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IMPROVING THE PERFORMANCE OF SOLAR CELLS BASED ON THIN FILM ELECTROGENERATED OF CuInSe2

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ABSTRACT
This study shows that thin films of $CuInSe_2$ and $CuIn(Se,S)_2$ may be developed by the electrochemical method of deposition using an electrolyte solution containing sulphate. The films obtained are almost amorphous and heat treatment selenizing or sulfurizing is always necessary to improve the crystallinity of the films and to confer the physical properties to them for their application in photovoltaic devices. The heat treatment in the presence of H_2S also allows the preparation of thin films of the quaternary $CuIn(Se,S)_2$. The analysis by X-ray diffraction shows that the films are well crystallized. The current-voltage characteristic of the cell $CuIn(Se,S)_2$ shows an efficiency of 6.37%.

KEYWORDS: Thin films, $CuInSe_2$, $CuIn(Se,S)_2$, Electrodeposition, potential pulsed method

INTRODUCTION
$CuInSe_2$ is a semiconductor material with a gap of 1.04 eV [1 - 2] and an efficiency of 20.3 % [3]. Its gap limits the tension of open circuit and thus the efficiency of the photovoltaic cell. Work on photovoltaic cells based on $CuInSe_2$ are turning more and more to wide band gap compounds which are quaternary alloys $Cu(In,Ga)Se_2$ [4, 5, 3] $CuIn(Se,S)_2$ [6 - 7] , $CuIn(Te,Se)_2$ [8] or types of alloys $Cu(In,Ga)(Se,S)_2$ [9].

Furthermore, it can be prepared by relatively simple and inexpensive technical [10, 11, 12, 13] which are appropriate perfectly for our conditions of research. The electrodeposition, part of these methods has enabled us to develop in particular to reach photovoltaic cells having a conversion efficiency record 9 % [14].

In this technique, the stabilization of the solution of deposit constitutes a limiting factor. We showed that the use of a buffer [14] (pH = 3, mixture of sulphamic acid and potassium biphthalate), which prevents the formation of metal oxides in solution and the precipitation of hydroxides, stabilizes the bath of deposit and helps keep for several weeks. Thus, the results obtained with the photovoltaic cells made with thin films of $CuInSe_2$ deposited in the presence of buffer, however, are lower than those obtained initially.

The objective of our work is of:
- to carry out the post-deposition treatment of $CuInSe_2$ thin films deposited in the presence of buffer, in a H_2S atmosphere to obtain the quaternary compound $CuIn(Se, S)_2$.
- to carry out the deposition of the thin film of $CuInSe_2$ pulsed potential in the presence of buffer.
- To make the characterization of materials and solar cells based of CIS films.

DEPOT OF PRECURSORS
Electrodeposition of $CuInSe_2$ was performed using aqueous solutions of acid mainly consisting of sulfate [10 - 13]. The precursors $CuSO_4.5H_2O$, $In_2(SO_4).H_2O$, SeO_2, $Li_2SO_4.H_2O$ and the buffer solution of pH = 3 are used without prior purification whose concentrations in ion are $[Cu^{2+}] = 2.00$ mM, $[In^{3+}] = 3.89$ mM and $[Se^{4+}] = 4.00$ mM. The buffer solution has a role to control the pH of the solution of deposit and to reduce the oxide and metal hydroxide precipitation in electronic bath. [14] These solutions are always made by mixing the solutions of Cu^{2+}, of In^{3+} to a solution of basic salt before diluting the whole in beaker containing of distilled water and the buffer beforehand dissolves to obtain a volume of solution of 500 ml. After the addition of buffer, stocks remain stable

during several weeks without metal precipitations of hydroxides. These precursors remain during the growth and about a dozen films of 2 microns can be obtained with 500 ml.

All depositions were carried out at ambient temperature by applying between the working electrode and the reference electrode a potential containing -0.550 V/SCE for the Mo substrates or -0.650 V/SCE for ITO substrates.

