Simulation of a thin-film solar cell based in kesterite using Matlab

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Abstract. The development of thin-film solar cells has led the researches to evaluate different materials to improve the conversion efficiency, avoid the use of non toxic raw materials or reduce the manufacturing costs. One option is to use simulation tools, which allow the variation of solar cell materials, parameters, dimensions and other variables in order to evaluate performance indicators of the cell without wasting material. This paper introduces a mathematical model for kesterite based thin-film solar cells with both theoretical and experimental solar irradiance spectra. The model is implemented in Matlab and it is used to evaluate four performance indicators: open-circuit voltage, short-circuit current density, conversion efficiency and fill factor. Those indicators are evaluated for a ZnO/CZTSSe/buffer solar cell with buffer layers implemented with CdS and ZnS considering different thickness. The results show that all performance indicators are significantly improved with the ZnS buffer layer; moreover, the results also evidence that the irradiance model affects the performance indicators. Particularly, experimental based irradiance model improves the performance indicators for both evaluated layers. Finally, the thickness does not affect considerably the performance of the cell with ZnS buffer layer, while a higher thickness reduces the performance of the cell with CdS buffer layer.

1. Introduction
Nowadays, solar energy is one of the most important energy sources. This can be evidenced in the 402 GW of peak generation capacity installed around the world, where 98 GW were installed just in 2017 [1, 2]. The market is dominated by crystalline silicon (c-Si) solar cells, due to the maturity of the technology, the cells stability and higher power conversion efficiencies. However, silicon is a band-gap indirect semiconductor, then, it requires more than 100 µm thickness to achieve an appreciable absorption of the incident radiation [3].

In contrast, thin-film solar cells are manufactured with a direct band-gap semiconductor, therefore, they require smaller thicknesses and, as consequence, less materials. This advantage is translated into a reduction in the manufacturing costs compared with c-Si cells. The market of thin-film solar cells is based on amorphous silicon (a-Si), cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS) [4]. Nevertheless, thin-film cells use scarce elements in nature, like the indium, and toxic materials, like Cd and Te [5]. Nowadays, new photovoltaic materials,
like kesterite, are emerging with significant advantages like the use of materials abundant in nature and high theoretical efficiency (greater than 32%).

In literature, it is possible to find some works about the efficiency evaluation of different thin-film solar cells [6–9]. However, some references [6, 7] use commercial software, like Solar Cell Capacitance Simulator (SCAPS), to evaluate the efficiency, which difficult the customization of the mathematical models and require an investment to acquire the software license. In [8], the authors introduce a mathematical model for a ZnO/buffer/Cu₂ZnSn(S-Se)₄(CZTSSe) thin-film solar cell, which allows efficiency evaluation for a theoretical solar spectrum. Such a model is implemented in a Matlab script whose outputs are the energy conversion efficiency (η), the fill-factor (FF), the short-circuit current density (J_s) and the open circuit voltage (V_oc). Nonetheless, the authors in [8] do not evaluate the solar cell performance for experimental values of solar spectrum and use a toxic material (CdS) as a buffer layer.

This paper evaluates the efficiencies of thin-film solar cells with two different materials in the buffer layer. The first one is CdS, since it is widely used in the manufacture of thin-film solar cells, and the second material is ZnS, because it is a non toxic alternative to replace CdS. The efficiency of the solar cells is evaluated by using the mathematical model of a ZnO/buffer/Cu₂ZnSn(S-Se)₄(CZTSSe) heterojunction solar cell introduced in [8], where the irradiance spectrum is improved by using experimental data [10]. Moreover, the efficiency evaluation results of the solar cells are also compared with the theoretical solar spectrum equation [9]. The mathematical model is implemented in Matlab to calculate η, FF, J_s, and V_oc for different thickness of buffer and absorption layers. The results show that the cell efficiency conversion increases when the CdS buffer layer is replaced by a ZnS layer; moreover, the values of η, FF, J_s and V_oc are significantly increased by using an experimental based model for the irradiance.

