2SO_4 system like the semiconductor/electrolyte interface was investigated as a function of time. It is an alternative procedure instead of the usual Tafel slope analysis. A small external signal with a low value of scan rate was applied in the electrochemical interface for promoting redox reactions on the surface of the semiconductor. The semiconductor/electrolyte system was analyzed for 12 days. The samples were analyzed using SEM and EDS. The results showed morphological changes on the sample surface but without substantial change in the chemical composition. It is likely that Cu^{2+}/Cu^{+} is dissolving in the electrolyte and then re-adsorbed by the semiconductor surface.

Keywords: CIGS photoelectrode; Electrochemical stability; Dissolution in H_2SO_4; CIGS photocorrosion

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1. Introduction

The stability and non-degradation reactions at the semiconductor/electrolyte interface are essential requirements for the application of a semiconductor as photoelectrode. The degradation reactions like photo-corrosion and dissolution must be avoided because they cause changes or losses in the chemical composition of the semiconductor, diminishing the electrical transport properties and photo-response of the system.

Copper indium diselenide (CIS) and copper indium gallium diselenide (CIGS) based semiconductors obtained by electrodeposition have shown good stability in different electrochemical systems [1–5], and they show similar physical properties. The use of gallium in controlled stoichiometric amounts in the CIS-matrix allows the formation of wide band gap semiconductors with promising characteristics for use in photoelectrochemical systems. The electrical characteristics of semiconductor based electrodes in electrochemical systems have been reported by Gerischer [6], considering the individual properties of charge carriers and the energy levels for establishing the charge transfer processes occurring at the electrode/electrolyte interface. The use of semiconductors in photoelectrochemical applications has been considered instead of metal based substrates. The charge transfer processes occurring at the semiconductor/electrolyte interface are usually complex or coupled mechanisms, and the use of electrochemical techniques is adequate for investigating the electrical characteristics and stability of the semiconductors. In this work, the stability of the electrochemical system formed by CIGS/H_2SO_4 was investigated using voltammetry measurements as a function of time. The occurrence of redox reactions at the semiconductor/electrolyte interface was studied by linear voltammetry during 12 days.

2. Experimental

2.1. Thin film preparation

The deposition bath used for the co-deposition of Cu–In–Se was 0.012 M $CuCl_2$, 0.025 M $InCl_3$, and 0.025 M H_2SeO_3 dissolved in high purity Millipore de-ionized water. The precursor CIGS films were electrodeposited by

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[*] Corresponding author. Tel.: +52-55-56229706;
fax: +52-77-73250018.
E-mail addresses: rcv@cie.unam.mx (R.C. Valderrama),
sjp@cie.unam.mx (P.J. Sebastián).

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applying a constant potential of −0.50 V versus saturated calomel electrode (SCE) during 50 min.

The CIS thin films were electrodeposited in a three-electrode electrochemical cell where the reference electrode was a saturated calomel electrode, the counter electrode was a graphite rod and the working electrode (substrates) was glass/Mo. The Mo film was about 1 μm thick and was deposited by dc sputtering. All electrodeposition experiments were performed at room temperature (24 °C), the pH was maintained at 1.5 and adjusted using 1N HCl solution. The film deposition was carried out under non-stirring conditions [7].

CIGS thin films were obtained by physical vapor deposition (PVD) to adjust the final composition of $CuIn_{1-X}Ga_XSe_2$ from previously electroplated CIS film. The optimization procedure for adjusting CIGS thin film composition by PVD was successfully established [8].

2.2. Photoelectrochemical measurements

The photoelectrochemical studies were carried out using a three-electrode electrochemical cell where 0.5 M H_2SO_4 was used as electrolyte. SCE and a graphite rod were used as reference and counter electrodes, respectively. Photo-electrodes or working electrodes were prepared using p-type $CuIn_{1-X}Ga_XSe_2$ thin films. The electrical contacts were done using a copper wire and conducting silver paste. The ohmic nature of the contacts was checked before measurements. The exposure area of the photo-electrode was 0.5 cm^2. The devices were illuminated using a tungsten halogen lamp and the flux on the device was measured as 100 mW/cm^2. The measurements were carried out in dark and under illumination. The photoelectrochemical cell (PEC) stayed in direct contact with the environment and, hence, the surrounding O_2 favors the oxidation processes.

