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Theoretical Study of Spectral Responses of Heterojunctions Based on CuInSe₂ and CuInS₂

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Abstract : In this work we study the spectral responses of thin films solar cells of heterojunctions based on CuInSe₂ and CuInS₂. Four-layer structures are studied according to the n⁺n/pp⁺ model. First we consider the structure ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺) where CuInS₂ represent the base and CuInSe₂ the substrate in this model. Secondly we consider the structure ZnO(n⁺)/CdS(n)/CuInSe₂(p)/ CuInS₂(p⁺), for this model CuInSe₂ represent the base and CuInS₂ the substrate. ZnO and CdS are used as window layers in each structure. Using the continuity equation that governs transport of carriers in semiconductor material, models for calculating spectral responses are proposed for heterojunctions type n⁺n/pp⁺ based on CuInSe₂ and CuInS₂. For each structure we have presented the energy band diagram based on the Anderson model [1] and determined the expression of the photocurrent. The theoretical results obtained allow to compare the performances of these two models by optimizing the different parameters of each structure (base thickness, diffusion length, recombination velocity at the interface, etc.) in order to improve the overall efficiency of the collection of carriers.

Keywords : Solar cells, Heterojunctions, CuInSe₂ and CuInS₂, Spectral Responses, base and substrate effects

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1. Introduction

The study of the performances of homojunction based on CuInSe₂ with a medium band gap window layer based on CuInS₂ (in order of 1.57 eV) according to 2-layer models (p/n : Homojunction), 3-layer models (p⁺/p/n : homojunction with window layer, p/n/n⁺ : homojunction deposited on substrate) and to 4-layer models (p⁺/p/n/n⁺ : homojunction with window layer deposited on substrate), showed that a wide band gap window layer would improve the spectral response and the short-circuit photocurrent [2,3].

In this work, we use window layers based on ZnO and CdS. These two materials have wide optical band gaps (in order of 2.35 eV for CdS [4] and 3 eV for ZnO [5]) and crystal lattice parameters compatible with some materials such as CuInSe₂ and CuInS₂ (see Table 1). The ZnO used as a window layer has an optical reflection coefficient less than 0.2 in the spectral range from 1 eV to 3 eV [54]. The CdS layer (called buffer layer) is also a window and allows a good electrical and structural transition between the absorbent layers (CuInSe₂ or CuInS₂) and the ZnO layer.

ZnO and CdS are n-doped [6 - 9] using aluminum (Al) for ZnO and indium (In) for CdS [10]. The structures studied in this work are mainly the n⁺n/pp⁺ model. In order to optimize the efficiency and choose the best performing structure, we consider first the model ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺) where CuInS₂ is used as a base and CuInSe₂ as a substrate. Secondly, we consider the model ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺), for this model CuInSe₂ is used as a base and CuInS₂ as substrate. For the two considered structures, the base and the substrate are different nature materials, we take into account the interface phenomena. Heterostructures are studied in this work.

2. Theory and method

For each structure, we propose a theoretical calculation model allowing to determine the internal quantum efficiency and the short-circuit photocurrent. It is assumed that the optical reflection coefficient is neglected at each interface in the spectral range used. It will also be considered that the space charge region is located only between the n and p regions of each structure and there is no electric field outside this region [2, 3]. Recombination phenomena are also neglected in the space charge region.

In figures 1 a-b, we represent the optical absorption coefficients of the different materials [2, 3, 4, 5]. These values are approximately completed by extrapolation.

The physical parameters of the different materials are listed in Table 1, they are taken from certain experimental values published in the literature [4, 6 - 9, 11 - 16].

Figure 1. Absorption coefficient versus photon energy

(a) CdS, CuInS₂, CuInSe₂ [2, 3, 4] ; (b) ZnO [5]

Table 1. Physical parameters of the materials used [4, 6 - 9, 11 - 16]

Material	E_g (gap)	a (crystal lattice parameter)	c (crystal lattice parameter)	χ (electron affinity)	Doping level (p, n)
CuInSe ₂ (p, n)	0.96 – 1.04 eV	5.78 Å	11.62 Å	4.58 eV	10^{14} - 10^{20} cm ⁻³
CuInS ₂ (p, n)	1.438 – 1.57 eV	5.51 Å	11 Å	4.04 eV	10^{14} - 10^{20} cm ⁻³
CdS (n)	2.35 – 2.42 eV	4.14 Å	6.72 Å	4.4 eV	10^{17} - 10^{20} cm ⁻³
ZnO (n)	3 – 3.3 eV	3.25 Å	5.21 Å	4.5 eV	10^{18} - 10^{20} cm ⁻³

By noting at the interface between two materials 1 and 2 :

$$\Delta E_{c0} = E_{c01} - E_{c02} = -(\chi_1 - \chi_2)$$

$$\Delta E_g = E_{g1} - E_{g2}$$

$$\Delta E_{v0} = E_{v01} - E_{v02} = \Delta E_{c0} - \Delta E_g$$

The variations of the parameters at the different interfaces are given in Table 2 below :

Table 2. Variation of the different physical parameters used at the interface

Interface (1/2)	ΔE_{c0}	ΔE_g	ΔE_{v0}
ZnO/CdS (1)	-0.1 eV	0.65 eV	-0.75 eV
CdS/CuInS ₂ (2)	-0.36 eV	0.78 eV	-1.14 eV
CdS/CuInSe ₂ (3)	0.18 eV	1.31 eV	-1.13 eV
CuInSe ₂ /CuInS ₂ (4)	-0.54 eV	-0.53 eV	-0.01 eV

The diagram of the structure with 4 layers according to the model n⁺ n/p p⁺ is shown in figure 2.

Figure 2 : Diagram of the model $n^+ n / p p^+$

Figure 3 : Energy band diagram of the structure $ZnO(n^+)/CdS(n)/CuInS_2(p)/CuInSe_2(p^+)$

Figure 4 : Energy band diagram of the structure $ZnO(n^+)/CdS(n)/CuInSe_2(p)/CuInS_2(p^+)$

Taking into account tables 1 and 2, and the doping level of the different layers, the energy band diagram for the structure $ZnO(n^+)/CdS(n)/CuInS_2(p)/CuInSe_2(p^+)$ is shown in figure 3. For the structure $ZnO(n^+)/CdS(n)/CuInSe_2(p)/CuInS_2(p^+)$, the energy band diagram is shown in figure 4. The construction of the energy band diagrams is based on the Anderson model [1].

