Optimization of Si (core)/CZTS/CZTSe (shell) nanowire array for solar cell

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Abstract
We present an optical simulation of a solar cell employing core (Si) /shell (Kesterite Cu2ZnSnS4 (CZTS) or/and Cu2ZnSnSe4 (CZTSe) vertically-aligned nanowire array. The method of the simulation is rigorous coupled wave analysis. In the first stage, we studied the case where the shell is composed of only CZTS or CZTSe. A larger absorptance of CZTSe led to a larger value of the ideal short circuit current (41 mA/cm²) in the case of CZTSe solar cell than in the case of CZTS solar cell (24 mA/cm²). In the second stage, to avoid the heat losses in CZTSe solar cell without reducing the current, we proposed a shell composed of a 3 µm of CZTS in the upper part and a 6 µm of CZTSe in the lower part. The maximum ideal current value in this structure is almost twice as large as that of a planar solar cell with the same amounts of used materials. Furthermore, the variation of this maximal ideal current with the incident angle of the sunlight shows that the investigated solar cell still has good performance as long as the incident angle doesn’t exceed 60°.

Keywords CZTS · CZTSe · Si · RCWA · Solar cell · Nanowire · Heat losses

1 Introduction
Thanks to its particular optical properties, like the light scattering and trapping (Ghosh et al. 2017; Sun et al. 2013; Melliti 2021), nanowires (NWs) configuration is economical than other configurations because solar cells (SC) have relatively less material. Among these solar cells, kesterite solar cells based on n-Si nanowires coated by p-type CZTS are emerging as the most auspicious candidate for scalable SC development (Peksu and Karaagac 2019; Peksu et al. 2020). Indeed, CZTS has outstanding electrical and optical features as direct optical band gap of 1.5 eV (Ericson et al. 2017) and large absorptance coefficient (10^4 cm⁻¹). Furthermore, the p-CZTS-n-Si heterojunction is of high quality and these solar cells are only consisting of earth-abundant and non-toxic constituents.
For better performance of SC based on coated Si NWs, numerical simulation can play a significant role that can save time and cost for the research community. Especially that the power of the conversion efficiency of solar cell based on Si/CZTS core–shell nanowire array (1–1.3%) (Peksu and Karaagac 2019; Peksu et al. 2020) is relatively weak compared to the one reported, for example, for CuIn_{1-x}Ga_xSe_2 (CIGS) thin film solar cell (22.9%) (Green et al. 2018). We need, among others, to optimize the geometrical parameters and to look for other materials or compositions of the shell.

In the present article, we present an optical simulation of a solar cell with core (Si)/shell (CZTS or/and CZTSe) vertically-aligned NWs array. It’s made using rigorous coupled wave analysis (RCWA) with Pavel Kwiecien’s rcwa-2d code for MATLAB (sourceforge.net/projects/rcwa-2d/), based on (Li 1997). The validation of the used code was made in previous work (Melliti 2021). In RCWA (Li 1997), Maxwell’s equations are solved by considering monochromatic polarized plane wave for the incident light and Bloch boundary conditions. The SC structure is divided into several layers with a constant profile in the xy plane. For each layer, the Fourier's series decompositions are performed along the x and y axis. The different layers are then assembled, such that the fields at the interface are continuous. For the layers containing NWs, the grid size is 200×200. The time taken to calculate the transmittance and the reflectance of the investigated NWs SC for each wavelength is 24.9 s.

To maximize its value, we calculated the ideal short circuit current density (J_{ph}) as a function of the thickness of the shell and the ratio between the period array and the NWs diameter for different values of NWs height. The maximal value obtained of J_{ph} is almost twice as large as that of a planar solar cell with the same amounts of used materials. A study of the variation of the ideal current density with the incident angle of the sunlight is also reported. According to our best knowledge, an optical simulation of solar cells based on Si nanowires decorated with a thin layer of CZTSe or CZTSe and CZTS has been reported for the first time in the present study.

