



Determination of the Diffusion Length of CuInSe₂ Thin Film Photovoltaic Cell Electrodeposited

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Abstract In this study we have realized photovoltaic devices using CIS thin films as absorber materials. These absorber films are obtained by electrodeposition which is a simple method and does not require expensive post-deposition treatments. In the case where a pH = 3 buffer is used to stabilize the solution for weeks the yields obtained are low. However, this study shows that there are ways to improve the performance of these cells. The sulfurizing thermal treatment which allows the formation of quaternary layers of CuIn(Se,S)₂ and the deposition of the absorber material by pulsed potential have allowed to improve the diffusion length of these cells.

Keywords CuInSe₂, electrodeposition, pulsed potential, diffusion length

Introduction

The semiconductor CuInSe₂ is among the best candidates for terrestrial photovoltaic applications. Solar cells fabricated on vacuum deposited CuInSe₂ thin films have demonstrated conversion efficiencies up to 21.7 % [1, 2, 3]. In our laboratory, a low-cost electrodeposition method has been developed to deposit thin films of CuInSe₂ [4, 5, 6]. For the heterojunction cells, two window materials (In-doped CdS and Al-doped ZnO) are used. The diffusion length of minority carrier is an important parameter characterizing properties of semiconductors. The diffusion length of minority carriers in the absorbing layer of a heterojunction solar cell plays an important role in determining the cell conversion efficiency. The diffusion length of electrons in the CuInSe₂ was measured using several methods [7, 8, 9]. In this study, we will first present the deposition techniques of the CuInSe₂ absorber film and the CdS buffer film, a post-deposition treatment of the absorber film in the presence of H₂S and finally we present the results.

Deposition of CuInSe₂ thin films

The production of CIS thin films can be carried out by a wide variety of techniques [4, 5, 6,]. The various parameters associated with the growth process in each of these techniques have a characteristic effect on the nucleation, microstructure of the layers, their composition as well as their adhesion and consequently on their physical properties. The choice of the growth method is therefore an important step in the development of high quality materials. The electrochemical technique presents a certain interest since it not only makes possible the control of the reactions and the properties of the deposits but is carried out at low temperature thus making it possible to remove certain constraints related to the substrate. It also offers a good reproducibility, a good yield and the possibility to treat large surfaces at lower costs; which makes it very attractive for industrial applications, in particular the production of thin film solar cells. Another advantage of the electrochemical method of synthesis of semiconductor or metallic materials in thin films is the great facility of its implementation. Indeed the very simple experimental device, is constituted within the framework of this work,



of a Potentiostat/Galvanostat Princeton Applied Research (PAR) Model 263A equipped with a digital coulometer and an electrochemical cell in which plunge three electrodes:

- a saturated calomel electrode (SCE) as reference electrode
- a platinum grid as counter electrode (CE)
- a glass slide of dimensions 2 cm x 2 cm covered with a layer of molybdenum (Mo) of 0.7 μ m thickness constitutes the working electrode (ET).

Bivalent copper (Cu^{2+}) and tetravalent selenium (Se^{4+}) salts are generally used for the electrochemical deposition of copper indium diselenide (CIS) and its derivatives due to their solubility but also their stability in aqueous medium.

The electrochemistry of these species is also well enough understood to allow for the optimization of the growth of Cu_xSe_y secondary phase. The electrodeposition of CIS was performed using acidic aqueous sulfate solutions. This solution consists of copper sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, indium sulfate hydrate, $\text{In}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, selenium dioxide SeO_2 and lithium sulfate hydrate, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ which serves as a bottom salt, all dissolved in distilled water. A packet of a buffer (pH = 3 pHydrion buffer) is dissolved in it, leading to a solution of pH 2.5. This pH = 3 pHydrion buffer is a mixture of sulphamic acid and potassium biphthalate. Its role is to control the pH of the deposition solution and to reduce the precipitation of metal oxides and hydroxides in the electrolytic bath.