2. Methods
This section introduces the mathematical model of heterojunction solar cells as well as the parameters used in the simulation. The model includes the equations of the buffer and absorption layer thickness, the definition of the experimental and theoretical solar spectrum irradiance, the description of the absorption coefficients, the definition of the current density and the solar cell characteristics.

2.1. Thickness of buffer and absorption layers
The modeled thin-film solar cell considers a ZnO/buffer/CZTSSe structure, where the buffer layer can be CdS or ZnS. The details of the cell dimensions with respect to the thickness of buffer and absorption layers are shown in Figure 1, where L is the thickness of the whole cell, w₁ and w₂ represent the thickness of the buffer and absorption layers, respectively, w₁ + w₂ is the Space Charge Zone (SCZ), and X_n is the thickness of the neutral charge zones of the N layer, X_p is defined as X_p = X_n + w₁ + w₂, and L' is the thickness of the neutral charge zone of the P layer.

Taking the initial point of the cell as zero (0) μm (see Figure 1), it is possible to define w₁ and w₂ as shown in Equation (1) [11], where V_d is the diffusion potential, ε₁ is the permittivity of the buffer layer, and ε₂ is the permittivity of the absorber layer (CZTSSe) [8].

\[
w₁ = \left( \frac{2N_a}{qN_d} \cdot \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 N_d + \varepsilon_2 N_a} \cdot V_d \right)^{1/2}, \quad w₂ = \left( \frac{2N_d}{qN_a} \cdot \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 N_d + \varepsilon_2 N_a} \cdot V_d \right)^{1/2} \quad (1)
\]

In turn, V_d is defined by Equation (2) [8], where x₁ and x₂ are the electronic affinities of the absorbent and buffer layers, respectively, U_t is the thermodynamic potential (25 mV), N_a and N_d are acceptors and donors concentrations, respectively, N_e is the effective conduction
band density of the states, $N_{v2}$ is the effective valence band density of the states, and $E_{g2}$ is the CZTSSe band-gap [8].

$$V_d = \frac{E_{g2} + (x_2 - x_1)}{e} + U_t \ln \left( \frac{N_a N_d}{N_{c1} N_{v2}} \right)$$  \hspace{1cm} (2)

2.2. Solar spectrum irradiance

Two models are used to determine the solar spectrum irradiance at ground level ($I_{rs}$) for a given light wavelength ($\lambda$). The first one is an approximated theoretical model introduced in Equation (4) [9], and the second one is a look up table of $I_{rs}$ for different values of $\lambda$, considering an air mass of 1.5 and a clear atmosphere provided by NASA [10]. Both, theoretical and experimental based models are introduced in Figure 2, where $I_{rs}$ is given in Wm$^{-2}$µm$^{-1}$.

$$I_{rs}(\lambda) = 0.00977 + 7.0625 \left( 1 - e^{-\frac{(\lambda-0.26053)}{0.15994}} \right)^2 2.28411 e^{-\frac{(\lambda-0.26053)}{0.15994}}$$  \hspace{1cm} (3)

Moreover, the solar flux for a given $\lambda$, i.e. $F(\lambda)$, is calculated from the solar spectrum irradiance at ground level ($I_{rs}(\lambda)$) as shown in Equation (4) [11].

$$F(\lambda) = \frac{I_{rs}(\lambda)}{hv}$$  \hspace{1cm} (4)
2.3. Absorption coefficients
The absorption coefficients are determined from the direct transition equations due to all the materials are characterized by a direct gap. The gaps considered for the semiconductor materials are: 2.4 eV for CdS [7], 3.52 eV for ZnS [12], and 1.5 eV for CZTSSe [13].