In Sect. 2 we described the structure of the SC simulated. The first part of Sect. 3 is devoted to the absorptance and optimization of the geometrical parameters of SC based on Si NWs coated by CZTS to maximize the ideal short circuit current. The results obtained were compared, in the second part, to that of SC with CZTSe shell. The third part is reserved to study the SC with a shell composed of CZTSe and CZTS layers. The fourth part is reserved to study the variation of the ideal current with the incident angle of the sunlight. In Sect. 5, we studied the effect of antireflection coating on the ideal short circuit current.

### 2 Device setup

The structure of the solar cell, with a square periodic array of NWs, investigated in this article is shown in Fig. 1a. The NWs have n-Si core used as a buffer layer and coated by a thin CZTS or/and CZTSe absorber layer. The NWs are deposited on n-Si seed layer of 0.15 µm thickness. The upper surface of the Si-cores is covered by a thin layer of CZTS. The thickness of this layer is kept constant in all calculations (20 nm) because this paper aims to study the NWs SC with radial junction and if the upper surface isn’t thin the SC will be with axial and radial junctions. The Si seed layer is covered by a thin CZTS or CZTSe absorber layer, of 20 nm thick, to connect all the absorber layers (blue cylinders in
Fig. 1  a Structure of a period of the investigated solar cells. H, D, p, and r_{cover} denote the height of the NWs, the diameter of the NWs, the array period, and the thickness of the CZTS or CZTSe layer covering the lateral surface of the NWs respectively. b Structure of the planar solar cell based on the same materials.
Fig. 1a) to the upper device contact (not shown) which is deposited on this thin layer. The n-Si seed layer is electrically connected to the device contact by a 0.3 µm FTO layer.

A schematic of a planar solar cell (PSC), used to assess the improvement of the investigated solar cells caused by the use of the NWs configuration, is shown in Fig. 1b.

Finally, we note that the optical constants of Si, CZTS, CZTSe, and FTO, used in the simulation were taken from references (Palik 1998; Gorji 2014; Cozza et al. 2016; Thomas et al. 2020). In Fig. 2, we plotted the variation of these optical constants with the wavelength.

3 Results and discussion

3.1 CZTS NWs-solar cell

3.1.1 Absorptance

To study the evolution of the absorptance of the NWs solar cell with the geometrical parameters,

we presented in Fig. 3 the absorptance spectrum obtained for different values of the thickness of CZTS layer covering the lateral surface of the NWs ($r_{\text{cover}}$) and the ratio between array period $p$ and the diameter $D$ of the coated NWs. The height of the NWs is 5 µm. We remark that the absorptance spectra present many resonances and these are more pronounced for larger $r_{\text{cover}}$. On the other hand, we remark that the absorptance is strongest for $r_{\text{cover}} = 80$ nm and $p/D = 2$. To interpret this result, we present in Fig. 4, the maps of

![Fig. 2 Optical constants used in the simulation (Palik 1998; Gorji 2014; Cozza et al. 2016; Thomas et al. 2020)](image-url)
the modulus of the component $E_x$ of the electric field at a light wavelength ($\lambda$) of 0.5 $\mu$m for the values of $p/D$ and $r_{cover}$ used in Fig. 3. We note that in the case of $p/D = 2$ and $r_{cover} = 80$ nm, the light is efficiently confined inside the NWs, unlike other cases where the intensity of the electric field is important outside the NWs. This is related to the NWs array effect which is strongest when the NWs are closest.