With the addition of the buffer, the solution stocks remain stable for several weeks without precipitation of metal hydroxides. They also remain stable during the growth of the layers and a dozen films of about 2 μ m thickness can be made with 500 ml of solution without appreciable depletion of electroactive species.

All the deposits are carried out at room temperature using either the continuous mode (in potential or in current) or the electrochemical technique in pulsed mode.

The fact of working in pulsed mode can modify the diffusion layer which feeds the interface of the deposit and also influence the reduction process in the vicinity of the working electrode by the rest phase which is a relaxation phase. Pulsed electrochemical deposition therefore has definite advantages in the development of thin films. This advanced form of electrodeposition is often cited in the literature as being able to improve the quality of the deposits, the mechanical and physical properties of the films and to increase the deposition rate.

In the continuous mode synthesis method, there is only one modulable parameter, which is the potential or the applied current density; this is generally insufficient for the quality control of the films. Pulsed mode electroplating, on the other hand, consists in varying the current or the potential over time. It offers additional parameters that can be modulated such as the shape, frequency or amplitude of the signal and the duty cycle. The form of the modulated electrical regimes often used in the literature is generally quite simple. Figure 1 shows the most common ones where the current is varied.

In the simple pulsed regime (Figure 1-a), a cathode current I_c is imposed for a time t_c and the circuit is opened for a time t_{off} , representing a pause at zero-current. In this type of regime, the cathode time t_c is more commonly used.

The pulsed current regime with periodic current reversal (Figure 1-b) is defined by a cathodic current I_c imposed for a time t_c and an anodic current I_a , of opposite sign, imposed for a time t_a .

The pulsed current regime with inversion and then interruption of the current (Figure 1-c) is a combination of the first two. Indeed, this regime is characterized by a cathodic current I_c imposed during a time t_c , then by an anodic current I_a imposed during a time t_a and finally a pause at zero current during a time t_{off} .