2.4. Current density
The total photocurrent density \( J_{ph} \) is the integral of the photocurrent for a particular wavelength \( J_{ph}(\lambda) \) over the entire solar spectrum, as introduced in Equation (5). In this paper \( \lambda_1 \) and \( \lambda_2 \) are 0.29 \( \mu \)m and 4.045 \( \mu \)m, respectively. In turn, \( J_{ph}(\lambda) \) is defined as the sum of the current density due to the holes in N region \( (J_n(\lambda)) \), the current density due to the electrons in the P region \( (J_p(\lambda)) \), and the current density in the space charge zone \( (J_{zce}(\lambda)) \).

\[
J_{ph} = \int_{\lambda_1}^{\lambda_2} J_{ph}(\lambda) \, d\lambda, \quad \text{where } J_{ph}(\lambda) = J_p(\lambda) + J_n(\lambda) + J_{zce}(\lambda)
\]  

The current densities \( J_p(\lambda), J_n(\lambda) \) and \( J_{zce}(\lambda) \) are defined as shown in Equation (6), Equation (7) and Equation (8), respectively, according to [11]. In those equations \( \alpha_1 \) is the absorption coefficient of the buffer layer (CdS o ZnS), \( \alpha_2 \) is the kesterite absorption coefficient, \( R \) is the reflectivity, \( D_n \) and \( D_p \) are the diffusion coefficients of electrons and holes, respectively, and \( L_n \) and \( L_p \) represent the electron and hole diffusion length, respectively.

\[
J_p(\lambda) = \left( \frac{q F_1(\lambda)(1 - R) \alpha_1 L_p}{\alpha_1^2 L_p^2 - 1} \right) \left( \frac{S_p L_p}{D_p} + \left( e^{-\alpha_1 X_n} \right) \frac{S_p L_p}{D_p} \frac{\sinh \left( \frac{X_n}{L_p} \right) + \cosh \left( \frac{X_n}{L_p} \right)}{\sinh \left( \frac{X_n}{L_p} \right) + \cosh \left( \frac{X_n}{L_p} \right)} \right) - \alpha_1 L_p \left( e^{-\alpha_1 X_n} \right) \]

\[
J_n(\lambda) = \left( \frac{q F_1(\lambda)(1 - R) \alpha_2 L_p}{\alpha_2^2 L_p^2 - 1} \right) \left( e^{-\alpha_1 (X_n + w_1) - \alpha_2 w_2} \right)
\]

\[
J_{zce}(\lambda) = q F_1(\lambda)(1 - R) e^{(\alpha_1 X_n(1 - e^{-\alpha_1 w_1 - \alpha_2 w_2}))}
\]

2.5. Solar cell characteristics
There are three key properties that describe the performance of a solar cell: the open-circuit voltage \( V_{oc} \), the fill factor \( (FF) \) and the power conversion efficiency \( (\eta) \), which are defined in Equation (9). In those equations \( J_o \) is the dark current density, \( I_{sc} \) is the cell short-circuit current, \( P_m \) is the maximum power and \( P_i \) is the incident power.

\[
V_{oc} = \frac{kT}{q} \ln \left( \frac{J_{ph}}{J_o} + 1 \right), \quad FF = \frac{P_m}{V_{oc} I_{sc}}, \quad \eta = \frac{P_m}{P_i} = \frac{P_m}{\int_{\lambda_1}^{\lambda_2} I_{rs}(\lambda) \, d\lambda}
\]

The solar cells parameters used in this paper to model the solar cells are introduced in Table 1.
Table 1. Solar cell parameters used in the simulations.