2-1. Calculation of the photocurrent in the frontal area (region 1 and region 2)

In regions 1 and 2 (ZnO and CdS), $0 \leq x \leq x_2$, the photocurrent is mainly due to the holes. The interface effects are characterized by a recombination velocity at the interface noted Sp_2 . We note Sp_1 the recombination velocity at the frontal surface (illuminated side). The continuity equations in regions 1 and 2 are respectively given by the following equations 1 and 2 :

$$\frac{d^2 \Delta p_1}{dx^2} - \frac{\Delta p_1}{L_{p1}^2} = \frac{-\alpha_1 F(1-R)e^{-\alpha_1 x}}{D_{p1}} \quad (1)$$

$$\frac{d^2 \Delta p_2}{dx^2} - \frac{\Delta p_2}{L_{p2}^2} = \frac{-\alpha_2 F(1-R)e^{-\alpha_1 x_1} e^{-\alpha_2 (x-x_1)}}{D_{p2}} \quad (2)$$

$$\text{With :} \quad L_{p1}^2 = D_{p1} \tau_{p1} \quad (3)$$

$$L_{p2}^2 = D_{p2} \tau_{p2} \quad (4)$$

The boundary conditions are given by [2, 3, 17-20] :

$$D_{p1} \left(\frac{d\Delta p_1}{dx} \right) = S_{p1} \Delta p_1 \quad \text{for } x = 0 \quad (5)$$

$$\Delta p_1 = 0 \quad \text{for } x = x_1 \quad (6)$$

$$D_{p2} \frac{d\Delta p_2}{dx} = S_{p2} \Delta p_2 + D_{p1} \frac{d\Delta p_1}{dx} \quad \text{for } x = x_1 \quad (7)$$

$$\Delta p_2 = 0 \quad \text{for } x = x_2 \quad (8)$$

The expression of the holes photocurrent density is given by

$$J_p = -q D_{p2} \left. \frac{d\Delta p_2}{dx} \right|_{x=x_2}, \text{ it is written as :}$$

$$J_p = \frac{q \alpha_2 F (1-R) L_{p2} e^{-\alpha_1 x_1}}{(\alpha_2^2 L_{p2}^2 - 1)} \left\{ \frac{\left(\frac{S_{p2} L_{p2}}{D_{p2}} + \alpha_2 L_{p2} \right)}{\left(\frac{S_{p2} L_{p2}}{D_{p2}} \text{sh} \left(\frac{x_2 - x_1}{L_{p2}} \right) + \text{ch} \left(\frac{x_2 - x_1}{L_{p2}} \right) \right)} - \frac{e^{-\alpha_2 (x_2 - x_1)} \left[\frac{S_{p2} L_{p2}}{D_{p2}} \text{ch} \left(\frac{x_2 - x_1}{L_{p2}} \right) + \text{sh} \left(\frac{x_2 - x_1}{L_{p2}} \right) \right]}{\frac{S_{p2} L_{p2}}{D_{p2}} \text{sh} \left(\frac{x_2 - x_1}{L_{p2}} \right) + \text{ch} \left(\frac{x_2 - x_1}{L_{p2}} \right)} - \alpha_2 L_{p2} e^{-\alpha_2 (x_2 - x_1)}} \right\} + \frac{q \alpha_1 F (1-R) L_{p1}}{(\alpha_1^2 L_{p1}^2 - 1) \left[\frac{S_{p2} L_{p2}}{D_{p2}} \text{sh} \left(\frac{x_2 - x_1}{L_{p2}} \right) + \text{ch} \left(\frac{x_2 - x_1}{L_{p2}} \right) \right]} \times \left\{ \left(\frac{S_{p1} L_{p1}}{D_{p1}} + \alpha_1 L_{p1} \right) - e^{-\alpha_1 x_1} \left[\frac{S_{p1} L_{p1}}{D_{p1}} \text{ch} \left(\frac{x_1}{L_{p1}} \right) + \text{sh} \left(\frac{x_1}{L_{p1}} \right) \right] \right. - \left. \frac{\frac{S_{p1} L_{p1}}{D_{p1}} \text{sh} \left(\frac{x_1}{L_{p1}} \right) + \text{ch} \left(\frac{x_1}{L_{p1}} \right)}{\alpha_1 L_{p1} e^{-\alpha_1 x_1}} \right\} \quad (9)$$

The first term of this expression is the photocurrent density generated by the region 2 itself and the second term is the one generated by the region 1.

2-2. Calculation of the photocurrent in the space charge region (SCR)

In the space charge region the recombinations are neglected, the expression of the resulting photocurrent is given by [17] :

$$J_{SCR} = -qF(1-R)e^{-\alpha_1 x_1} e^{-\alpha_2(x_2-x_1)} \times [e^{-\alpha_2 w_1} - 1] - qF(1-R)e^{-\alpha_1 x_1} e^{-\alpha_2[(x_2+w_1)-x_1]} \times [e^{-\alpha_3 w_2} - 1] \quad (10)$$

2-3. Calculation of the photocurrent of electrons in the rear area (regions 3 and 4: base and substrate)

In regions 3 and 4 (base and substrate: CuInS₂, CuInSe₂), the photocurrent is due to electrons, the continuity equations are respectively given by the following equations (11) and (12) :

$$\frac{d^2 \Delta n_3}{dx^2} - \frac{\Delta n_3}{L_{n3}^2} = \frac{-\alpha_3}{D_{n3}} F(1-R)e^{-\alpha_1 x_1} e^{-\alpha_2[(x_2+w_1)-x_1]} \times e^{\alpha_3(x_2+w_1)} e^{-\alpha_3 x} \quad (11)$$

$$\frac{d^2 \Delta n_4}{dx^2} - \frac{\Delta n_4}{L_{n4}^2} = \frac{-\alpha_4}{D_{n4}} F(1-R)e^{-\alpha_1 x_1} e^{-\alpha_2[(x_2+w_1)-x_1]} \times e^{-\alpha_3[x_3-(x_2+w_1)]} e^{\alpha_4 x_3} e^{-\alpha_4 x} \quad (12)$$

The boundary conditions are given by [17] :

$$\Delta n_3 = 0 \quad \text{for} \quad x = x_2 + w \quad (13)$$

$$D_{n3} \frac{d\Delta n_3}{dx} = -S_{n3} \Delta n_3 + D_{n4} \frac{d\Delta n_4}{dx} \quad \text{for} \quad x = x_3 \quad (14)$$

$$\Delta n_4 = 0 \quad \text{for} \quad x = x_3 \quad (15)$$

$$D_{n4} \frac{d\Delta n_4}{dx} = -S_{n4} \Delta n_4 \quad \text{for} \quad x = H \quad (16)$$

Since the substrate and the base are different materials, the interface phenomena are taken into account and are modeled by a recombination velocity at the interface noted S_{n3} , a parameter which characterizes the state of the interface between the base and the substrate. We note S_{n4} the recombination velocity at the back surface (substrate).

The electrons photocurrent which results from the contribution of regions 3 and 4 (base and substrate) is given by :

$$J_n = qD_{n3} \left. \frac{d\Delta n_3}{dx} \right|_{x=x_2+w}, \text{ it is written as :}$$