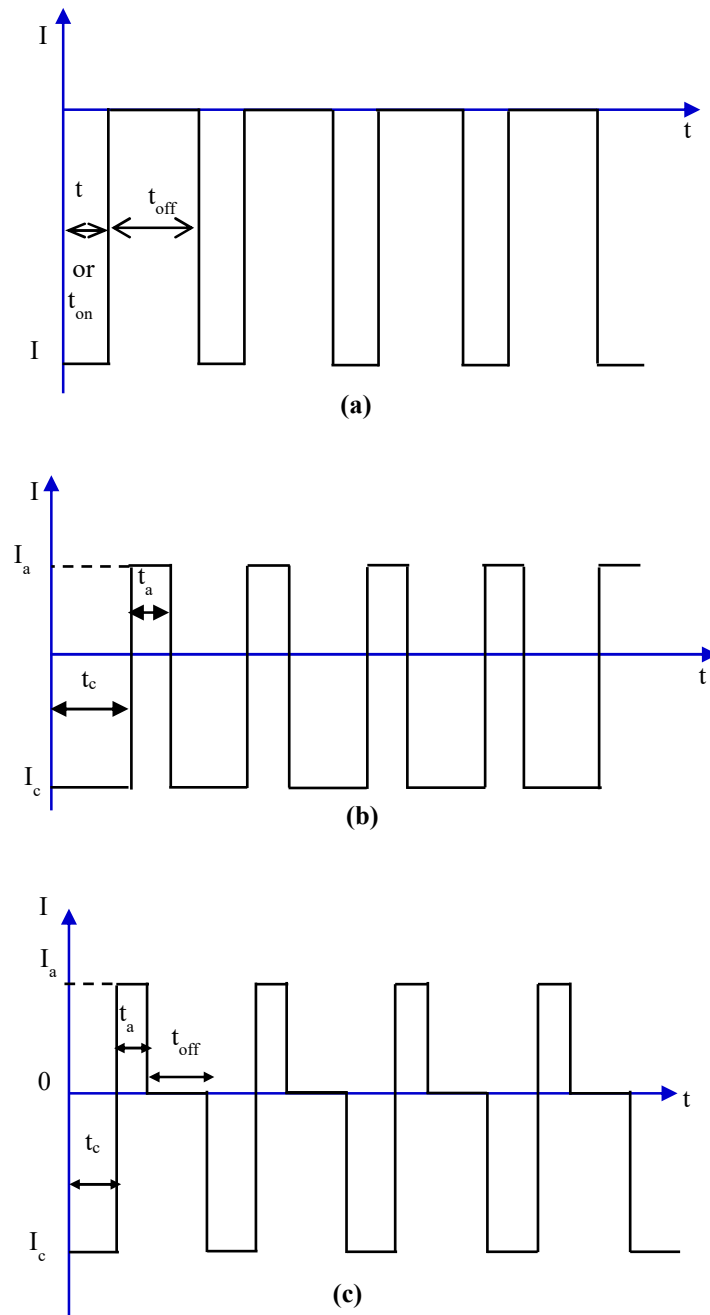


Figure 1: Examples of pulsed current regimes: simple regime (a), regime with current reversal (b), regime with current reversal then interruption (c).

Buffer layer deposition (CdS)

Chemical Bath Deposition (CBD) is a deposition method similar to Chemical Vapor Deposition (CVD). It is a method that has long been used for the deposition of chalcogenides: metal sulfides and selenides such as PbS, CdSe, CdS. For the deposition of a given chalcogenide, a wide variety of compounds or precursor ions can be used.

In the particular case of the elaboration of the CdS buffer layer in CIS-based photovoltaic cells, an alkaline aqueous solution ($\text{pH} \approx 9$) containing a cadmium salt (cadmium sulfate, CdSO_4 , cadmium chloride CdCl_2 ,

cadmium iodide CdI_2 , cadmium acetate, $\text{Cd}(\text{CH}_3\text{COO})_2$, ...), a complexing agent which is usually ammonia NH_3 and a precursor sulfide often thiourea, $\text{SC}(\text{NH}_2)_2$.

The structure of the CdS film formed depends on the operating conditions. In particular, we can obtain CdS of cubic or hexagonal structure or a mixture of these two structures in the material. Under our operating conditions, the growth of CdS is carried out according to the process of condensation ion by ion, thus leading us to homogeneous and dense layers with a mixed cubic-hexagonal structure or with a predominant hexagonal structure.

It is shown that CdS thin films formed by chemical bath are generally not stoichiometric. In particular, they are slightly deficient in sulfur and contain a substantial amount of oxygen and significant concentrations of hydrogen, carbon and nitrogen are also detected. The concentration of these impurities is linked to a phenomenon of reduction of the optical gap observed in these layers but also to the importance of the cubic phase compared to the hexagonal phase in the material.

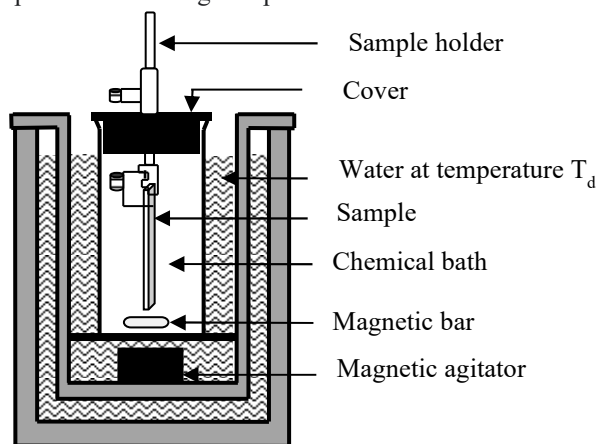


Figure 2: Experimental setup for chemical bath deposition of the CdS layer

Post-deposit treatment of the layers

The CIS thin films deposited at low temperature are very weakly crystallized or even quasi-amorphous. In the case of electroplating, the layers are very often composed of small grains and quite often polyphase with the presence of CuInSe_2 , In_2Se_3 or Cu_2Se . In some cases, the simultaneous presence of these last two phases is observed in the films before annealing.