From our previous studies [9] we knew that the H_2 evolution reaction for p-$CuIn_{1-X}Ga_XSe_2/H_2SO_4$ system under conditions of illumination starts around −0.2 V versus SCE. With the purpose of evaluating how stable is the system during the process of H_2 evolution, we simulated the experimental conditions by means of linear and cyclic voltammetries as a function of time and potential range between ±0.15 V versus SCE. Also, the open circuit potential (V_{oc}) was monitored as a function of time for a period of 12 days. The potentials were controlled with a Radiometer PGP201 potentiostat coupled to a computer. The acquisition and analysis of data were carried out by Voltamaster software.

3. Result and discussions

3.1. Measurement of open circuit potential (V_{oc})

Fig. 1 shows the variation of V_{oc} with the time (in h) corresponding to the p-CIGS/H_2SO_4 system in dark and under illumination. As we can see in Fig. 1 V_{oc} measured in dark decreases with time from ∼0.12 V versus SCE (first day) to ∼0.04 V versus SCE (fifth day) and after that it remains constant. Under illumination V_{oc} does not vary too much, changing from 0.05 V versus SCE to ∼0.04 V versus SCE. Starting from fifth day onwards, the changes in V_{oc} in dark and under illumination are not significant and have a tendency to stabilize around 0.04 V versus SCE. This variation in V_{oc} may to be due to the photocorrosion reaction of one of the elements present in the photocathode and that it tends to oxidize around 0.04 V versus SCE. Under illumination this reaction is accelerated.

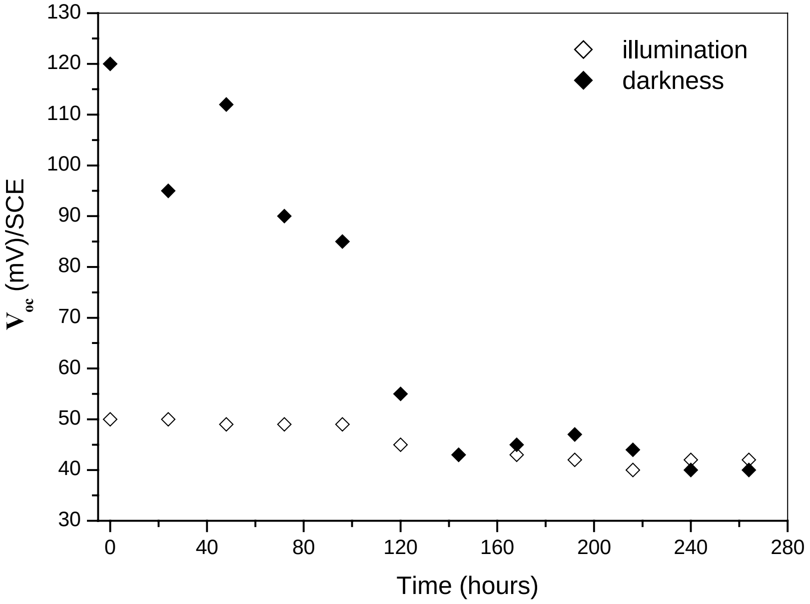


Fig. 1. The open-circuit potential vs. time curve for a p-CIGS/H_2SO_4 system in dark and under illumination.

3.2. Linear voltammetry studies

Figs. 2 and 3 show the typical current–voltage response for p-CIGS/H_2SO_4 system in dark and under illumination. Linear voltammetry studies were initiated at open circuit potential in either negative or positive direction: with a scan rate of $\upsilon = 5\,\text{mV/s}$ in the potential range ±0.150 V versus SCE. Fig. 2 shows the typical current–voltage response of the p-CIGS/electrolyte system in dark and under illumination for various days in the cathodic direction, using linear voltammetry as a function of time (in days). Fig. 2 shows that under illumination there appears a reduction peak on the first day. In dark for the first 2 days there was no significant change in the recorded current density. From the third day onwards there appears a reduction peak, indicating that soluble species are present in the system which is involved in the reduction processes. From the sixth day onwards the cathodic peak (E_p^c) is well defined at the potential region from −0.075 to −0.10 V versus SCE. No significant changes were observed in the potential peak position, indicating that the