$$J_n = -\frac{q \alpha_3 L_{n3} F(1-R) e^{[(\alpha_2 - \alpha_1)x_1]} e^{[(\alpha_3 - \alpha_2)(x_2+w_1)]}}{(\alpha_3^2 L_{n3}^2 - 1)} \times \left[\left(\alpha_3 L_{n3} - \frac{S_{n3} L_{n3}}{D_{n3}} \right) e^{-\alpha_3 x_3} + \frac{\left[\frac{S_{n3} L_{n3}}{D_{n3}} \operatorname{sh} \left(\frac{x_3 - (x_2+w)}{L_{n3}} \right) + \operatorname{ch} \left(\frac{x_3 - (x_2+w)}{L_{n3}} \right) \right]}{e^{-\alpha_3(x_2+w)} \left[\frac{S_{n3} L_{n3}}{D_{n3}} \operatorname{ch} \left(\frac{x_3 - (x_2+w)}{L_{n3}} \right) + \operatorname{sh} \left(\frac{x_3 - (x_2+w)}{L_{n3}} \right) \right]} - \frac{\left[\frac{S_{n3} L_{n3}}{D_{n3}} \operatorname{sh} \left(\frac{x_3 - (x_2+w)}{L_{n3}} \right) + \operatorname{ch} \left(\frac{x_3 - (x_2+w)}{L_{n3}} \right) \right]}{\alpha_3 L_{n3} e^{-\alpha_3(x_2+w)}} \right] - \frac{q \alpha_4 L_{n4} F(1-R) e^{[(\alpha_2 - \alpha_1)x_1]} e^{[(\alpha_3 - \alpha_2)(x_2+w_1)]} e^{[(\alpha_4 - \alpha_3)x_3]}}{(\alpha_4^2 L_{n4}^2 - 1) \left\{ \frac{S_{n3} L_{n3}}{D_{n3}} \operatorname{sh} \left(\frac{x_3 - (x_2+w)}{L_{n3}} \right) + \operatorname{ch} \left(\frac{x_3 - (x_2+w)}{L_{n3}} \right) \right\}} \times \left[\left(\alpha_4 L_{n4} - \frac{S_{n4} L_{n4}}{D_{n4}} \right) e^{-\alpha_4 H} + \frac{\left[\frac{S_{n4} L_{n4}}{D_{n4}} \operatorname{sh} \left(\frac{H-x_3}{L_{n4}} \right) + \operatorname{ch} \left(\frac{H-x_3}{L_{n4}} \right) \right]}{e^{-\alpha_4 x_3} \left[\frac{S_{n4} L_{n4}}{D_{n4}} \operatorname{ch} \left(\frac{H-x_3}{L_{n4}} \right) + \operatorname{sh} \left(\frac{H-x_3}{L_{n4}} \right) \right]} - \alpha_4 L_{n4} e^{-\alpha_4 x_3} \right] \quad (17)$$

The first term of this expression is the photocurrent density generated by the region 3 (base) itself and the second term is the one generated by the region 4 (substrate).

2-4. Calculation of the global photocurrent

The global (total) photocurrent is due by the contribution of the different areas of the structure, it is given by :

$$J_{ph} = J_p + J_{SCR} + J_n \quad (18)$$

The internal quantum efficiency (or spectral response) is given by [17, 21] :

$$RS = \left| \frac{J_{ph}}{J_0} \right| \quad (19)$$

$$\text{With } J_0 = qF(1-R)$$

By noting :

$$H_1 = x_1 ; H_2 = x_2 - x_1 ; w = (x_2 + w) - x_2 ;$$

$$H_3 = x_3 - (x_2 + w) ; H_4 = H - x_3 ;$$

$$H = H_1 + H_2 + H_3 + H_4 + w ; w = w_1 + w_2$$

With H_i the thickness of region i and H the thickness of the structure.

w is the thickness of the space charge region, w_1 is the thickness of the first area of the space charge region and w_2 is the thickness of the second area of the space charge region.

The photocurrent expressions established in equations 9, 10 and 17, can be respectively written as equations 20, 21 and 22. They are given as function as the thickness H_i of region i .

$$J_p = \frac{q\alpha_2 F(1-R)L_{p2}e^{-\alpha_1 H_1}}{(\alpha_2^2 L_{p2}^2 - 1)} \left\{ \frac{\left(\frac{S_{p2}L_{p2}}{D_{p2}} + \alpha_2 L_{p2} \right)}{\left(\frac{S_{p2}L_{p2}}{D_{p2}} \sinh\left(\frac{H_2}{L_{p2}}\right) + \cosh\left(\frac{H_2}{L_{p2}}\right) \right)} - \frac{e^{-\alpha_2 H_2} \left[\frac{S_{p2}L_{p2}}{D_{p2}} \cosh\left(\frac{H_2}{L_{p2}}\right) + \sinh\left(\frac{H_2}{L_{p2}}\right) \right]}{\frac{S_{p2}L_{p2}}{D_{p2}} \sinh\left(\frac{H_2}{L_{p2}}\right) + \cosh\left(\frac{H_2}{L_{p2}}\right)} - \alpha_2 L_{p2} e^{-\alpha_2 H_2}} \right\} + \frac{q\alpha_1 F(1-R)L_{p1}}{(\alpha_1^2 L_{p1}^2 - 1) \left[\frac{S_{p2}L_{p2}}{D_{p2}} \sinh\left(\frac{H_2}{L_{p2}}\right) + \cosh\left(\frac{H_2}{L_{p2}}\right) \right]} \times \left\{ \frac{\left(\frac{S_{p1}L_{p1}}{D_{p1}} + \alpha_1 L_{p1} \right) - e^{-\alpha_1 H_1} \left[\frac{S_{p1}L_{p1}}{D_{p1}} \cosh\left(\frac{H_1}{L_{p1}}\right) + \sinh\left(\frac{H_1}{L_{p1}}\right) \right]}{\frac{S_{p1}L_{p1}}{D_{p1}} \sinh\left(\frac{H_1}{L_{p1}}\right) + \cosh\left(\frac{H_1}{L_{p1}}\right)} - \alpha_1 L_{p1} e^{-\alpha_1 H_1}} \right\} \quad (20)$$

$$J_{SCR} = -qF(1-R)e^{-\alpha_1 H_1} e^{-\alpha_2 H_2} [e^{-\alpha_2 W_1} e^{-\alpha_3 W_2} - 1] \quad (21)$$

$$J_n = -\frac{q\alpha_3 L_{n3} F(1-R) e^{[(\alpha_2 - \alpha_1)H_1]} e^{[(\alpha_3 - \alpha_2)(H_1 + H_2 + W_1)]}}{(\alpha_3^2 L_{n3}^2 - 1)} \times \left[\frac{\left(\alpha_3 L_{n3} - \frac{S_{n3}L_{n3}}{D_{n3}} \right) e^{-\alpha_3 (H-H_4)}}{\frac{S_{n3}L_{n3}}{D_{n3}} \sinh\left(\frac{H_3}{L_{n3}}\right) + \cosh\left(\frac{H_3}{L_{n3}}\right)} + \frac{e^{-\alpha_3 (H_1 + H_2 + W)} \left[\frac{S_{n3}L_{n3}}{D_{n3}} \cosh\left(\frac{H_3}{L_{n3}}\right) + \sinh\left(\frac{H_3}{L_{n3}}\right) \right]}{\frac{S_{n3}L_{n3}}{D_{n3}} \sinh\left(\frac{H_3}{L_{n3}}\right) + \cosh\left(\frac{H_3}{L_{n3}}\right)} - \alpha_3 L_{n3} e^{-\alpha_3 (H_1 + H_2 + W)} \right] - q\alpha_4 L_{n4} F(1-R) \times \frac{e^{[(\alpha_2 - \alpha_1)H_1]} e^{[(\alpha_3 - \alpha_2)(H_1 + H_2 + W_1)]} e^{[(\alpha_4 - \alpha_3)(H-H_4)]}}{(\alpha_4^2 L_{n4}^2 - 1) \left\{ \frac{S_{n3}L_{n3}}{D_{n3}} \sinh\left(\frac{H_3}{L_{n3}}\right) + \cosh\left(\frac{H_3}{L_{n3}}\right) \right\}} \times \left[\frac{\left(\alpha_4 L_{n4} - \frac{S_{n4}L_{n4}}{D_{n4}} \right) e^{-\alpha_4 H}}{\frac{S_{n4}L_{n4}}{D_{n4}} \sinh\left(\frac{H_4}{L_{n4}}\right) + \cosh\left(\frac{H_4}{L_{n4}}\right)} + \frac{e^{-\alpha_4 (H-H_4)} \left[\frac{S_{n4}L_{n4}}{D_{n4}} \cosh\left(\frac{H_4}{L_{n4}}\right) + \sinh\left(\frac{H_4}{L_{n4}}\right) \right]}{\frac{S_{n4}L_{n4}}{D_{n4}} \sinh\left(\frac{H_4}{L_{n4}}\right) + \cosh\left(\frac{H_4}{L_{n4}}\right)} - \alpha_4 L_{n4} e^{-\alpha_4 (H-H_4)} \right] \quad (22)$$