Heat treatment in an inert atmosphere, in a vacuum or in a controlled atmosphere of chalcogen allows to remarkably improve the crystallinity of the layers, their charge transport properties and to reduce the presence of secondary phases.

At CIS recrystallization temperatures, selenium is more volatile than other elements such as copper and indium. Moreover, to give the layers a p-type semiconductor character, they must have a slight excess of selenium. Thus in this work, the post-deposition treatment consists of an annealing under controlled atmosphere of a chalcogen: atmosphere of selenium or "selenization" and atmosphere of sulfur or "sulfurization". In addition to improving the crystallinity and the electronic properties of the deposits, this last type of thermal treatment allows the formation of the quaternary material $\text{CuIn}(\text{Se},\text{S})_2$, by a partial substitution of selenium by sulfur.

In this annealing process, a laminar flow CVD thermal reactor is used to impose a well controlled pressure on the chalcogen. The latter is dissolved in a carrier gas which is argon (Ar). A mantle heated to a uniform temperature by means of four thermocouples, allows to control the temperature through the tube. Typical treatment conditions are a temperature of 500°C , a concentration of chalcogen in the carrier gas of 0.35% and a carrier gas velocity of 76 cm/min.

A constant flow of $\text{H}_2\text{Se}/\text{Ar}$ or $\text{H}_2\text{S}/\text{Ar}$ is maintained through the tube during the whole process. For electrogenerated CIS layers, two parameters remain decisive in the heat treatment: temperature and annealing time. For thin films obtained in the presence of the buffer solution, a better recrystallization is obtained at 50°C for a duration of at least 25 minutes. A slight selenium deposit on the tube walls is usually observed after the



operation; this indicates a loss of Se during the heat treatment. In the particular case of sulfurization, the formation of the quaternary $\text{CuIn}(\text{Se},\text{S})_2$ is carried out by partial substitution of selenium (Se) by sulfur (S) during the heat treatment in the presence of a constant $\text{H}_2\text{S}/\text{Ar}$ flow. This phenomenon of S incorporation in CuInSe_2 , CuGaSe_2 and $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ films has been quantitatively studied and has provided a scientific basis for the fabrication of homogeneous or compositionally graded $\text{CuIn}(\text{Se},\text{S})_2$ thin films (Figure 3). It constitutes, in the case of CuInSe_2 a useful means to modulate the gap from 1.02eV for CuInSe_2 to 1.55 eV for CuInS_2 .

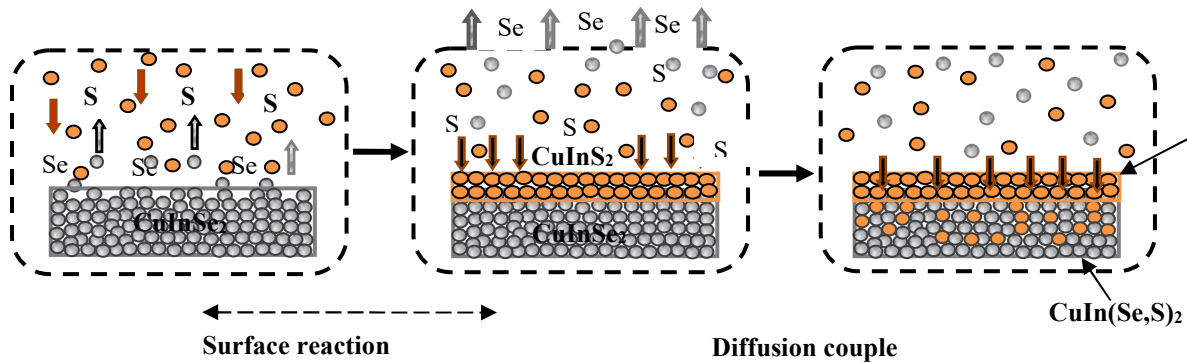


Figure 3: Formation process of $\text{CuIn}(\text{Se},\text{S})_2$ by substitution-diffusion