However, the deposit by pulsed potential is controlled by computer. We use the same solution as for the deposit above.

FORMATION OF THE FILMS CuIn(Se, S)2
Several approaches are used for the realization of thin films of CuIn(Se,S)$_2$. All these approaches rest however on the same principle: the chalcogenisation of alloy or precursors definite compounds [15, 16, 13].

The formation of the quaternary CuIn(Se, S)$_2$ is carried out by heat treatment under atmosphere of sulfur, electrogenerated thin films. For that a constant flow of H$_2$S/Ar is maintained through the tube during the operation. It then occurs a partial substitution of selenium by sulfur. This phenomenon of incorporation of sulfur in the films of CuInSe$_2$, CuGaSe$_2$ and Cu(In,Ga)Se$_2$ was the objet many quantitative studies which made it possible to establish a scientific basis for the manufacture of thin films of CuIn(Se,S)$_2$ homogeneous or of graduated compositions [17, 18]. It constitutes in the case of CuInSe$_2$ a means useful to modulate the gap of 1.02 eV for CuInSe$_2$ to 1.55 eV for CuInS$_2$.

In the gas hydrogen sulfide H$_2$S, the chemical reaction of substitution leading to quaternary is:

$$CuInSe_2(s) + 2H_2S(g) \leftrightarrow CuInS_2 + 2H_2Se(g) \qquad (1)$$
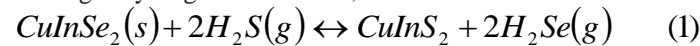
The equilibrium constant of this reaction is given by:

$$k = \frac{[CuInS_2][H_2Se]^2}{[CuInSe_2][H_2S]^2} = \left(\frac{1-x}{x}\right)\left(\frac{y}{1-y}\right) \qquad (2)$$

where

$$x = \frac{[H_2S]}{[H_2S] + [H_2Se]} \qquad (3) \text{ in the gas phase}$$

and

$$y = \frac{[S]}{[S] + [Se]} \qquad (4) \text{ in the film}$$

A phenomenological model of the process of diffusion reaction was developed which the H$_2$S reacts with CuInSe$_2$ to the surface to form a layer of CuInS$_2$ and to release selenium figure 1.
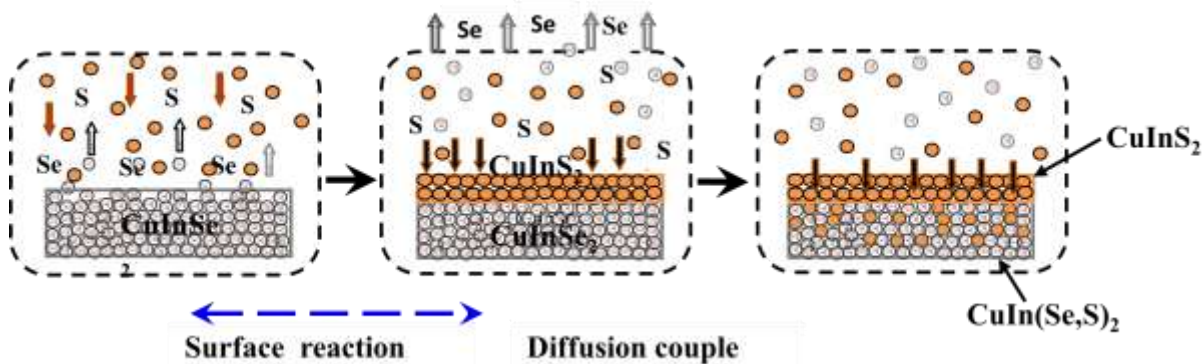

Figure 1: Phenomenological model for the reaction / diffusion formation process of CuIn(Se,S)$_2$
The films of CuInSe$_2$ and CuInS$_2$ inter- diffuse to give a gradient of [S]/[Se] in the structure. The concentration of solid phases in the reaction corresponds to the molar fractions in the compound CuIn (Se,S)$_2$.