3. Results and discussion

3-1. Model ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺)

3-1-1. Effect of the base thickness (CuInS₂)

Figure 5. Global (total) internal quantum efficiency vs. photon energy for different thicknesses of the base model ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺)

($s_{p1}=2 \times 10^7 \text{ cm.s}^{-1}$; $H_1=0.3 \mu\text{m}$; $L_{p1}=0.4 \mu\text{m}$; $s_{p2}=2 \times 10^4 \text{ cm.s}^{-1}$; $H_2=0.1 \mu\text{m}$; $L_{p2}=0.5 \mu\text{m}$; $s_{n3}=2 \times 10^5 \text{ cm.s}^{-1}$; $L_{n3}=3 \mu\text{m}$ (a) and $6 \mu\text{m}$ (b, c and d); $s_{n4}=2 \times 10^7 \text{ cm.s}^{-1}$; $L_{n4}=1 \mu\text{m}$; $W_1=0.02 \mu\text{m}$; $W_2=0.08 \mu\text{m}$; $W=0.1 \mu\text{m}$; $H=100 \mu\text{m}$; $D_{p1}=0.51 \text{ cm}^2.\text{s}^{-1}$; $D_{p2}=0.64 \text{ cm}^2.\text{s}^{-1}$; $D_{n3}=5.13 \text{ cm}^2.\text{s}^{-1}$; $D_{n4}=10.27 \text{ cm}^2.\text{s}^{-1}$)

In Figure 5, we represent the internal quantum efficiency versus photon energy for different thicknesses of the base. The diffusion length L_{n3} is fixed at $3 \mu\text{m}$. In the energy range from 1.04 eV to 1.57 eV (part E₁), the internal quantum efficiency is only due to the absorption of photons by the substrate (CuInSe₂). We note that it increases when we reduce the thickness of the base.

Figure 6. Internal quantum efficiency vs. photon energy and base thickness H_3 model ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺)

Above 1.57 eV corresponding to the absorption of CuInS₂ (part E₂) is the absorption of the base and a part of the space charge region ($x_2 + w_1 \leq x \leq x_2 + w_1 + w_2$), the evolution of the internal quantum efficiency changes. We note that the absorption of the base and the space charge region (CuInS₂) increases considerably the spectral response for photon energies ranging from 1.57 eV to 2.4 eV (part E₂). This efficiency ranges from 65% to 100% for a base thickness $H_3 = 0.1 \mu\text{m}$. In contrast to the behavior of the substrate, the contribution of the base increases when we increase its thickness H_3 .

In figure 6, we represent the internal quantum efficiency versus photon energy and base thickness H_3 . We show in three dimensions the graphs studied in figure 5, the diffusion length in the base is fixed at $L_{n3} = 3 \mu\text{m}$ and the recombination velocity at the base-substrate interface at $S_{n3} = 2.10^5 \text{ cm.s}^{-1}$.

3-1-2. Diffusion length effect in the base and the substrate (CuInS₂ and CuInSe₂)

In figures 7-a, 7-b and 7-c, we highlight the effect of the diffusion length in the base L_{n3} to the internal quantum efficiency. The base thickness is fixed respectively at 0.1 μm , 0.5 μm and 1 μm .

We note that the effect of the diffusion length depends on the thickness of the base. The efficiency increases with the diffusion length when $H_3 > L_{n3}$, it is independent of the diffusion length when $H_3 < L_{n3}$ (see part E₁ and E₂). We also note that despite a high value of the diffusion length ($L_{n3} = 10 \mu\text{m}$), the contribution of the substrate (part E₁ : 1.04 eV < E < 1.57 eV) is lower for a base thickness greater than 0.5 μm , it does not exceed 20% for $H_3 = 1 \mu\text{m}$. This low contribution of the substrate may be due to carrier recombinations at the base-substrate interface characterized by the presence of spike effect in the conduction and valence bands. The recombination velocity at the interface is fixed at $S_{n3} = 2.10^5 \text{ cm.s}^{-1}$. Another effect which can cause this low contribution of the substrate for H_3 values greater than 1 μm , is the decrease of the diffusion current by increasing the base thickness; this phenomenon can be highlighted by representing the densities of minority carriers (electrons) in the base and the substrate.

The absorption of photons by the base and the space charge region for radiation energies $1.57 \text{ eV} < E < 2.4 \text{ eV}$ (part E₂), considerably increases the internal quantum efficiency, it varies between 20% and 100% when $H_3 < L_{n3}$.

In figure 7-d, we highlight the effect of the diffusion length in the substrate L_{n4} . In the base, the thickness H_3 is fixed at 1 μm , the diffusion length L_{n3} at 6 μm and the recombination velocity at the base-substrate interface S_{n3} always at 2.10^5 cm.s^{-1} . We note that, despite the high values of the diffusion length L_{n4} which ranging between 1 μm and 10 μm , the substrate contribution is controlled by the base effects (base thickness and state of the base-substrate interface). Its contribution to the internal quantum efficiency does not always exceed 20% for base thickness H_3 equal to (or greater than) 1 μm (part E₁ : 1.04 eV < E < 1.57 eV).

Figure 7. Internal quantum efficiency vs. photon energy for different diffusion lengths of electrons in the base (figures a, b and c) and in the substrate (figure d) : (a) $H_3 = 0.1 \mu\text{m}$; (b) $H_3 = 0.5 \mu\text{m}$; (c) $H_3 = 1 \mu\text{m}$; (d) $H_3 = 1 \mu\text{m}$ and $L_{n3} = 6 \mu\text{m}$ model $\text{ZnO}(n^+)/\text{CdS}(n)/\text{CuInS}_2(p)/\text{CuInSe}_2(p^+)$

($s_{p1} = 2 \times 10^7 \text{ cm.s}^{-1}$; $H_1 = 0.3 \mu\text{m}$; $L_{p1} = 0.4 \mu\text{m}$; $s_{p2} = 2 \times 10^4 \text{ cm.s}^{-1}$; $H_2 = 0.1 \mu\text{m}$; $L_{p2} = 0.5 \mu\text{m}$; $s_{n3} = 2 \times 10^5 \text{ cm.s}^{-1}$; $L_{n3} = 6 \mu\text{m}$ (d); $H_3 = 1 \mu\text{m}$ (d); $s_{n4} = 2 \times 10^7 \text{ cm.s}^{-1}$; $L_{n4} = 1 \mu\text{m}$ (a, b and c); $W_1 = 0.02 \mu\text{m}$; $W_2 = 0.08 \mu\text{m}$; $W = 0.1 \mu\text{m}$; $H = 100 \mu\text{m}$; $D_{p1} = 0.51 \text{ cm}^2.\text{s}^{-1}$; $D_{p2} = 0.64 \text{ cm}^2.\text{s}^{-1}$; $D_{n3} = 5.13 \text{ cm}^2.\text{s}^{-1}$; $D_{n4} = 10.27 \text{ cm}^2.\text{s}^{-1}$)

A three-dimensional representation of the different results obtained in figures 7, is shown in figures 8 and 9. We simultaneously show the evolution of the internal quantum efficiency versus photon energy and the electron diffusion length in the base (figure 8), and in the substrate (figure 9).