Results and discussions

Minority carrier diffusion length and surface recombination rate are fundamental parameters that determine the performance of p-n junctions, bipolar transistors and solar cells. In the semiconductor industry, the diffusion length is an indicator of contamination (impurities) and localized micro-defects the material [7]. The diffusion length directly affects the performance of solar cells through both the open circuit voltage and the short circuit current. Furthermore, a sufficiently low surface recombination rate is also necessary to allow the generated carriers not to recombine at the surface and thus cause a decrease in the open circuit voltage. The measurement of these parameters is therefore essential for the characterization of the devices.

Thus, the most intuitive analysis for the extraction of this parameter is the internal quantum efficiency (IQE), defined as the ratio of the photocurrent to the amount of photons absorbed in the device. The internal quantum efficiency can be further analyzed using one-dimensional models to determine the minority carrier scattering length L_n and the recombination rate at the back surface of the device.

$$\text{IQE}_n = \frac{J_{\text{ph}}(\lambda)}{e \phi(\lambda)(1 - R)} \quad (1)$$

Most models describing the internal quantum efficiency of p-n devices use only a small portion of the wavelength that is uniquely absorbed in the base for scattering length extraction. Thus, absorption and recombination in the emitter region can be neglected. The solution of the one-dimensional continuity equation in the basis is used to determine J_{sc} . Using this solution, the expression for the internal quantum efficiency IQE_n in the basis can be described as a function of the recombination factors of the basis, namely the scattering length L_n of the basis and the recombination rate at the back surface S_n . This is a complex function of L_n and S_n that allows the use of different approximations for the internal quantum efficiency IQE_n .

The simplest model is based on the linearity between the inverse of the efficiency between the inverse of the internal quantum efficiency of the IQE_n base and the penetration depth $1/\alpha$ of light [7]:

$$\frac{1}{\text{IQE}_n} \approx 1 + \frac{1}{L_n} \left(\frac{1}{\alpha} \right) \quad (2)$$

This model involves a linear fit of $1/\text{IQE}_n$ as a function of $1/\alpha$ that yields a linear part whose directing coefficient is used to determine the diffusion length.

If the absorption depth exceeds the thickness of the photovoltaic cell, only an effective scattering length L_{eff} is measured, i.e., a scattering length that is influenced by surface recombination. In this case, the model is only applicable if L_n is larger than the penetration depth. However, L_{eff} is defined as follows

$$L_{\text{eff}} = L_n \frac{\frac{S_n L_n}{D_n} \sinh\left(\frac{w_b}{L_n}\right) + \cosh\left(\frac{w_b}{L_n}\right)}{\sinh\left(\frac{w_b}{L_n}\right) + \frac{S_n L_n}{D_n} \cosh\left(\frac{w_b}{L_n}\right)} \quad (3)$$

where w_b is the thickness and D_n is the diffusion constant of the base.

Due to the high degree of approximation in the calculation of the linear model, the application is limited or may lead to erroneous results. However, several effects cause the limitations of the linear model: linearity is not achieved for all cell models, the influence of the emitter becomes more important when the cell thickness is reduced, and the influence of the back reflection cannot be completely neglected [7].

Several authors, including Spiegel [10], have highlighted the limits of applicability of the relation. Thus, they showed that this method could be used by neglecting the contributions of the emitter and the space charge region, volume scattering lengths much smaller than the substrate thickness and low recombination velocities but in the case of thin cells and/or scattering length larger than the substrate thickness, the relation did not apply. In order to improve the extraction of the diffusion length by relation, Spiegel [16] replaced the expression for the short circuit current established by [11] and given by the formula:

$$J_{\text{sc}}(\alpha) = \frac{qL_n\alpha(1-R)\phi_0 e^{-\alpha x_j}}{1 + \alpha L_n} \left\{ \frac{D_n \left(e^{-\frac{w}{L_n}} - \alpha L_n e^{-\alpha w} \right) - L_n S_n \left(e^{-\frac{w}{L_n}} - e^{-\alpha w} \right)}{(\alpha L_n - 1) \left[L_n S_n \sinh\left(\frac{w}{L_n}\right) - \cosh\left(\frac{w}{L_n}\right) \right]} + 1 \right\} \quad (4)$$

here x_j is the junction depth and ϕ_0 the photon flux in the expression of the internal spectral response defined by the relation (1).