RESULTS AND DISCUSSION
1) Characterization of Films
During this work, various physical methods of characterization were used. These analyzes are necessary to evaluate the quality of thin films in order to optimize the conditions of electrochemical deposition and post-deposition treatment of thin film CuInSe$_2$. These analyzes include:
- Optical microscopy and scanning electron microscopy SEM to study the textural of the films;
- Analysis composition performed by a system of dispersive microanalysis in energy EDS;
- The X-ray diffraction for the study of the structural properties of the films;
- The study of optical properties by spectrometry UV-visible-IR
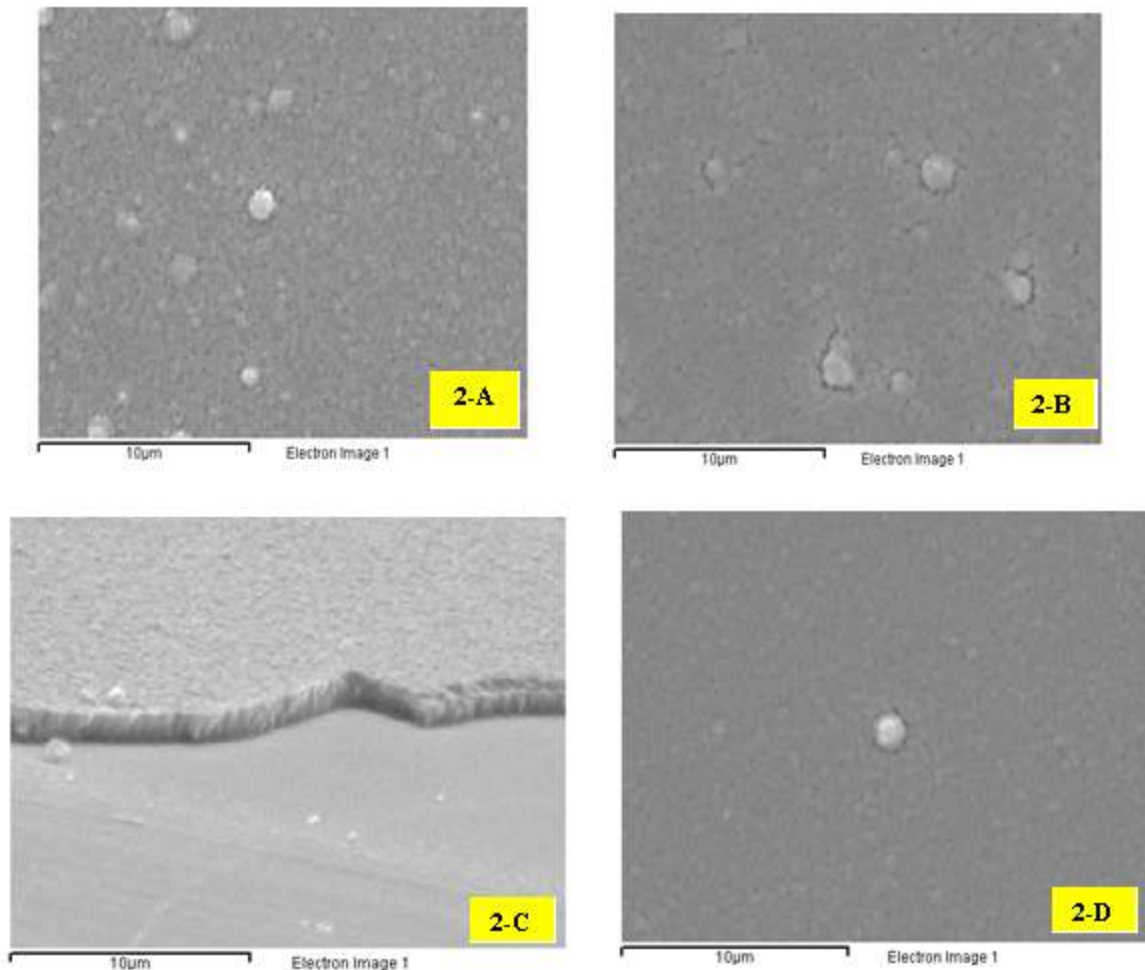
A. Composition and morphology
The analysis of the chemical composition is carried out by dispersive microanalysis in energy. The dispersive analysis is an analytical technique used for chemical microanalysis. It is based on the detection and analysis of X-rays emitted by a sample during its interaction with an electron beam primary which bombards it.