| Description                          | Value         | Reference |
|--------------------------------------|---------------|-----------|
| Acceptor concentration ($N_a$)       | $10^{17}$ cm$^{-3}$ | [8]       |
| Donor concentration ($N_d$)          | $10^{15}$ cm$^{-3}$ | [8]       |
| Relative permittivity CdS ($\varepsilon_{r1}$) | 10 | [8]       |
| Relative permittivity CZTSSe ($\varepsilon_{r1}$) | 13.6 | [8]       |
| Relative permittivity ZnS ($\varepsilon_{r1}$) | 9 | [8]       |
| Electronic affinity CdS ($x_1$)      | 4.2 eV        | [8]       |
| Electronic affinity CZTSSe ($x_2$)   | 4.1 eV        | [8]       |
| Electronic affinity ZnS ($x_1$)      | 3.9 eV        | [8]       |
| Effective conduction band density of states ($N_{C1}$) | $2.2 \times 10^{18}$ cm$^{-3}$ | [8]       |
| Effective valence band density of states ($N_{v2}$) | $1.8 \times 10^{19}$ cm$^{-3}$ | [8]       |
| Reflectivity ($R$)                   | 0.1           | [11]      |
| Holes mobility ($\mu_p$) (CdS)       | $25$ cm$^2$V$^{-1}$s$^{-1}$ | [8]       |
| Holes mobility ($\mu_p$) (ZnS)       | $40$ cm$^2$V$^{-1}$s$^{-1}$ | [8]       |
| Electrons mobility ($\mu_e$) (CdS)   | $230$ cm$^2$V$^{-1}$s$^{-1}$ | [8]       |
| Electrons mobility ($\mu_e$) (ZnS)   | $25$ cm$^2$V$^{-1}$s$^{-1}$ | [8]       |
| Hole capture cross section ($\sigma_p$) CdS | $10^{-13}$ cm$^2$ | [11]      |
| Hole capture cross section ($\sigma_p$) CZTSSe | $10^{-14}$ cm$^2$ | [11]      |
| Hole capture cross section ($\sigma_p$) ZnS | $10^{-12}$ cm$^2$ | [11]      |
| Electron capture cross section ($\sigma_n$) CZTSSe | $10^{-14}$ cm$^2$ | [11]      |
| Electron capture cross section ($\sigma_n$) CdS | $10^{-17}$ cm$^2$ | [11]      |
| Electron capture cross section ($\sigma_n$) ZnS | $10^{-17}$ cm$^2$ | [11]      |
| Thermal speed ($v_{th}$)             | $10^7$ cm s$^{-1}$ | [11]      |
| Defect density ($N_{tp}$) CZTSSe     | $10^{17}$ cm$^{-3}$ | [11]      |
| Defect density ($N_{tn}$) CdS        | $1.35 \times 10^{15}$ cm$^{-3}$ | [11]      |
| Defect density ($N_{tn}$) ZnS        | $10^{10}$ cm$^{-3}$ | [11]      |
| Recombination speed of the holes (front surface) CdS ($S_p$) | $10^7$ cm s$^{-1}$ | [11]      |
| Recombination speed of the holes (front surface) ZnS ($S_p$) | $10^3$ cm s$^{-1}$ | [11]      |
| Recombination rate electrons (rear surface) CZTSSe ($S_n$) | $10^7$ cm s$^{-1}$ | [11]      |
| Ideal diode factor                   | 1.45          | [11]      |

3. Results and discussion

A solar cell, with the parameters described in Table 1, was simulated for different thickness of the buffer layer in order to evaluate the open-circuit voltage, the short-circuit current, the fill factor and the conversion efficiency. Those simulations were performed for two different materials in the buffer layer (i.e. CdS and ZnS) considering the theoretical solar spectrum model, shown in Equation (3), and the lookup table constructed from experimental measurements [10].

In Figure 3, it can be observed that the data obtained for the ZnO/CZTSSe/CdS cell with Model 1 of the solar spectrum irradiance (theoretical [11]) agrees with the results reported in [8]. Moreover, the cell efficiency considering the Model 2 of the solar spectrum irradiance is more than 1% higher for all the evaluated thicknesses, because most of the irradiance values in Model 2 are higher than the values in Model 1 for wavelength less than $0.83 \mu m \approx 1.5$ eV (gap considered for the CZTSSe), see Figure 2. It is worth noting that the cell efficiency decreases from a buffer thickness of $13.9 \eta m$, which is related to the edge of the SCZ.

Figure 4 illustrates the behavior of $V_{oc}$, $J_{sc}$, $\eta$ and $FF$ of the ZnO/CZTSSe/ZnS cell for variations in the buffer layer thickness and considering the two solar spectrum irradiance models.
It can be observed that the performance of the cell is less affected by the thickness compared with ZnO/CZTSSe/CdS. Additionally, the values of $V_{oc}$, $J_{sc}$, $\eta$ and $FF$ of the ZnO/CZTSSe/ZnS are significantly higher than the ones of the ZnO/CZTSSe/CdS cell, and it is evident that the irradiance model significantly affects the calculation of the performance indicators.

