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Research Article

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Study of the Impact of the Thickness of the Cu_2ZnSnS_4 (CZTS) Absorber Layer Deposited by CSVT on the Performance of the Cells

M. S. Mané, A. Sagna, B. Ndiaye, E. M. Keita, A. Sow, C. Sene

Laboratoire des Semiconducteurs et d'Energie Solaire, Département de Physique, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal
Corresponding author: manesolmats@yahool.fr

Abstract The objective of this work is to perform a simulation of a Cu_2ZnSnS_4 (CZTS) based thin film photovoltaic solar cell to relate the characteristics of this cell with the material parameters to improve its performance. A device model for the n-CdS/p-CZTS solar cell was used to study the internal quantum efficiency that takes into account the influence of loss mechanisms on the solar cell performance. The effects of the thickness of the CZTS absorber layer were investigated.

Keywords Cu_2ZnSnS_4, thickness, absorber layer, internal quantum efficiency

Introduction

In recent years, the renewable energy sector continues to produce great interest in the minds of researchers; in particular, photovoltaic cell technology continues to grow due to the development of new manufacturing techniques and improvements in the efficiency conversion of solar cells. Nowadays, the solar cell market is still dominated by crystalline silicon which occupies about 80% of the market [1]. The high cost of these solar cells is mainly due to the large use of the material and the manufacturing processes that use complicated and very expensive techniques. Making the production processes simple and cheaper or manufacturing solar cells that consume less material could reduce the costs of these. One of the alternatives is the thin film solar cell because it consumes less material. The best cells CdTe and CIGS made in the laboratory have efficiencies of 22.1% and 22.6%, respectively [2]. However, these thin films contain rare and toxic elements (In, Te, Cd, Ga, Se), which limits the relevance of these two technologies for terawatt-scale energy production. Faced with these difficulties, measures will have to be taken to counteract these problems of scarcity and toxicity in order to produce low-cost solar cells that respect the environment. The quaternary material made of copper, zinc, tin and sulfur **(**Cu_2ZnSnS_4**)** known as CZTS is one such measure.

With a direct and tunable gap energy of about 1.5 eV [3, 4] and a high absorption coefficient of 10^4 cm-1 [5, 6], CZTS is an ideal candidate to be used as an absorber layer in thin film solar cells. The constituent elements of this material namely copper, zinc, tin and sulfur are still available in the earth's crust and are safe for the environment [1]. Several physical and chemical deposition techniques have been used to fabricate CZTS-based solar cells such as sputtering [7, 8, 9, 10, 11], thermal evaporation [12, 13, 14], pulsed laser deposition (PLD) [15, 16, 17], sol gel [18, 19, 20], spray pyrolysis [21, 22, 23, 24], electrodeposition [25, 26, 27], Close Spaced Vapor Transport (CSVT) [28, 29]. The efficiency conversion of this cell has been improved from 0.66% in 1996 [1] to 12.6% by the International Business Machines laboratory in 2014 [10]. Despite the development of different manufacturing techniques and efficiency improvements, our understanding of this type of cell remains relatively limited compared to CIGS and CdTe solar cells [1, 2]. In order to fabricate solar cells with high efficiencies, a thorough study of the synthesis and fabrication mechanisms is required as well as an understanding of the solar cell performance. This work focuses on the study of the impact of the absorber layer thickness of the CZTS thin film deposited by CSVT following a mathematical model, the physical and geometrical parameters of the different layers of a CZTS-based thin film photovoltaic solar cell in order to improve the performance of this cell.

Materials and Methods

Structure of the Cell

The cell structure considered in this study consists of the following materials: n-CdS as a buffer layer, p-CZTS acts as an absorber layer. Figure 1 illustrates the dimensions and the different regions of the CdS(n)/CZTS(p) heterojunction. The recombination profile and carrier transport are studied in one dimension using the Poisson equation and continuity equations for electrons and holes.