The dispersive in energy is generally coupled with scanning electron microscopy. This characterization makes it possible to visualize the surface of the thin films. To characterize our thin film on a macroscopic scale, we used a scanning electron microscope SEM. Its principle is the following: in a vacuum enclosure, an energy electron beam is sent on the surface of the sample and the image obtained is the result of interaction of these electrons and the sample.

The figures 2-A and 2-B show the images for a thin film of CuInSe$_2$ before and after its heat treatment under atmosphere of sulfur. We note very little change in the morphological structure of these films after the sulfurizing treatment. The composition of this layer before and after sulphurizing annealing is given in table 1.

Table 1: Chemical composition of thin Film CIS before and after selenization and the sulfurization processes.

As-deposited film composition (at.%)			Annealing atmosphere	Annealed film composition (at.%)			
Cu	In	Se		Cu	In	Se	S
22,18	23,25	54,58	0,35% H$_2$Se Ar(g)	24,05	24,68	51,27	0,00
22,32	23,46	54,22	0,35% H$_2$S Ar(g)	23,95	24,98	39,60	11,47

Figure 2: Morphology of the surface of a thin film of CIS deposited in potentiostat mode:
2-A) before sulfurizing , 2 -B) after sulfurization and 2 -C) cross section of a film before annealing. 2 -D)
morphology of surface of a thin film of CIS deposited in mode pulsed after selenizatio

B.   Structural study thin films of CuIn (Se, S)$_2$

The X-ray diffraction technique is a method which is based on Bragg's law relating to the conditions of X-ray diffraction by a crystal:

$$2d \sin \theta = n\lambda \quad (5)$$

This technique makes it possible to have quantitative information covering the crystalline characteristics (nature of the material, phases present, preferred orientation, crystallite size, etc.). It also highlights noted qualitative made starting from electronic microscopy on the level of the texture layer and the crystallite size. This study is very important in the case of the CIS given the probable coexistence of several phases in the depot.