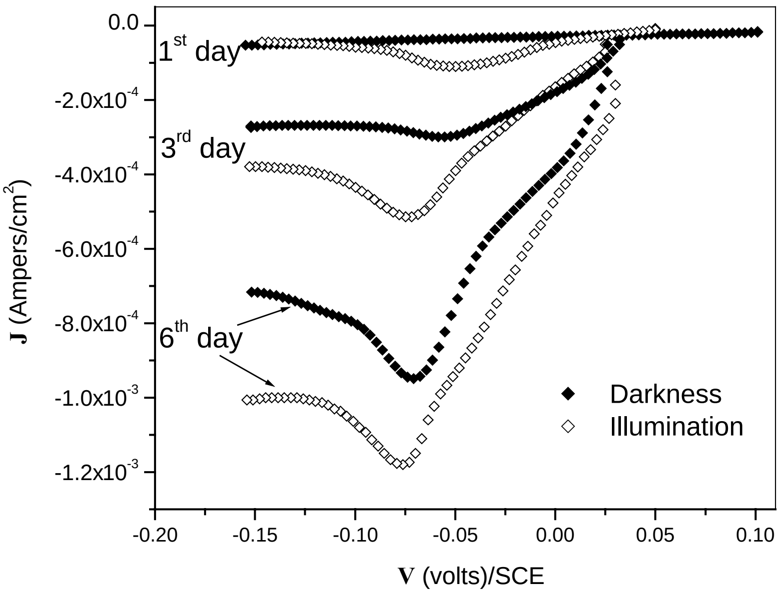


Fig. 2. The current vs. potential curve for a p-CIGS in dark and under illumination. Electrolyte −0.5 M H_2SO_4, scan direction $V_{oc} \rightarrow -0.15$ V vs. SCE, scan rate 5 mV/s.

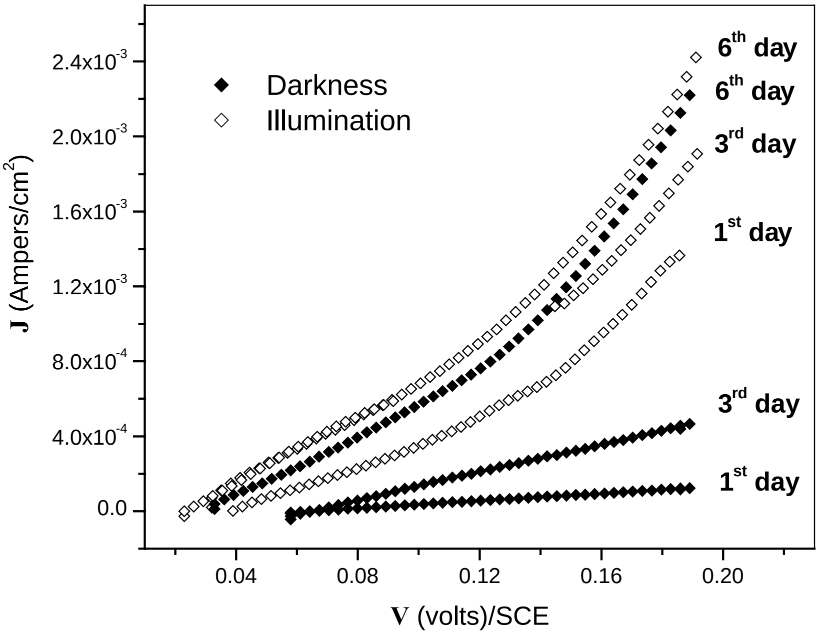


Fig. 3. The current vs. potential curve for a p-CIGS in dark and under illumination. Electrolyte −0.5 M H_2SO_4, scan direction $V_{oc} \rightarrow +0.20$ V vs. SCE, scan rate 5 mV/s.

cathodic peak corresponds to the same species that has been reduced in the process. It is observed that there is a systematic displacement of the open circuit potential towards more cathodic potentials corresponding to the data registered in Section 3.1.

Fig. 3 shows the linear voltammetry results corresponding to the positive direction in dark and under illumination. On the first day, the dark current density is practically zero and increases with time. Under illumination, from the first day of exposure there observed a high current density compared to that in dark. Under illumination also the current density increases with time. From the sixth day onwards the dark and illumination response of current density are very similar with respect to the value and tendency. A systematic displacement of the open circuit potential towards more cathodic potentials was observed. Other important factors are the absence of oxidation peaks in the anodic region and the presence of two slopes in the response curve. The two slopes in the curve mean the presence of two oxidation reaction in the p-CIGS/H_2SO_4 system.