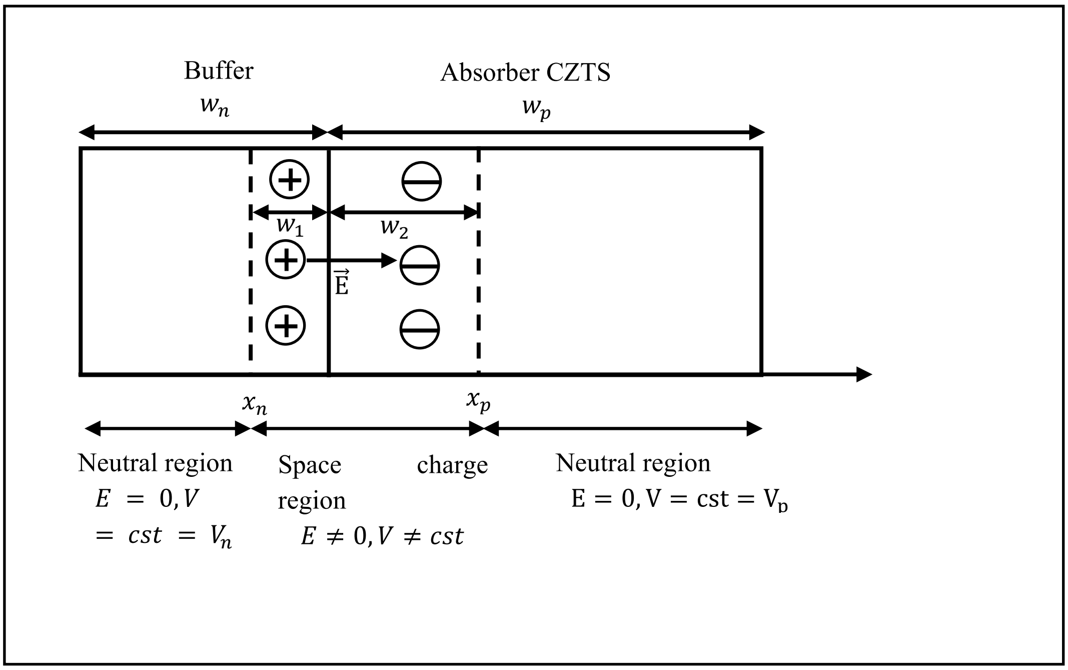

Figure 1: Dimensions and differents regions of CdS(n)/CZTS(p) heterojunction

The transport of the majority charge carriers at the back metal-semiconductor interface is described by the thermionic emission. The transport of minority carriers is described by their surface recombination rates (Sp). Recombination at deep bulk levels and their occupancy are treated according to the Shockley-Read-Hall (SRH) mechanism [31].

In these three regions, solving the continuity equation combined with the Poisson equation and the current density equation allows us to calculate the current density in each of these three regions.

Considering the phenomenon of the generation rate presented by the rate G(λ, x) given by :

$$G(\lambda, x) = \alpha(\lambda)F(\lambda)\big(1 - R(\lambda)\big)e^{-\alpha(\lambda)x} \qquad (1)$$

And those of the recombination rates presented by U_n and U_p as follows:

- For electrons in the neutral p region of CZTS:

$$U_n = \frac{\Delta n}{\tau_n} = \frac{n - n_0}{\tau_n} \qquad (2)$$

- For holes in the neutral n region of CdS:

$$U_p = \frac{\Delta p}{\tau_p} = \frac{p - p_0}{\tau_p} \qquad (3)$$

Where R(λ) is the fraction of photons reflected from the front surface, n is the concentration of electrons in the p-CZTS layer and p is that of holes in the n-CdS layer, n0 and p0 are the equilibrium concentrations of electrons and holes, respectively.

In the first neutral zone N (CdS), the electric field E = 0 and the minority carriers are holes, which, according to the formula :

$$J_p = \left(\frac{qF(1-R)\alpha_1 L_p}{\alpha_1^2 L_p^2 - 1}\right)\left\{\frac{\frac{S_pL_p}{D_p} + \alpha_1 L_p - \left[\frac{S_pL_p}{D_p}\cosh\left(\frac{x_n}{L_p}\right) + \sinh\left(\frac{x_n}{L_p}\right)\right]e^{-\alpha_1 x_n}}{\frac{S_pL_p}{D_p}\sinh\left(\frac{x_n}{L_p}\right)+\cosh\left(\frac{x_n}{L_p}\right)} - \alpha_1 L_p e^{-\alpha_1 x_n}\right\}$$

Where L_p **et** D_p **are respectively the hole diffusion length and the diffusion coefficient.** S_p **is the hole recombination rate at the CdS front surface.**

In the second neutral zone P (CZTS), the electric field E = 0 and the minority carriers are electrons, so according to :

$$J_n = \left(\frac{qF(1-R)L_n}{\alpha_2^2 L_n^2-1}\right)e^{[-\alpha_1(x_n+w_1)-\alpha_2 w_2]}\left\{\alpha_2 L_n - \frac{\frac{S_nL_n}{D_n}\left[\cosh\left(\frac{H'}{L_n}\right) - e^{-\alpha_2 H'}\right] + \sinh\left(\frac{H'}{L_n}\right) + \alpha_2 L_n e^{-\alpha_2 H'}}{\frac{S_nL_n}{D_n}\sinh\left(\frac{H'}{L_n}\right)+\cosh\left(\frac{H'}{L_n}\right)}\right\}$$

Where L_p **et** D_p **are the electron diffusion length and the diffusion coefficient, respectively.** S_n **is the electron recombination rate at the back surface of the CZTS.**

In the space charge region, the electric field E ≠ 0, according to:

$$J_{ZCE} = qF(1-R)e^{-\alpha_1 x_n}(1-e^{-\alpha_1 w_1 - \alpha_2 w_2})$$

And the photocurrent density is given by:

$$J_{ph}(\lambda) = J_p(\lambda) + J_{ZCE}(\lambda) + J_n(\lambda)$$

For this analytical study, we developed the collection efficiency model for thin-film solar cells and established its mathematical expression. The internal quantum efficiency is the ratio of the number of charge carriers collected by the photovoltaic device to the number of photons of a given wavelength or energy on the device [32].