The substitution of selenium by sulfur and the diffusion of this last in the volume of the material results in a slight displacement of the peaks of diffraction of the structure chalcopyrite into the great values of the diffraction angle. Figure 3 shows the spectra of diffraction of the two films of CuInSe$_2$ after the treatments selenisant and sulfurizing. The small box in this figure shows the displacement of the peak of diffraction characteristic of the reflection (112) which passes from $2\theta = 26.58°$ to 26.86. In more selenium substitution by sulfur led to slight decrease interplanar spacings (Table 2) and consequently a reduction of the lattice parameters.
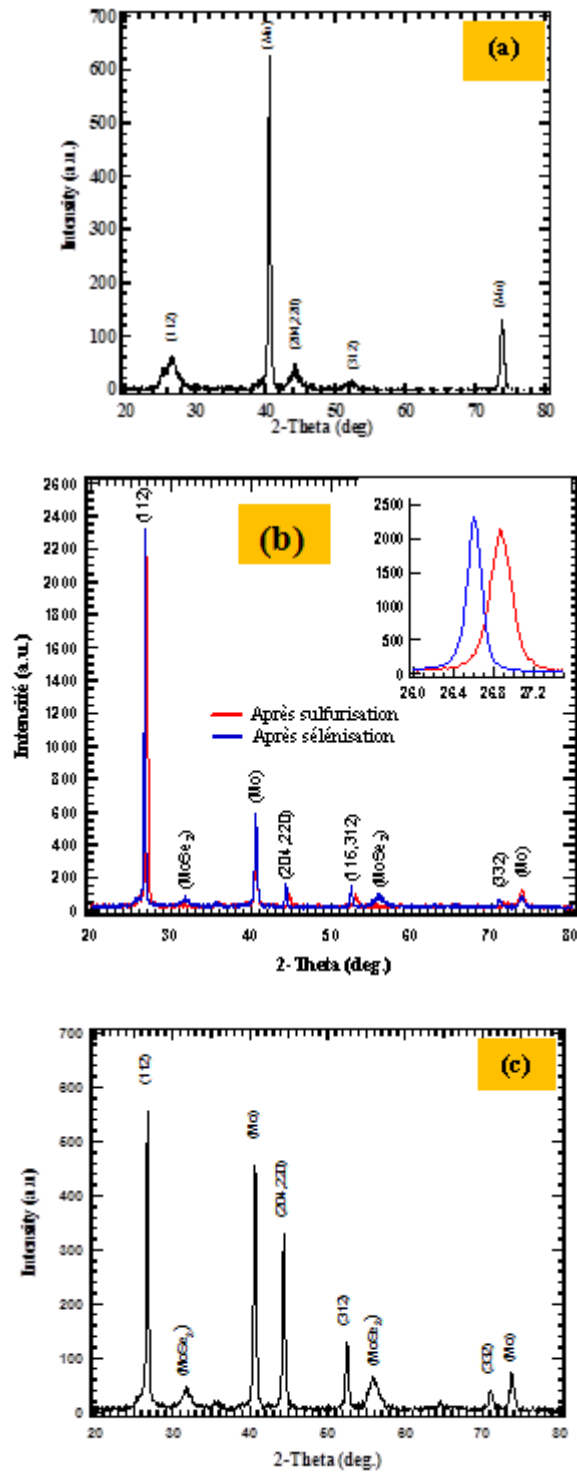
Figure 3 : XRD patterns of:
(a) film of CuInSe₂ before heat treatment (potentiostatic and pulsed mode)
(b) Selenized and sulfurized samples deposited in solution without buffer
(c) Samples deposited in the presence of buffer after sulfurisation

Table 2: Peak positions and corresponding lattice d-spacing of the copper based chalcopyrite structure

(hkl)	$CuInSe_2$		$CuIn(Se,S)_2$		$CuInS_2$	
	2θ	d(Å)	2θ	d(Å)	2θ	d(Å)
(112)	26,58	3,35	26,86	3,32	28,24	3,20
(220)	44,18	2,05	44,66	2,03	46,84	1,95
(312)	52,34	1,75	52,86	1,73	55,36	1,67
(332)	70,90	1,33	71,42	1,32	75,04	1,27

C. Optical Properties

The study of the optical characteristics of the semiconductor makes it possible to obtain information on their structure of band and their aptitude to contribute effectively in photovoltaic devices.

In the case of $CuIn(Se,S)_2$, the study of the absorption spectra or transition from the layers before the heat treatment does not allow any comparison . Indeed, these layers do not generally show semiconductor characteristics.

The values of energies of band transition of the conduction and valence band that of the bursting due to the spin-orbit interface can be evaluated from the optical spectra.
From the measurements of transmission and reflection, we can determine the absorption coefficient by the following equation:

$$\alpha = \frac{1}{d} \ln\left(\frac{100 - R\%}{T\%}\right) \quad (6)$$

Where R% is the reflection and T% is the transmission
The absorption coefficient α of $CuIn(Se,S)_2$ is with energy hv of photons by :