The base thickness is fixed at $H_3 = 1 \mu\text{m}$ and the recombination velocity at the base-substrate interface at $\text{Sn}_3 = 2 \cdot 10^5 \text{ cm.s}^{-1}$.

Figure 8. Internal quantum efficiency vs. photon energy and the electron diffusion length in the base L_{n3}
model $\text{ZnO}(n^+)/\text{CdS}(n)/\text{CuInS}_2(p)/\text{CuInSe}_2(p^+)$

Figure 9. Internal quantum efficiency vs. photon energy and the electron diffusion length in the substrate L_{n4}
model $\text{ZnO}(n^+)/\text{CdS}(n)/\text{CuInS}_2(p)/\text{CuInSe}_2(p^+)$

3-1-3. Effect of recombination velocity at the base-substrate interface (CuInS₂/CuInSe₂)

In figures 10-a, 10-b, 10-c and 10-d, we represent the internal quantum efficiency versus photon energy for different values of the recombination velocity at the base-substrate interface Sn_3 . The diffusion length L_{n3} is fixed at $6 \mu\text{m}$.

We always note that the substrate contribution strongly depends on the interface effects characterized by Sn_3 and the base thickness H_3 :

- For low recombination velocities ($\text{Sn}_3 < 2 \cdot 10^3 \text{ cm.s}^{-1}$): the substrate contribution (part E_1 : $1.04 \text{ eV} < E < 1.57 \text{ eV}$) exceeds 90% for thin base thicknesses ($H_3 < 1 \mu\text{m}$) (figures 10-a and 10-b) and the global internal quantum efficiency is between 80% and 100% in the range of non-absorption of the window layers (part E_1 and E_2 : $E < 2.5 \text{ eV}$). For larger base thicknesses ranging between $1 \mu\text{m}$ and $3 \mu\text{m}$ (figure

10-c and 10-d), the substrate contribution (part E_1 : $1.04 \text{ eV} < E < 1.57 \text{ eV}$) becomes less than 80%, and the global internal quantum efficiency is between 70% and 100% for $E < 2.5 \text{ eV}$ (part E_1 and E_2).

Figure 10. Internal quantum efficiency evolution versus photon energy for different values of the recombination velocity at the base-substrate interface : (a) $H_3 = 0.2 \mu\text{m}$; (b) $H_3 = 1 \mu\text{m}$; (c) $H_3 = 3 \mu\text{m}$
model $\text{ZnO}(n^+)/\text{CdS}(n)/\text{CuInS}_2(p)/\text{CuInSe}_2(p^+)$

($s_{p1} = 2 \times 10^7 \text{ cm.s}^{-1}$; $H_1 = 0.3 \mu\text{m}$; $L_{p1} = 0.4 \mu\text{m}$; $s_{p2} = 2 \times 10^4 \text{ cm.s}^{-1}$; $H_2 = 0.1 \mu\text{m}$; $L_{p2} = 0.5 \mu\text{m}$; $H_3 = 1 \mu\text{m}$ (d); $L_{n3} = 6 \mu\text{m}$ (a, b and c) and $3 \mu\text{m}$ (d); $s_{n4} = 2 \times 10^7 \text{ cm.s}^{-1}$; $L_{n4} = 1 \mu\text{m}$; $W_1 = 0.02 \mu\text{m}$; $W_2 = 0.08 \mu\text{m}$; $W = 0.1 \mu\text{m}$; $H = 100 \mu\text{m}$; $D_{p1} = 0.51 \text{ cm}^2.\text{s}^{-1}$; $D_{p2} = 0.64 \text{ cm}^2.\text{s}^{-1}$; $D_{n3} = 5.13 \text{ cm}^2.\text{s}^{-1}$; $D_{n4} = 10.27 \text{ cm}^2.\text{s}^{-1}$)

- For more elevated recombination velocities at the interface Sn_3 ($2 \cdot 10^4 \text{ cm.s}^{-1} < \text{Sn}_3 < 2 \cdot 10^5 \text{ cm.s}^{-1}$), the quantum internal efficiency decreases and ranges between 20% and 100% for $H_3 < 1 \mu\text{m}$ (figures 10-a and 10-b) and between 5% and 100% for $1 \mu\text{m} < H_3 < 3 \mu\text{m}$ (figure 10-c). The high values of the recombination velocity ($\text{Sn}_3 > 2 \cdot 10^6 \text{ cm.s}^{-1}$) considerably reduce the substrate contribution (part E_1 : $1.04 \text{ eV} < E < 1.57 \text{ eV}$) which becomes less than 5% for $H_3 < 3 \mu\text{m}$. The photon absorption by the base and the space charge zone (part E_2) increases the efficiency between 95% and 100% for radiation energy ranging

between 1.57 and 2.4 eV.

Therefore, we note that, increasing the base thickness H_3 reduces the substrate contribution even if the recombination velocity at the interface is weak ($S_{n3} < 2.10^3 \text{ cm.s}^{-1}$) and the diffusion length in the base is sufficient or great ($L_{n3} > H_3$).

On each figure, the internal quantum efficiency decreases slightly for photon energy neighboring 2.4 eV, corresponding to the CdS absorption (region 2 : part E_3). We also note that, the spectral response no longer depends on the base thickness H_3 above 2.4 eV, which means that all the incident photons are absorbed by the region 2 (CdS) and the space charge region (CdS/CuInS₂). A second drastic decrease in the internal quantum efficiency is observed above 3 eV (part E_4), which corresponds to the photon absorption by ZnO (Frontal layer).

Figure 11. Three-dimensional representation of the internal quantum efficiency vs. photon energy and the recombination velocity at the base-substrate interface S_{n3} : figures (a) and (b) are identical only the view angles differ

model $\text{ZnO}(n^+)/\text{CdS}(n)/\text{CuInS}_2(p)/\text{CuInSe}_2(p^+)$

Figures 11 a-b show the internal quantum efficiency evolution versus photon energy and recombination velocity at the base-substrate interface, we represent in three dimensions the graphs studied in figures 10. The thickness of the base H_3 is fixed at 1 μm and the diffusion length L_{n3} at 3 μm .