By positing $x_j = 0$, we can then verify that:

$$IQE(\alpha) = \frac{1 - (\alpha L_{\text{eff}})^{-1}}{1 - (\alpha L_n)^{-2}} \quad (5)$$

This relation allows us to obtain the volume diffusion lengths and the effective diffusion lengths simultaneously. In the case of our study, we used the linear method for the estimation of the scattering lengths in the absorber material for the three types of cells realized. For this purpose, measurements of the quantum yields have been performed on the three types of cells studied here. Figure 4 shows that the graphical representation of $(1/IQE)$ as a function of $(1/\alpha)$ has a linear part for each of the three cells. The slope of this allowed us to estimate the diffusion length. The results obtained are grouped in Table.



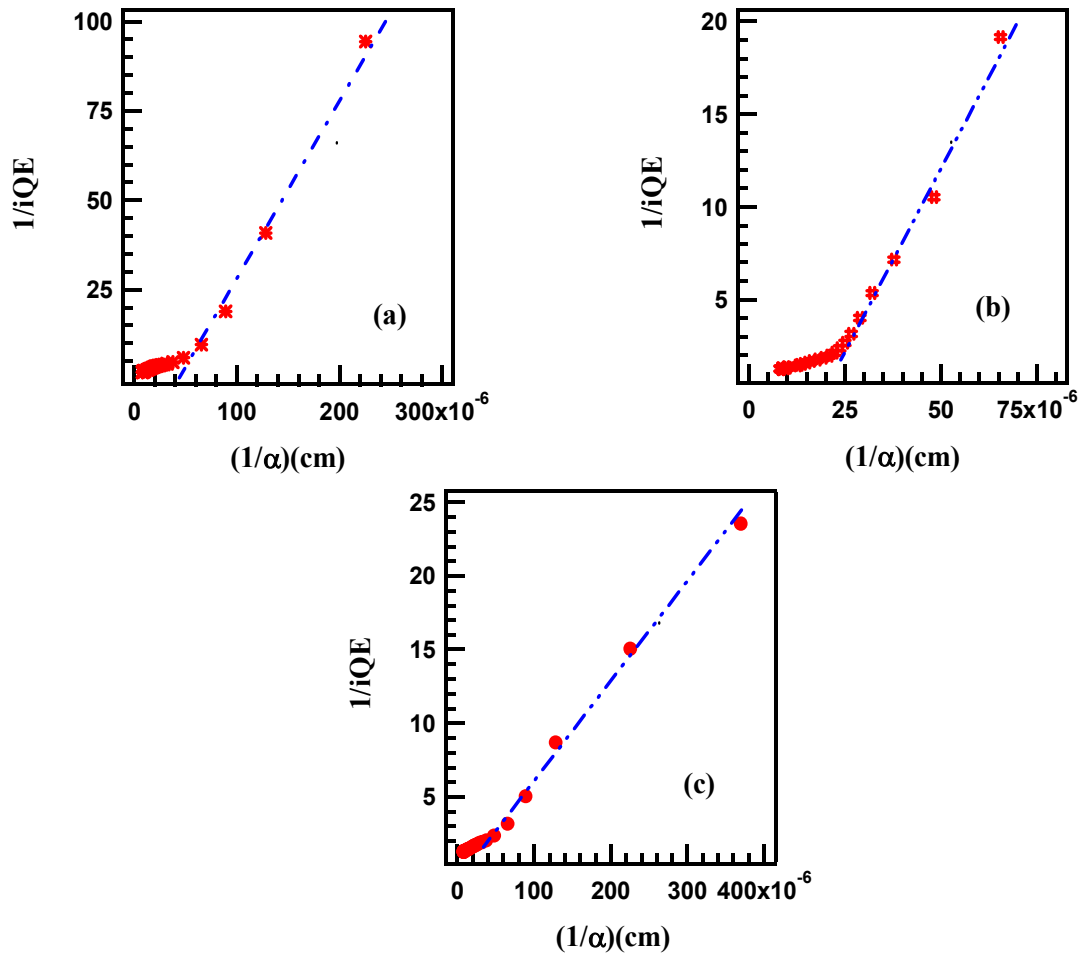


Figure 4: Inverse of quantum yield versus inverse of absorption coefficient for the three types of Mo/CuInSe₂/CdS/ZnO cells. The CIS layer is deposited from a solution containing the buffer. (a) At constant current followed by selenization, (b) At constant current followed by sulfurization, and (c) By pulsed potential from the buffer-containing solution followed by selenization

Table 1: Diffusion length values L_n for CuInSe₂ layers deposited from the solution containing the buffer solution

(a) constant potential deposition followed by selenization, (b) constant potential deposition followed by sulfurization, and (c) pulsed potential deposition from the solution containing the buffer solution followed by selenization.

| (a) | (b) | (c) |
|--------------------------|--------------------------|--------------------------|
| L _n = 0,02 μm | L _n = 0,03 μm | L _n = 0,20 μm |