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (7)$$

Figure 3 shows the transmission spectra and reflection thin film of $CuIn(Se,S)_2$. These spectra present two distinct zones. In the wavelength range between 400 and 1000 nm; the transmission rate is relatively low so the incident radiation is well absorbed. Beyond of 1000 nm, the transmission rate increases quickly to maximum values. For reflection, a slight variation in the wavelength domain is observed between 400 and 1000 nm. Beyond this area, the interference phenomena occur.
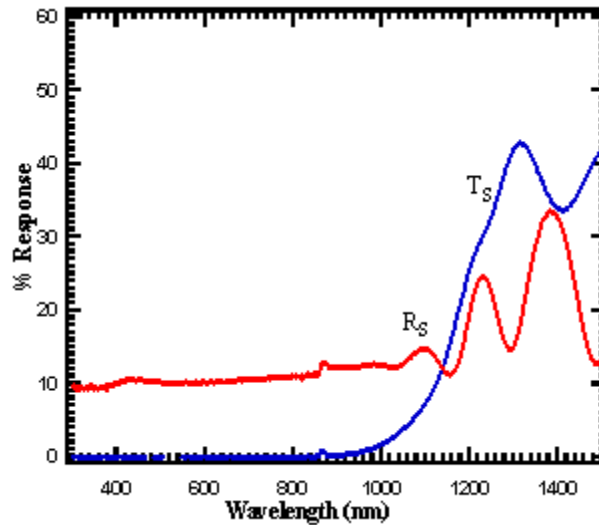
Figure 3 : Transmission and reflection spectra of a CIS sample grown in a solution with a buffer hydrion on ITO substrate after the sulfurization

The representation of $(\alpha h\nu)^2$ according to energy $h\nu$ of the photons presents a linear part. The extrapolation of this linear part to the axis of energies makes it possible to determine the value of Eg energy of the transition figure 4.
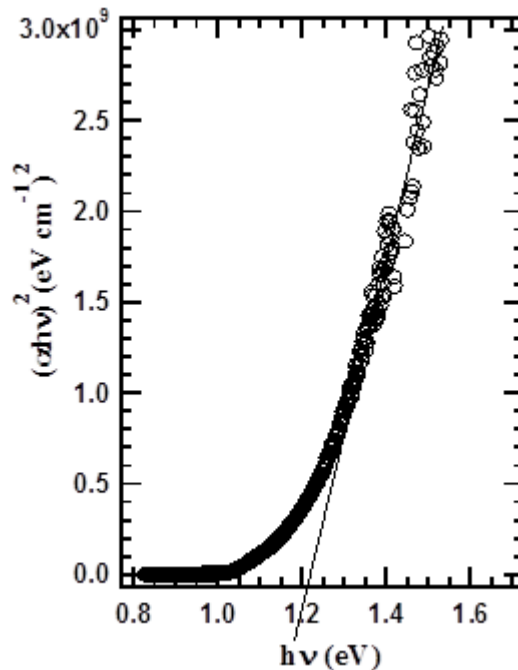
<u>Figure 4</u> : Variation of $(\alpha h\nu)^2$ according to the energy of the photon for samples of CIS electrodeposited on ITO after sulfurization: the precursory film of CIS is deposited in a solution containing the buffer.

2) Current-voltage characterization

The main feature of a solar cell is that of the variation of the current density delivered by the cell based on the tension at its terminals, commonly called characteristic J-V from this, we can easily deduce the current density short circuit Jcc (Vcc = 0), the open circuit voltage Voc (Jco = 0) and maximum power Pm that can charge the cell and the fill factor FF.