3-1-4. Contribution of the different regions of the structure to the internal quantum efficiency

Figure 12. Internal quantum efficiency evolution versus photon energy : contribution of the different regions of the structure for different values of the recombination velocity at the base-substrate interface S_{n3}

(a) $H_3 = 1 \mu\text{m}$ and $S_{n3} = 2.10^3 \text{ cm.s}^{-1}$; (b) $H_3 = 1 \mu\text{m}$ and $S_{n3} = 2.10^5 \text{ cm.s}^{-1}$; (c) $H_3 = 1 \mu\text{m}$ and $S_{n3} = 2.10^7 \text{ cm.s}^{-1}$

model $\text{ZnO}(n^+)/\text{CdS}(n)/\text{CuInS}_2(p)/\text{CuInSe}_2(p^+)$

($s_{p1} = 2 \times 10^7 \text{ cm.s}^{-1}$; $H_1 = 0.3 \mu\text{m}$; $L_{p1} = 0.4 \mu\text{m}$; $s_{p2} = 2 \times 10^4 \text{ cm.s}^{-1}$; $H_2 = 0.1 \mu\text{m}$; $L_{p2} = 0.5 \mu\text{m}$; $H_3 = 1 \mu\text{m}$; $L_{n3} = 3 \mu\text{m}$; $s_{n4} = 2 \times 10^7 \text{ cm.s}^{-1}$; $L_{n4} = 1 \mu\text{m}$; $W_1 = 0.02 \mu\text{m}$; $W_2 = 0.08 \mu\text{m}$; $W = 0.1 \mu\text{m}$; $H = 100 \mu\text{m}$; $D_{p1} = 0.51 \text{ cm}^2.\text{s}^{-1}$; $D_{p2} = 0.64 \text{ cm}^2.\text{s}^{-1}$; $D_{n3} = 5.13 \text{ cm}^2.\text{s}^{-1}$; $D_{n4} = 10.27 \text{ cm}^2.\text{s}^{-1}$)

In figures 12-a, 12-b and 12-c, we represent the contribution of each region to the internal quantum efficiency versus the radiation energy, for different values of the recombination velocity at the base-substrate interface Sn_3 . The base thickness is fixed at $H_3 = 1 \mu\text{m}$ and the diffusion length at $Ln_3 = 3 \mu\text{m}$ for each case.

By fixing the recombination velocity Sn_3 at 2.10^3 cm.s^{-1} , characterizing low carrier losses at the base-substrate interface, figure 12-a shows that the contributions of the substrate (region 4 : part E_1) and the base (region 3: part E_2) are very important, their maximum values exceed 80% and 65% respectively.

For $Sn_3 = 2.10^5 \text{ cm.s}^{-1}$, the contribution of each region is shown in Figure 12-b. Many carriers generated in the substrate (region 4 : part E_1) are lost and the substrate contribution is less than 20%. These losses are caused by the increase of the recombination velocity at the interface and are higher when the base thickness is great.

In Figure 12-c, losses are assumed high at the interface ($Sn_3 = 2.10^7 \text{ cm.s}^{-1}$), the efficiency becomes practically zero from 1.04 eV to 1.57 eV (substrate absorption : part E_1), all the carriers (electrons) generated in the substrate are lost by recombination phenomenon at the base-substrate interface, the efficiency depends only on the base and space charge region absorptions (part E_2).

The contribution of the space charge region ($E > 1.57 \text{ eV}$: part E_2) is important, it does not depend on the recombination velocity at the base-substrate interface and the base thickness. Its maximum contribution is in order of 90% for photon energy neighboring 2.3 eV.

Absorption of the frontal layers (CdS and ZnO) above 2.4 eV (part E_3 and part E_4) reduces the overall efficiency, it is due to carrier losses by recombination phenomenon at the frontal surface ($Sp_1 = 2.10^7 \text{ cm.s}^{-1}$) and at the ZnO/CdS interface ($Sp_2 = 2.10^4 \text{ cm.s}^{-1}$).

3-2. Model ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺)

3-2-1. Effect of the base thickness (CuInSe₂) on the internal quantum efficiency

In figure 13-a, we represent the internal quantum efficiency versus photon energy for different thicknesses of the base (CuInSe₂). We note that the internal quantum efficiency is important with a low diffusion length in the base ($Ln_3 = 0.3 \mu\text{m}$), it is practically equal to 100% for photon energy ranging between 2 eV and 2.4 eV (part E'_2). This efficiency decreases for Radiation energy greater than 2.4 eV, this decrease is due to the photon absorption by CdS and ZnO (regions 1 and 2).

For a diffusion length $Ln_3 = 3 \mu\text{m}$ (Figure 13-b), we note that the spectral response becomes higher and wider compared to the previous structure. The internal quantum efficiency is close to 100% for photon energy ranging between 1.5 eV to 2.4 eV (part E'_2) when $H_3 \geq 1 \mu\text{m}$. This is explained by the fact that the photons are practically all absorbed by the space

charge region (CdS ($0.02 \mu\text{m}$) / CuInSe₂ ($0.08 \mu\text{m}$)) and on a thin thickness of the base. The base is formed by CuInSe₂ layer, the energy band gap of this material is smaller than that of the substrate formed by CuInS₂ layer.

Figure 13. Internal quantum efficiency evolution vs. photon energy for different thicknesses of the base (region 3) : (a) $Ln_3 = 0.3 \mu\text{m}$; (b) $Ln_3 = 3 \mu\text{m}$

Model ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺)

($sp_1 = 2 \times 10^7 \text{ cm.s}^{-1}$; $H_1 = 0.3 \mu\text{m}$; $Lp_1 = 0.4 \mu\text{m}$; $sp_2 = 2 \times 10^4 \text{ cm.s}^{-1}$; $H_2 = 0.1 \mu\text{m}$; $Lp_2 = 0.5 \mu\text{m}$; $sn_3 = 2 \times 10^3 \text{ cm.s}^{-1}$; $sn_4 = 2 \times 10^7 \text{ cm.s}^{-1}$; $Ln_4 = 1 \mu\text{m}$; $W_1 = 0.02 \mu\text{m}$; $W_2 = 0.08 \mu\text{m}$; $W = 0.1 \mu\text{m}$; $H = 100 \mu\text{m}$; $Dp_1 = 0.51 \text{ cm}^2.\text{s}^{-1}$; $Dp_2 = 0.64 \text{ cm}^2.\text{s}^{-1}$; $Dn_3 = 10.27 \text{ cm}^2.\text{s}^{-1}$; $Dn_4 = 5.13 \text{ cm}^2.\text{s}^{-1}$)

Figure 14. Internal quantum efficiency vs. photon energy and base thickness H_3

Model ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺)

Therefore CuInSe₂ layer (base and space charge region) with its high photon absorption coefficient, absorbs practically all photons having energy ranging between 1.04 eV (gap of

CuInSe₂) and 2.4 eV (gap of CdS). The photons do not reach the substrate which starts to absorb above 1.57 eV (gap of CuInS₂).

The graphs studied in figures 13 are represented in three dimensions in figure 14. We show the internal quantum efficiency evolution versus photon energy and base thickness H_3 simultaneously. The electron diffusion length in the base is fixed at 3 μm and the recombination velocity at the base-substrate interface at $S_{n3} = 2 \cdot 10^3 \text{ cm.s}^{-1}$.

3-2-2. Diffusion length effect in the base (CuInSe₂)

Figure 15 shows the internal quantum efficiency evolution versus different values of the electron diffusion length in the base L_{n3} . In Figures 15-a and 15-b, the base thickness is fixed respectively at 1 μm and at 3 μm , the diffusion length ranging from 0.3 μm to 10 μm . The recombination velocity at the base-substrate interface is set at $S_{n3} = 2 \cdot 10^3 \text{ cm.s}^{-1}$ (no spike effect)

Figure 15. Internal quantum efficiency evolution vs. photon energy for different diffusion lengths of electrons in the base : (a) $H_3 = 1 \mu\text{m}$; (b) $H_3 = 3 \mu\text{m}$.