![Figure 3](image1.png)

**Figure 3.** Open-circuit ($V_{oc}$), short-circuit current density ($J_{sc}$), conversion efficiency ($\eta$) and fill factor ($FF$), as a function of the CdS buffer layer thickness.

![Figure 4](image2.png)

**Figure 4.** Open-circuit ($V_{oc}$), short-circuit current density ($J_{sc}$), conversion efficiency ($\eta$) and fill factor ($FF$), as a function of the ZnS buffer layer thickness.
Finally, Figure 5 shows the effect of replacing the buffer layer in a thin film ZnO/CZTSSe/buffer cell from CdS to ZnS. The results show that a ZnS buffer produces an increment of around 180% in the conversion efficiency; additionally, it reduces toxic materials in the manufacturing process and the final disposal of the cells at the end of their useful life.

![Figure 5](image1.png)

**Figure 5.** Comparison of ZnO/CZTSSe/buffer solar cell conversion efficiency with CdS and ZnS buffer layers and theoretical (Model 1) and experimental based (Model 2) model of the solar spectrum irradiance.

4. Conclusions
In this paper, the effect of replacing the buffer layer in a ZnO/CZTSSe/buffer from CdS to ZnS has been analyzed. Such an analysis was developed by using a mathematical model with two different solar spectrum irradiance models: one theoretical (Model 1) and one experimental based (Model 2). The mathematical model was implemented in Matlab to perform different simulations in order to evaluate four solar cell performance parameters \( V_{oc}, J_{sc}, \eta \) and \( FF \) as a function of the buffer layer thickness.

Simulation results showed that modifying the buffer layer from CdS to ZnS, it is possible to increase the conversion efficiency around 180% and to reduce the use of toxic materials in the manufacturing of thin-film solar cells. Moreover, the results also put into evidence that the performance indicators \( V_{oc}, J_{sc}, \eta \) and \( FF \) are significantly affected by the irradiance model, since the experimental based irradiance model improved the performance indicators for both of the buffer layers evaluated in a ZnO/CZTSSe/buffer cell.

Finally, simulation results show that the increment in the thickness of the buffer layer reduces the performance of the cell, therefore, it is important to determine the material and the thickness of the buffer layer to achieve the desired performance and to reduce the manufacturing costs.

References
[1] IEA 2018 *Snapshot of global photovoltaic markets* (Paris: International Energy Agency)
[2] REN21 2018 *Renewables 2018 global status report* (Paris: Renewable Energy Policy Network for the 21st Century)
[3] Mitzi D B, Gunawan O, Todorov T K, Wang K and Guha S 2011 Solar Energy Materials and Solar Cells 95(6) 1421–1436
[4] Abermann S 2013 *Solar Energy* 94 37–70
[5] Kim J S, Kim D H and Hwang D K 2018 *Journal of Power Sources* 400 9–15
[6] Minbashi M, Omrani M K, Memarian N and Kim D H 2017 *Current Applied Physics* 17(10) 1238–1243
[7] Cherouana A and Labbani R 2017 *Applied Surface Science* 424 251–255
[8] Bennir A and Aida M S 2016 *Superlattices and Microstructures* 91 70–77
[9] Bennir A and Aida M 2013 *Energy Procedia* 36 618–627
[10] Mecherikunnel A T and Richmond J C 1980 *Spectral distribution of solar radiation* (Greenbelt: National Aeronautics and Space Administration)
[11] Luque A and Hegedus S 2003 *Handbook of Photovoltaic Science and Engineering* (England: John Wiley & Sons Inc.)
[12] Londón O A B 2008 *Síntesis y caracterización de nuevos materiales no tóxicos empleados como capa buffer y capa absorbente en la fabricación de celdas solares* (Bogotá: Universidad Nacional de Colombia)
[13] Li J, Shen H, Shang H, Li Y and Wu W 2017 *Materials Letters* 190 188–190