### 3.1.2 Optimization of the geometrical parameters

The geometrical parameters (period, the thickness of the absorber layer as well as the NWs height) were optimized to maximize the ideal short circuit current created in the absorber layer assuming that every generated electron–hole pairs are collected. This current is estimated by:

$$J_{ph} = J_{ph}^w - J_{ph}^{Si}$$  \hspace{1cm} (1)

where $J_{ph}^w$ is the ideal short circuit current created in the whole SC and $J_{ph}^{Si}$ is that created in the structure of the SC without the absorber layer. $J_{ph}^w$ and $J_{ph}^{Si}$ are given by:

$$J_{ph}^{w(Si)} = \frac{e}{h} \cdot \int_0^\infty A^{w(Si)}(\lambda) \cdot I(\lambda) \cdot \lambda \cdot d\lambda$$  \hspace{1cm} (2)

Fig. 3 Absorptance spectrum of CZTS NWs-SC obtained for different values of the thickness of CZTS layer ($r_{cover}$) and the ratio between array period $p$ and the diameter $D$ of the coated NWs. The height of the NWs is 5 $\mu$m
Fig. 4 Component $E_x$ of the electric field in CZTS NWs-SC at a light wavelength of 0.5 µm and for the ratio between array period $p$ and the diameter $D$ of the coated NWs (the thickness of CZTS layer) of 2 (80 nm) (a), 2 (400 nm) (b), and 4 (80 nm) (c). The height of the NWs is 5 µm. The white lines are guides for the eyes to show the underlying nanowire structure described in Fig. 1.
where $A_w^{(Si)}(\lambda)$ is the wavelength-dependent optical absorptance, $I(\lambda)$ denotes the ASTM AM1.5G solar irradiance taken from Ref. (ASTM 2020), $e$, $h$, and $c$ are fundamental physics constants: electron charge, Plank constant, and light celerity, respectively. The integration has been performed every 0.01 µm from 300 nm to the wavelength of the threshold of absorptance of the absorber layer ($\lambda_g = 0.826$ µm for CZTS and 1.239 µm for CZTSe). We chose to begin the integration from 300 nm because the solar power is very weak below this wavelength. To validate our calculations, we calculated $J_{ph}$ for the values of the geometrical parameters used in Peksu and Karaagac (2019) which investigated experimentally NWs SCs similar to that investigated in this paper. The values of $r_{cover}$ and the height of the NWs are 0.6 µm and 3.5 µm respectively. We estimated from SEM images that the ratio between array period $p$ and the diameter $D$ of the coated NWs is of the order of 2. The experimental value of $J_{ph}$, reported in Peksu and Karaagac (2019), is 9.6 mA/cm$^2$. Our calculated value is 13.4 mA/cm$^2$. Given that in the calculation of $J_{ph}$ we assume that every generated electron–hole pairs are collected, we can conclude that our calculation is in good agreement with the experimental results reported by Peksu and Karaagac (2019). On the other hand, Mihailetchi et al. (2004) shows that only 60% of the generated bound electron–hole pairs are dissociated and contribute to the short-circuit current. The ratio $(9.6/13.4 = 71\%)$ is then in good agreement with this experimental value.

To optimize the geometrical parameters, we calculated $J_{ph}$ as a function of the thickness of the absorber layer ($r_{cover}$) and the ratio between the array period and the diameter of the coated NWs ($p/D$) for different values of Si NWs height ($H$). In Fig. 5a, we presented the mapping obtained for $H = 3$ µm. The maximum value of $J_{ph}$ (23.7 mA/cm$^2$) is obtained for the optimal values of $r_{cover} = 82$ nm and of $p/D = 2.01$. To interpret the existence of this maximum, we presented in Fig. 5b the evolution with $r_{cover}$ and $p/D$ of the ratio of the absorber volume (volume of CZTS) and the volume of the period ($v_a/v_p$).

$$v_a = \pi \left[ (R_s + r_{cover})^2 - R_s^2 \right] H$$
$$v_p = p^2 H$$

where $R_s$ is the radius of the Si NWs.

We remark the absence of a maximum in the obtained mapping. We deduce that the existence of the maximum in $J_{ph}$ mapping is related to NWs effect.