model $\text{ZnO}(n^+)/\text{CdS}(n)/\text{CuInSe}_2(p)/\text{CuInS}_2(p^+)$

$(s_{p1}=2 \times 10^7 \text{ cm.s}^{-1}; H_1=0.3 \mu\text{m}; L_{p1}=0.4 \mu\text{m}; s_{p2}=2 \times 10^4 \text{ cm.s}^{-1}; H_2=0.1 \mu\text{m}; L_{p2}=0.5 \mu\text{m}; s_{n3}=2 \times 10^3 \text{ cm.s}^{-1}; H_3=1 \mu\text{m} \text{ (a) and } 3 \mu\text{m} \text{ (b)}; s_{n4}=2 \times 10^7 \text{ cm.s}^{-1}; L_{n4}=1 \mu\text{m}; W_1=0.02 \mu\text{m}; W_2=0.08 \mu\text{m}; W=0.1 \mu\text{m}; H=100 \mu\text{m}; D_{p1}=0.51 \text{ cm}^2.\text{s}^{-1}; D_{p2}=0.64 \text{ cm}^2.\text{s}^{-1}; D_{n3}=10.27 \text{ cm}^2.\text{s}^{-1}; D_{n4}=5.13 \text{ cm}^2.\text{s}^{-1})$

We note that, for photon energy ranging between 1.04 eV and 2 eV (part E'_1), the efficiency increases with the diffusion length and becomes no dependent on it when $L_{n3} > H_3$. In this energy range (part E'_1 : 1.04 eV $< E < 2$ eV) the photons

reach the base. For photon energy ranging between 2 eV and 2.5 eV (part E'_2) the quantum internal efficiency is no dependent on the diffusion length and is almost 100%. In this energy range (part E'_2 : 2 eV $< E < 2.5$ eV) all carriers are generated in the space charge region and are collected because of the high electric field which exists in this area. In fact, the thickness of the CuInSe₂ layer in the space charge region is fixed at 0.08 μm , this thickness is sufficient to absorb all the photons above 2 eV because of the high absorption coefficient of this material in this energy range (see Figure 1-a). The drastic decrease of efficiency above 2.5 eV (parts E'_3 et E'_4) is due to the photon absorption by the frontal layers, CdS and ZnO (regions 1 and 2).

In figure 16, we simultaneously represent the quantum internal efficiency evolution versus photon energy and the diffusion length. This is the 3-dimensional representation of figures 15. The base thickness is fixed at $H_3 = 1 \mu\text{m}$ and the recombination velocity at the base-substrate interface at $S_{n3} = 2 \cdot 10^3 \text{ cm.s}^{-1}$.

Figure 16. Internal quantum efficiency evolution vs. photon energy and the electron diffusion length in the base L_{n3} : figures (a) and (b) are identical only the view angles differ

Model $\text{ZnO}(n^+)/\text{CdS}(n)/\text{CuInSe}_2(p)/\text{CuInS}_2(p^+)$

3-2-3. Effect of the recombination velocity at the base-substrate interface (CuInSe₂-CuInS₂) to the internal quantum efficiency

Figure 17. Internal quantum efficiency evolution versus photon energy : contribution of the different regions of the structure

(a) $H_3 = 0.3 \mu\text{m}$ and $Sn_3 = 2.10^3 \text{ cm.s}^{-1}$; (b) $H_3 = 0.3 \mu\text{m}$ and $Sn_3 = 2.10^7 \text{ cm.s}^{-1}$; (c) $H_3 = 3 \mu\text{m}$ and $Sn_3 = 2.10^3 \text{ cm.s}^{-1}$; (d) $H_3 = 3 \mu\text{m}$ and $Sn_3 = 2.10^7 \text{ cm.s}^{-1}$

Model ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺)

($s_{p1} = 2 \times 10^7 \text{ cm.s}^{-1}$; $H_1 = 0.3 \mu\text{m}$; $L_{p1} = 0.4 \mu\text{m}$; $s_{p2} = 2 \times 10^4 \text{ cm.s}^{-1}$; $H_2 = 0.1 \mu\text{m}$; $L_{p2} = 0.5 \mu\text{m}$; $L_{n3} = 3 \mu\text{m}$; $s_{n4} = 2 \times 10^7 \text{ cm.s}^{-1}$; $L_{n4} = 1 \mu\text{m}$; $W_1 = 0.02 \mu\text{m}$; $W_2 = 0.08 \mu\text{m}$; $W = 0.1 \mu\text{m}$; $H = 100 \mu\text{m}$; $D_{p1} = 0.51 \text{ cm}^2.\text{s}^{-1}$; $D_{p2} = 0.64 \text{ cm}^2.\text{s}^{-1}$; $D_{n3} = 10.27 \text{ cm}^2.\text{s}^{-1}$; $D_{n4} = 5.13 \text{ cm}^2.\text{s}^{-1}$)

Figure 17 shows the contribution of the different regions to the global efficiency versus photon energy, the effect of the recombination velocity at the base-substrate interface is highlighted.

Since the incident photons do not reach practically the substrate, the effect of the recombination velocity only affects the base behavior. We note that, this effect becomes more important for thin thicknesses of the base as we can see with $H_3 = 0.3 \mu\text{m}$ in Figures 17-a and 17-b where the recombination velocities are respectively fixed at 2.10^3 cm.s^{-1} and 2.10^7 cm.s^{-1} .

An increase of the base thickness reduces the recombination velocity influence at the interface and greatly enhances the base contribution to the internal quantum efficiency. This effect is illustrated in figures 17-c and 17-d where $H_3 = 3 \mu\text{m}$, Sn_3 is fixed at 2.10^3 cm.s^{-1} in figure 17-c and at 2.10^7 cm.s^{-1} in figure 17-d. The diffusion length is fixed at $L_{n3} = 3 \mu\text{m}$.

We also note a high contribution of the space charge region to the spectral response compared to the other regions. This important contribution of the space charge region to the efficiency is due to the widening of the CuInSe₂ thickness in this region, it is fixed at $0.08 \mu\text{m}$.

3-3. Comparative study of the behavior of the two structures considered (n⁺n/pp⁺)

Figures 18 a-f represent the comparison of the spectral responses of the two considered structures ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺) and ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺).

The base thickness is fixed respectively at $0.2 \mu\text{m}$ (thin thickness, figures 18-a and 18-b, $1 \mu\text{m}$ (figures 18-c and 18-d) and $3 \mu\text{m}$ (wide thickness, figures 18-e and 18-f). For each thickness, two recombination velocities at the base-substrate interface is considered, 2.10^3 cm.s^{-1} for low recombination losses (figures 18-a, 18-c, 18-e) and $Sn_3 = 2.10^5 \text{ cm.s}^{-1}$ for more recombination losses (figures 18-b, 18-d, 18-f). For each case the diffusion length is fixed at $L_{n3} = 3 \mu\text{m}$.

- For the model ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺) where the materials are arranged by decreasing energy band gap, the quantum internal efficiency depends on the responses of the different layers of the structure. Since the spectral response begins with the photon absorption by the smaller energy band gap materials, the back layers absorb at first incident photons. The curves of the internal quantum efficiency show that, the substrate response's (CuInS₂) strongly depends on the recombination velocity at the base - substrate interface and the diffusion length of minority carriers in the base and substrate layers. The diffusion length must be greater than the base thickness's in order that carriers generated in the substrate can be collected.

The substrate contribution increases by decreasing base thickness's and with a low recombination velocity at the base - substrate interface. Therefore, a thin thickness of the base is sufficient (in order of $0.1 \mu\text{m}$ to $0.3 \mu\text{m}$) when the carrier losses at the interface are lower ($Sn_3 < 2.10^5 \text{ cm.s}^{-1}$). However, the widening of the region 2 of the space charge region ($w_2 = 0.08$

μm) allows to reduce the base thickness's, and to improve consequently substrate contribution.