The internal quantum efficiencies are given by:

$$\eta = \frac{J_{ph}}{qF(1-R)}$$

$$\eta_1 = \frac{J_p}{qF(1-R)}$$

$$\eta_2 = \frac{J_n}{qF(1-R)}$$

$$\eta_3 = \frac{J_{ZCE}}{qF(1-R)}$$

With η the total internal quantum efficiency, η_1 he emitter or buffer zone (CdS) internal quantum efficiency, η_2 the base internal quantum efficiency (CZTS), and η_3 the space charge zone internal quantum efficiency.

RESULTS & DISCUSSION

In this study we present a simulation of the developed theoretical model, investigating the effects of thickness on the internal quantum efficiency.

Contribution of the different parts of the CdS/CZTS cell

Figures 2 represent the contribution of each part of the cell on the internal quantum efficiency as a function of the photon energy.

We notice that the contributions of the absorbing layer (p-CZTS) and the space charge zone are very important compared to the contributions of the buffer layer (n-CdS) corresponding to the volume absorptions. In the range of higher energies (far from the absorption threshold or the gap of the CZTS), the absorption of incident photons is superficial, they are almost absorbed by the front; the surface phenomena become decisive leading to the fall of the efficiency.

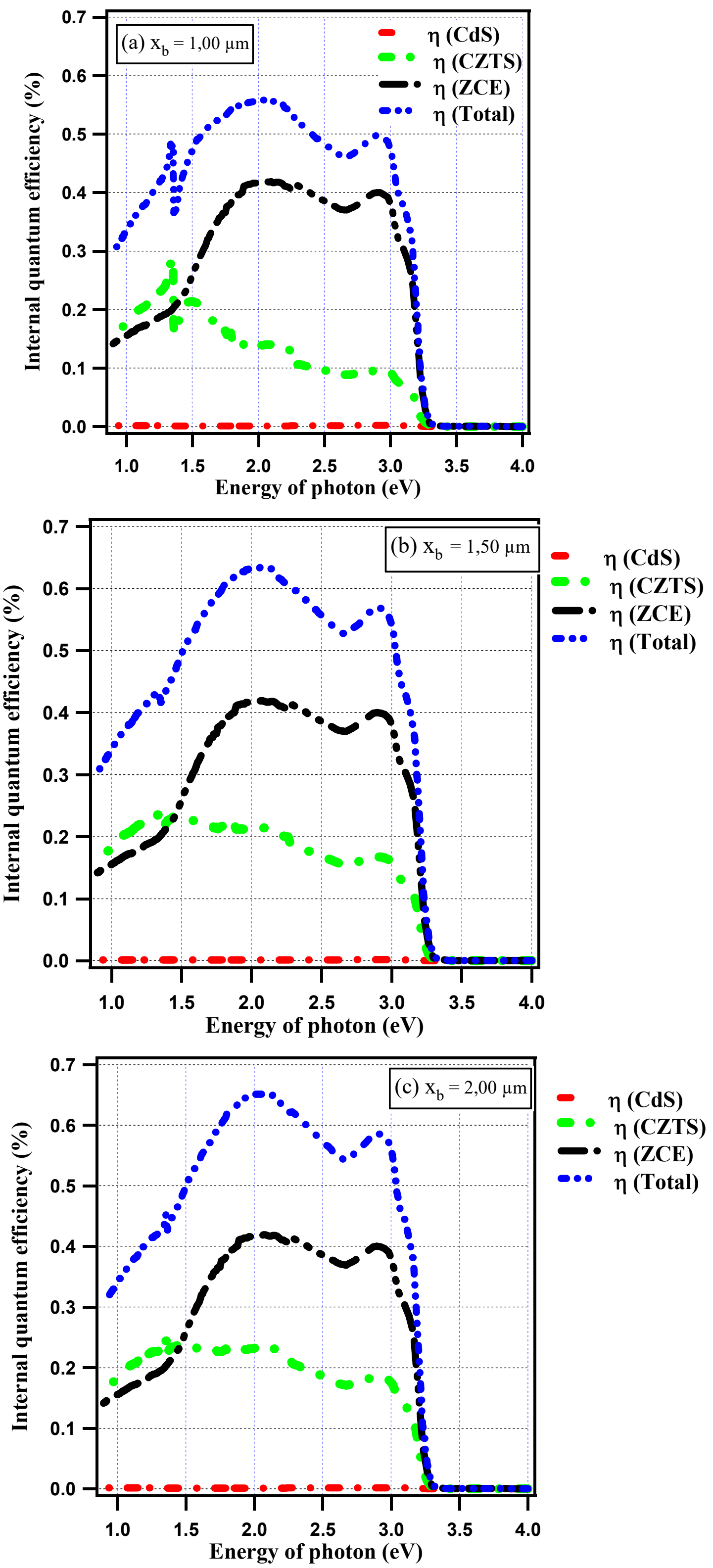

Figure 2: Contribution of the different parts of the n-CdS/p-CZTSS cell

Effect of the thickness of the base

The absorber layer is the most important component of the solar cell, where incident photons are absorbed and excess carriers are generated. The absorption of photons in a semiconductor material follows the Beer-Lambert law. Therefore, as the thickness of the absorber layer increases, more long wavelength photons (low energy photons) are absorbed, which generates a greater number of excess carriers. This leads to a higher internal quantum efficiency and thus an increase in cell efficiency. In the present study, the effect of absorber layer thickness on the internal quantum efficiency of the cell is simulated