Figure 5c shows the evolution with $H$ of the optimal values of $r_{cover}$ and $p/D$ that give the maximal value of $J_{ph}$ for a given value of $H$. We note that the optimal value of $r_{cover}$ (82 nm) is independent of $H$. In contrast, the optimal value of $p/D$ increases from 2 to 3 when $H$ varies from 1 to 5 µm and remains constant for the greater value of $H$. This increase is explained by the fact that with increasing $H$, we need less absorber material, consequently a greater $p/D$ ratio, to reach the maximum value of $J_{ph}$.

Figure 5d shows that the maximal value of $J_{ph}$ saturates at about 24 mA/cm$^2$ and the enhancement of $J_{ph}$ from $H = 3$ µm isn’t important (about 1%). Thus, the optimal value of $H$ is 3 µm. The optimal values of $p/D$ and $r_{cover}$ corresponding to this value of $H$ are 2 and 82 nm respectively.

In the following, we compare the optimal value of $J_{ph}$ to the one of a P SC (Fig. 1b) involving the same amount of materials (CZTS and Si). We obtained a value of 17 mA/cm$^2$ for $J_{ph}$ created in the CZTS layer (without taking into account the $J_{ph}$ created in Si layer). Then, the optimal value of $J_{ph}$ of the NWs SC (24 mA/cm$^2$) is greater by about 41% than the one of P SC. This improvement of $J_{ph}$ added to the improvement of the collection
of generated minority carriers in CZTS layer, due to the radial geometry of the NWs SC, shows the superiority of the NWs SC.

3.2 CZTSe NWs-solar cell

In this section, we present the results obtained when using CZTSe as an absorber instead of CZTS. As shown by Fig. 6, the CZTSe solar cell absorbs very efficiently for a wavelength smaller than 1.1 µm. In Fig. 7, we present the evolution as a function of Si NW height of the optimal values of the thickness of CZTSe layer ($r_{\text{cover}}$) and of $p/D$ and the maximal value of $J_{\text{ph}}$ obtained for the optimal values of $r_{\text{cover}}$ and $p/D$. We remark that $J_{\text{ph}}$ saturates at about 41 mA/cm$^2$ and the enhancement of $J_{\text{ph}}$ from $H = 6$ µm is small (about 1%). Thus, the optimal value of $H$ is about 6 µm. This corresponds to optimal values of $r_{\text{cover}}$ and $p/D$ of 102 nm and 2.98 respectively. We remark that the saturation
value of Jph is much larger in the case of CZTSe SC than in the case of CZTS SC. This is explained by the strong absorptance of CZTSe for wavelength between 0.826 and 1.236 µm, as shown by Fig. 6, that isn’t the case of CZTS. On the other hand, the NW height of saturation of Jph is larger in the case of CZTSe SC than in the case of CZTS SC. Indeed, the penetration depth increases with wavelength and CZTSe absorbs long wavelengths, longer than 826 nm, that aren’t absorbed by CZTS.

On the other hand, the value of Jph of a P SC (Fig. 1b) involving the same amount of materials is 21 mA/cm² (without taking into account the Jph in Si layer). Then, the
maximal value of Jph of the NWs SC (41 mA/cm²) is greater by about 95% than the one of P SC.

Given previous results, CZTSe NWs SC is more performant than CZTS NWs SC, but in this section, we didn’t take into account the heat loss of a part of the energy of generated carriers in CZTSe (Dharmadasa et al. 2013; Contreras et al. 1996). Indeed, an important part of the photons of the sunlight has energy larger than CZTSe bandgap. Then, a part of their energy is wasted as heat. Consequently, this process reduces the efficiency of the cell. To avoid this problem, we propose in the following section a graded absorber SC.

3.3 Graded absorber solar cell

In this section, we replace the uniform CZTS or CZTSe shell by an upper CZTS shell and a lower CZTSe shell. The height of each shell is the optimal height found in the previous sections. In other words, 3 µm for CZTS shell and 6 µm for CZTSe shell. In this structure, most the photons with larger energy will be absorbed by CZTS layer. So, the amount of loss will be reduced.