The results obtained in dark present evidence of dissolution of the material in the electrolyte. In the case of illumination the significant increase in current density corresponds to a photocorrosion reaction. In order to verify which species are being dissolved in the electrolyte the following cyclic voltammetry studies were performed.

3.3. Cyclic voltammetry studies

Some typical current–voltage curves in dark for the p-CIGS/H_2SO_4 system are shown in Fig. 4. The potential sweep was initiated from the negative direction in the potential range −0.150 to 0.200 V versus SCE. It is important to note that these studies were carried out on samples with different exposure times. These studies were done in order to identify the species involved in dissolution and photo-corrosion process. Initially, the current–voltage response is almost zero, this means that there is no charge transfer. The current density increases with time of exposure and for long exposure periods there appear a reduction and an oxidation peak. These peaks are appeared around −0.100 and 0.100 V versus SCE, respectively.

Fig. 5 shows some typical current–voltage curves under illumination for the p-CIGS/H_2SO_4 system. The illumination accelerates the redox reactions. One can see from Fig. 5 that the reduction peaks E_p^c are appeared at the potential region between −0.05 and −0.10 V versus SCE and the oxidation peaks E_p^A between 0.08 and 0.10 V versus SCE. In both Figs. 4 and 5, the peaks are wide and with certain symmetry but the system does not get reversible. Nevertheless, we can consider that there occurs a redox reaction. From Figs. 4 and 5 it is observed that on the first day the CIGS does not react with the electrolyte but after some time (days) an element or some elements of the semiconductor dissolve in the electrolyte (anodic peak) and are re-adsorbed during the cathodic scan (cathodic peak).

3.4. Possible reactions that take place in the PEC (CIGS/H_2SO_4)

The linear and cyclic voltammetry studies indicate the presence of a redox reaction in the system, this reaction is due to the dissolution and re-adsorption

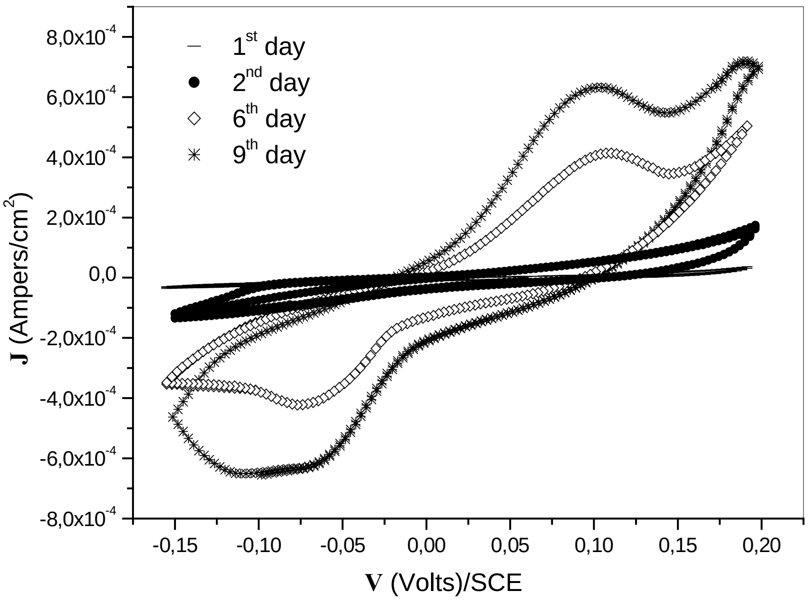


Fig. 4. The cyclic voltammograms for a p-CIGS photo-electrode in dark. Electrolyte 0.5 M H_2SO_4, scan direction $V_{oc} \rightarrow +0.20\,V \rightarrow -0.15\,V$, scan rate 5 mV/s.