by changing the thickness of CZTS from 1 to 5 nm (Figure 2). The efficiency of the solar cell initially increases with increasing CZTS layer thickness and almost saturates at higher values. This saturation of the efficiency is due to an increased probability of SRH recombination (due to the finite carrier diffusion length) with increasing absorber thickness.

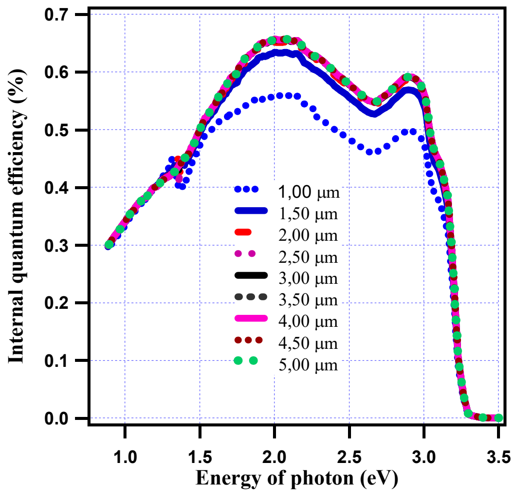

Figure 3: Evolution of internal quantum efficiency as function of photon energy: effect of absorber layer thickness (CZTS)

On this plot the internal quantum efficiency drops slightly near 2.4 eV corresponding to the absorption of CdS. We also notice that the signal does not depend any more on the thickness of the absorbing layer xb beyond 2.4 eV, showing that all the incident photons are absorbed by the CdS and the space charge zone (CdS/CZTS). A second drastic drop in efficiency is observed beyond 3 eV, which corresponds to the absorption of photons by the ZnO (Front).

Three dimensional representation of the internal quantum efficiency

The graph studied on figure 4 is represented in three dimensions. This three-dimensional representation allows to show simultaneously the evolution of the internal quantum efficiency as a function of the photon energy and of the considered parameter such as: the thickness of the absorber layer.

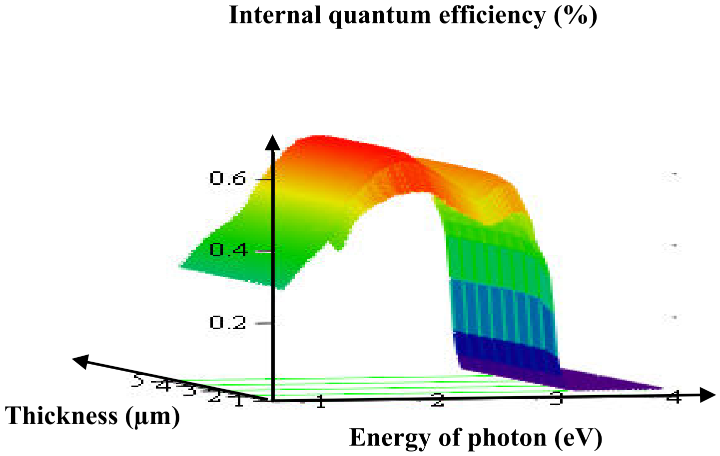

Figure 4: Evolution of the internal quantum efficiency as a function of photon energy and base thickness

Conclusion

In this work, we studied the internal quantum efficiency of CZTS-based solar cells. We have developed a theoretical model for two layers. We performed a theoretical simulation on all the spectral responses studied by varying the physical parameters such as the thickness of the absorber layer in order to improve the device performance. We have shown that the internal quantum efficiency increases with the thickness of the absorber layer.

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