The extraction of the diffusion length L_n at constant flux is slightly lower. The values obtained by the films (a) and (b) are lower than those obtained for (c) deposited by electrochemical pulsed method.

The values found are well below the thickness of the absorber layers, which is between 2.0 and 2.5 μm. This is one of the characteristics of the linear model.

Conclusion

CuInSe₂ thin films have been electrodeposited onto Mo and Mo-coated glass. We have developed our CIS cell from the solution containing the buffer. The minority carrier diffusion length of the CuInSe₂ was measured using the linear method.

References

- [1]. K. Ramanathan, G. Teeter, J. C. Keane, R. Noufi, *Thin Solid Films*, 480-481 (2008) 499.
- [2]. M. A. Contreras, K. Ramanathan, J. Abushama, F. Hasoon, D. L. Young, B. Egaas, R. Noufi, *Prog. Phot. Volt. Res. Appl.* 13 (2005) 209.
- [3]. P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T. M. Friedlmeier, and M. Powalla, *Phys. Status Solid RRL* 9, No. 1, 28-31 (2015).
- [4]. C. Sene, M. E. Calixto, K. D. Dobson, R. W. Birkmire, *Thin Solid Films* 516 (2008) 2188–2194.
- [5]. M. S. Mané, B. Ndiaye, E. M. Keita, B. Mbow and C. Sène, *International Journal of Engineering Sciences & Research Technology*, 4 (12) December 2015 pp.455-464.
- [6]. B. Ndiaye, C. Mbow, M.S. Mane and C. Sène, *Revue des Energies Renouvelables* Vol. 15 N°4 (2012) 609 – 620.
- [7]. H. Mäckel, A. Cuevas, *Journal of Applied Physics* 98, 08378 (2005).
- [8]. S.N. Qiu, C.X. Qiu, I. Shih, *Applied Surface Science* 92 (1996) 306-310.
- [9]. J. Tousek, S. Dolhov, J. Tuskova, *Solar Energy Materials & Solar Cells* 76 (2003) 205–210.
- [10]. M. Spiegel, B. Fisher, S. Keller, E. Bucher, 28th IEEE Photovoltaic Specialists Conference, 2000, pp. 311-314.
- [11]. J. H. Reynolds and A. Meulenber, *J. Appl. Phys.*, 1974, vol. 45, n° 6, pp. 2582-2592.