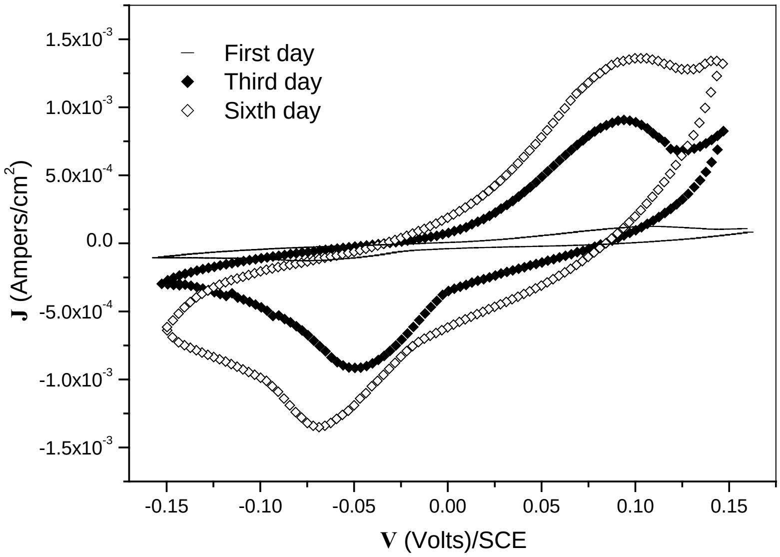


Fig. 5. The cyclic voltammograms for a p-CIGS photo-electrode under illumination. Electrolyte −0.5 M H_2SO_4, scan direction $V_{oc} \rightarrow +0.15\,V \rightarrow -0.15\,V$, scan rate 5 mV/s.

(oxidation–reduction) of an element or some elements of the CIGS/H_2SO_4 system.

The possible redox reactions in the system are the following [10]:

$$Cu^0 - 2e^- \rightleftarrows Cu^{2+}, \quad E^\circ \text{ versus SCE} = +0.099 \tag{1}$$

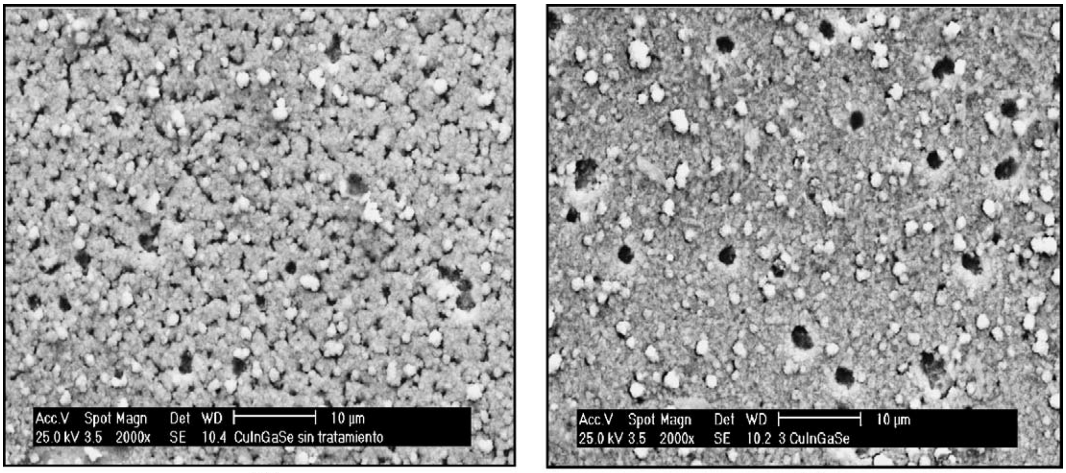
$$Cu^{1+} - e^- \rightleftarrows Cu^{2+}, \quad E^\circ \text{ versus SCE} = -0.083 \tag{2}$$

Under the present experimental conditions, the reaction which involves H_2SO_4 is not very probable. From the characteristics of the wide oxidation peaks in the cyclic voltammetry (Figs. 4 and 5), there is no evidence of a metallic reduction (Cu^0). Thus, the most probable reaction is $Cu^{1+} - e^- \rightleftarrows Cu^{2+}$ where Cu^{1+} dissolves in the electrolyte and then adsorbed by the semiconductor surface.