The base contribution increases by increasing the diffusion length L_{n3} and the thickness H_3 in this area. The thin thicknesses of the base increase losses of carriers generated in this region when recombination velocities at the base-substrate interface are high ($S_{n3} > 2.10^6 \text{ cm.s}^{-1}$).

Figure 18. Internal quantum efficiency evolution versus photon energy: Comparison two considered structures ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺) and ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺).

($s_{p1}=2 \times 10^7 \text{ cm.s}^{-1}$; $H_1=0.3 \mu\text{m}$; $L_{p1}=0.4 \mu\text{m}$; $s_{p2}=2 \times 10^4 \text{ cm.s}^{-1}$; $H_2=0.1 \mu\text{m}$; $L_{p2}=0.5 \mu\text{m}$; $L_{n3}=3 \mu\text{m}$; $s_{n4}=2 \times 10^7 \text{ cm.s}^{-1}$; $L_{n4}=1 \mu\text{m}$; $W_1=0.02 \mu\text{m}$; $W_2=0.08 \mu\text{m}$; $W=0.1 \mu\text{m}$; $H=100 \mu\text{m}$; $D_{p1}=0.51 \text{ cm}^2.\text{s}^{-1}$; $D_{p2}=0.64 \text{ cm}^2.\text{s}^{-1}$; $D_{n3}=10.27 \text{ cm}^2.\text{s}^{-1}$; $D_{n4}=5.13 \text{ cm}^2.\text{s}^{-1}$)

- For the model ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺), the materials are not arranged with a decreasing energy band gap. The base (CuInSe₂) has the smallest energy band gap and a high photon absorption coefficient, it absorbs at first the incident photons and reduces substrate contribution.

However, the spectral response curves show that, the internal quantum efficiency obtained with this structure (ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺)) is wider and higher compared to that obtained with the previous model (ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺)). Interface effects or high recombination velocities at the base-substrate interface ($S_{n3} > 2.10^6 \text{ cm.s}^{-1}$) become less influential on the internal quantum efficiency. Substrate contribution is lower. All photons are absorbed by the space charge region and a thin thickness of the base, the spectral response essentially depends on these regions.

4. Conclusion

A comparative theoretical study of solar cell performances based on CuInSe₂ heterojunctions has been developed in this work. We considered the model with four layers formed by two window layers (ZnO and CdS), a base and a substrate with different natures (CuInSe₂ and CuInS₂) according to the model n⁺/n/p/p⁺. In order to optimize the performances and choose the best structure of the solar cell, the following two models were considered : ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺) and ZnO(n⁺)/CdS(n)/ CuInSe₂(p)/CuInS₂(p⁺). The internal quantum efficiency was studied for each model of structure, by varying some geometrical and electrical parameters (base thickness's, diffusion length, recombination velocity at the interface, etc.). As we have used window layers in the frontal area (ZnO and CdS), the variation of the geometrical and electrical parameters concerns only the rear area (base and substrate : CuInSe₂, CuInS₂). The results obtained show that the spectral response depends on the structure and the juxtaposition of layers forming the solar cell.

For the model ZnO(n⁺)/CdS(n)/CuInS₂(p)/CuInSe₂(p⁺), the efficiency depends on the substrate, base and space charge region responses. This structure is a decreasing energy band gap model, the behavior of each layer is visible on the spectral response. This model of structure requires a low recombination velocity at the base-substrate interface (less than 2.10^3 cm.s^{-1}) and a diffusion length of the photocarriers greater than the base thickness. This model exploits the rear area, it allows to absorb a wide range of the solar spectrum by avoiding the hot carrier generation.

Thus, by fixing $w_2 = 0.08 \mu\text{m}$ (region 2 of the space charge region), the optimal base thickness's is ranging between $0.1 \mu\text{m}$ and $0.3 \mu\text{m}$ for recombination velocities at the base-substrate interface lower than 2.10^5 cm.s^{-1} . For those greater than 2.10^6 cm.s^{-1} , the interest is to increase the thickness of the base, a thickness greater than $3 \mu\text{m}$ is optimal.

-For the model ZnO(n⁺)/CdS(n)/CuInSe₂(p⁺)/CuInS₂(p), the efficiency depends only on the thicknesses of the space charge region and the base. This model of structure allows to avoid carrier losses due to surface or interface recombination phenomena. This structure exploits the space charge region and the base. Therefore, generation of hot carriers can be observed with this model, it can temporarily reduce the performance of the solar cell because the hot carriers participate in the electrical conduction after thermalization. Also, the widening of the space charge region can decrease the open-circuit voltage, which reduces the energy conversion efficiency.

By fixing $w_2 = 0.08 \mu\text{m}$ (region 2 of the space charge region) and the base thickness's at $3 \mu\text{m}$, the theoretical internal quantum efficiency is ranging between 85% to 100% for photon energy less than the energy band gap of the window layers. A thickness of the base greater than (or equal to) $3 \mu\text{m}$ is optimal for this model (ZnO(n⁺)/CdS(n)/CuInSe₂(p)/CuInS₂(p⁺)).

This study is very useful for manufacturers to calculate the dimensions and optimize the different photoconductive layers during their growth. It allows to optimize the performance of the solar cell according to the structure of the considered materials. It also allows to determine theoretically the model of structure that gives the best short- circuit photocurrent.

Nomenclature :

β : n (electrons) or p (holes)
 i : region (1, 2, 3 or 4)
 α_i : Absorption coefficient of region i (cm^{-1})
 F : Incident photon flux ($\text{cm}^{-2}.\text{s}^{-1}$)
 R : Reflection coefficient
 τ_{β_i} : Lifetime of free electrons or holes photocreated in region i (μs)
 $\Delta\beta_i(x)$: Density of free electrons or holes photocreated in region i at the point of x coordinate (cm^{-3})
 $J_{\beta_i}(x)$: Photocurrent density of free electrons or holes photocreated in region i at the point of x coordinate ($\text{A}.\text{cm}^{-2}$)

J_{β} : Photocurrent density of free electrons or holes photocreated ($\text{A}.\text{cm}^{-2}$)
 J_{SCR} : Photocurrent density in the space charge zone ($\text{A}.\text{cm}^{-2}$)
 J_{ph} : Total density of photocurrent ($\text{A}.\text{cm}^{-2}$)
 D_{β_i} : Diffusion coefficient of free electrons or holes photocreated in region i ($\text{cm}^2.\text{s}^{-1}$) ($D_{p_{ZnO}} = 0.51 \text{ cm}^2.\text{s}^{-1}$; $D_{p_{CdS}} = 0.64 \text{ cm}^2.\text{s}^{-1}$; $D_{n_{CuInS_2}} = 5.13 \text{ cm}^2.\text{s}^{-1}$; $D_{n_{CuInSe_2}} = 10.27 \text{ cm}^2.\text{s}^{-1}$)
 L_{β_i} : Diffusion length of free electrons or holes photocreated in region i (μm)
 S_{β_i} : Recombination velocity on the surface (or to the interface) of region i ($\text{cm}.\text{s}^{-1}$)
 H : Thickness of the structure (μm)
 H_i : Thickness of the region i (μm)
 w_i : Thickness of the region i of the space charge zone (SCZ) (μm)
 q : Elementary charge ($1.6 \times 10^{-19}\text{C}$)
 B : Base
 Sub. : Substrate
 SCR : Space Charge Region

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Please locate eventual acknowledgements here following this format.

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