Figure 5 represents the photovoltaic cell of thin film of $CuIn(Se,S)_2$ with the different parts of the solar cell .
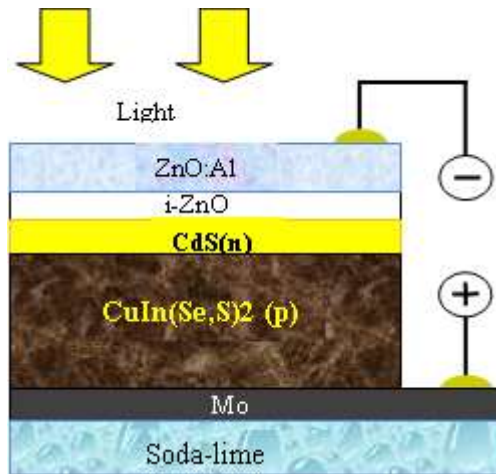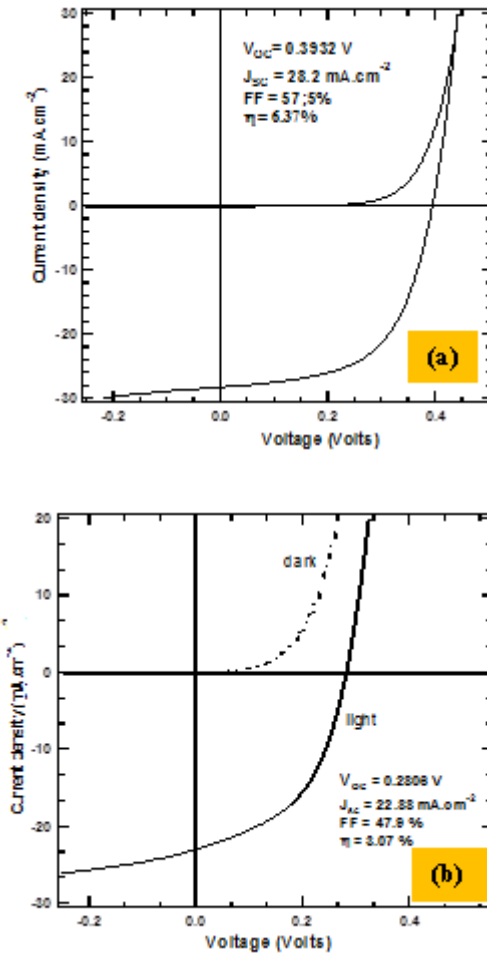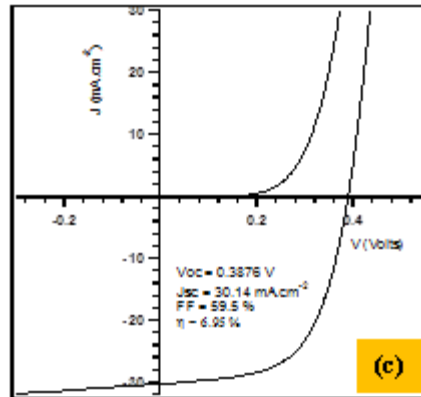
Figure 5 : Conventional structure of the solar cell based CIS

Figure 6 represents the current-voltage characteristics of a photovoltaic cell based on $CuInSe_2$ and $CuIn(Se,S)_2$

Figure 5: characteristics J-V of solar cells (AM 1.5).

(a): A device made with a thin film of CIS deposited in the presence of buffer then sselenized : Mo/CIS/CdS/ZnO

(b): A device made with a thin film of CIS deposited in the presence of buffer and then sulfurized : Mo/CISS/CdS/ZnO

(c) : A device made with a thin layer of CIS deposited in pulsed mode then selenized : Mo/CISS/CdS/ZnO

CONCLUSION

The use of a buffer (pH=3) in the electrolytic solution makes it possible to stabilize the solution of deposit of $CuInSe_2$ but produced films leading to photovoltaic cells having relatively low efficiencies of conversion (3,07%).We showed that the post-deposition treatment in an atmosphere of sulfur, which supports a reaction of exchange between selenium and sulfur led to thin films of $CuIn(Se,S)_2$.These films, crystallized well, gave access higher efficiencies of conversion (6,37%).The technique of electrodeposition by potential pulsed controlled by computer, that we developed, also made it possible to improve the physical properties of the films and to thus increase the efficiency of the photovoltaic cells (6,95%).

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