3.5. SEM and EDS results

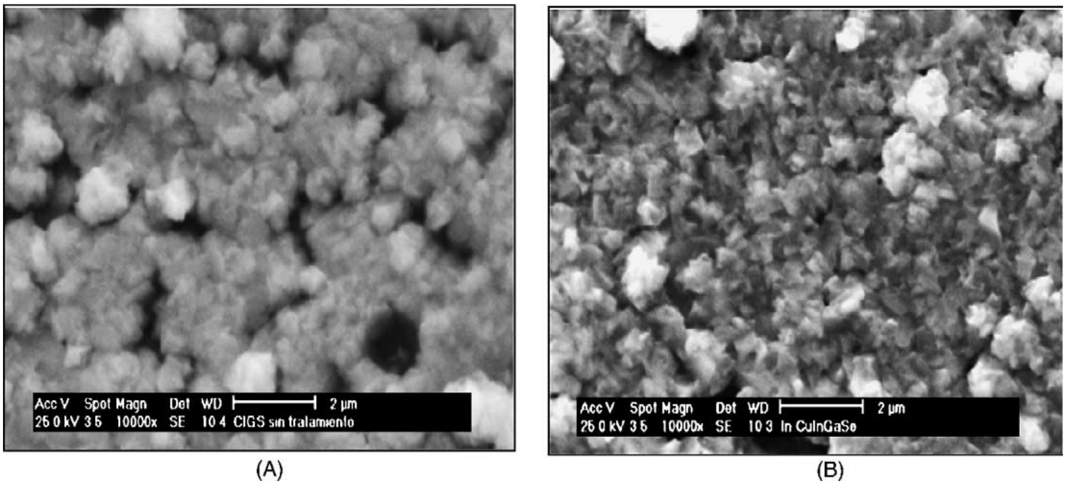
To observe the morphological and chemical composition changes we carried out SEM and EDS measurements before and after electrochemical measurements. Fig. 6A shows the SEM image of the CIGS sample before immersing in H_2SO_4, and Fig. 6B the image of the same sample after remaining 12 days in H_2SO_4. The images were taken under similar conditions (voltage 25 kV, magnification 2000×) with secondary electrons, which give information up to a depth of 5–10 nm below the surface of the thin film.

While comparing both images it appeared that there is an etching of the surface (Fig. 6B) due to the exposure of the film in the acid medium. A similar behavior has been reported for p-$CuInSe_2$ [11,12]. In both images it is observed that the chemical structures are arranged in different planes,



(A) (B)

Fig. 6. The SEM images (2000×) for the CIGS sample: (A) before immersion in H_2SO_4, (B) after immersion in H_2SO_4 during 12 days.



(A) (B)

Fig. 7. The SEM images (10,000×) for the CIGS sample: (A) before immersion in H_2SO_4, (B) after immersion in H_2SO_4 during 12 days.

Table 1
The composition data for the CIGS films analyzed by EDS, before and after the film was immersed for 12 days in sulfuric acid

Composition (%)	Cu	In	Ga	Se
Before immersion	17.3	8.45	19.57	54.68
After immersion	16.94	5.63	22.07	55.36

hence, the images have different contrasts. However, the chemical analysis of the different contrast places shows a uniform distribution of the four elements of CIGS. In order to analyze more these morphological changes the SEM analysis was carried out with a higher magnification of 10,000× with secondary electrons (Fig. 7). Similar to the previous cases, Fig. 7A and B shows the SEM images of CIGS before and after exposure in H_2SO_4. In Fig. 7B there appeared a more compact surface than in Fig. 7A.

Table 1 gives the chemical composition of CIGS film before and after exposure to H_2SO_4 for 12 days. There is no significant change in the Cu and Se content in the film composition after exposure, but there is a noticeable change in the relative proportion of In and Ga content in the film composition. But, the total percentage of In and Ga before and after exposure remains almost the same in the quaternary compound $CuIn_{1-X}Ga_XSe_2$.

4. Conclusion

In this work, we studied the stability of the p-CIGS/H_2SO_4 system in a small potential interval with the purpose of simulating the conditions of use. From the voltammetry analysis of the samples it is seen that p-CIGS is susceptible to dissolution or photocorrosion in H_2SO_4. Considering the SEM and EDS results for CIGS immersed in H_2SO_4 for 12 days, an important morphological change is observed, which may be caused by the Cu^{1+} dissolution in the electrolyte and re-adsorbed in the semiconductor. This affects the superficial aspects of the film. The hydrogen evolution potential is normally more negative than the redox potential of Cu^{2+}/Cu^{1+}. Hence, the dissolution and re-adsorption of Cu^{1+} does not impede with the hydrogen evolution reaction. Also the compositional changes are not appreciable with respect to the final composition of $CuIn_{1-X}Ga_XSe_2$.

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