In Fig. 8 we present the absorbance spectrum of the gradient SC obtained for \( p/D = 3 \) and \( r_{\text{cover}} = 80 \) nm. We remark that for a wavelength smaller than 1.1 µm, the absorbance is almost 1.

In Fig. 9, we present the map of the modulus of the component \( E_x \) of the electric field at light wavelengths (\( \lambda \)) of 0.5 and 1 µm and for the values of \( p/D \) and \( r_{\text{cover}} \) of 3 and 80 nm respectively. We note that for a wavelength of 0.5 µm, the intensity of the field is very weak outside the NWs. On the other hand, for 1 µm and in the region of CZTS shell, the radiant modes are dominant unlike in the CZTSe shell where the light is efficiently confined inside the NWs. Given the refractive index of CZTS and CZTSe are close, these results are

![Absorbance spectrum of gradient NW-SC. The thickness of the absorber layer and the ratio between the array period p and the diameter D of the coated NWs are 100 nm and 3 respectively](image-url)
related to the fact that at 1 µm, CZTS is transparent and CZTSe is absorbent that isn’t the case at 0.5 µm where CZTS and CZTSe are absorbent.

In Fig. 10 we presented a mapping showing the variation of Jph with r_cover and the ratio p/D. We note that the maximal value of the current is 41 mA/cm² and it’s obtained for r_cover = 102 nm and p/D = 2.98. This value, as in the case of CZTSe SC, is greater by about 95% than the one of P SC involving the same amount of materials.
4 Variation of the ideal current with the incident angle of the sunlight

Taking the change in the sun’s incidence angle into account, the relationship between $J_{ph}$ with the incident angle of the sunlight for the gradient solar cell is illustrated in Fig. 11. The angle 0 corresponds to the normal incidence. The values of the geometrical parameters are optimum. We remark that $J_{ph}$ decreases slowly for incident angle smaller than 60° and it remains greater than 37 mA/cm$^2$. Then, $J_{ph}$ decreases rapidly. We conclude that the gradient SC still has an important ideal current when the incident angle doesn’t exceed 60°.

5 Effect of antireflection coating

In this section, we study the effect of Al$_2$O$_3$ antireflection coating (ARC) layer on $J_{ph}$. The choice of Al$_2$O$_3$ is based on previous work (Melliti 2021) that showed that Al$_2$O$_3$ is appropriate to solar cells similar to that studied in this paper and where the CZTS layer is the upper layer of the solar cell. In Fig. 12 we plotted the difference between $J_{ph}$ obtained with and without ARC layer (Al$_2$O$_3$). We remark that the difference is about 1 mA/cm$^2$ which is negligible (optimal value of $J_{ph}$ is 41.4 mA/cm$^2$). This result can be explained by the fact the upper surface of the CZTS layer (the CZTS layer that cover the lateral surface of Si NWs) is small compared to the surface of the period that isn’t the case of the SC studied in Melliti (2021). This interpretation is confirmed by the result of the calculation of $J_{ph}$ of planar cell with Al$_2$O$_3$ ARC where the surface of CZTS exposed to sunlight covers the whole solar cell surface. We found that the increase of $J_{ph}$ caused by the antireflection coating is about 14%.

![Graph showing variation of ideal current density with incident angle](image-url)

**Fig. 11** Variation of the ideal short circuit current density ($J_{ph}$) of the gradient solar cell with the incident angle of the sunlight. The values of the geometrical parameters are optimum.
In this article, we optically simulated a solar cell with core (Si)/shell (CZTS or and CZTSe) vertically-aligned NWs array to optimize the structural morphology. An optimum value of 41 mA/cm² has been found when the NWs are coated by an upper 3 µm-CZTS shell and a lower 6 µm-CZTSe shell. This configuration offers an excellent absorptance of the sunlight and minimizes heat loss. The optimal shell thickness and the ratio of period and NWs diameter are 102 nm and 2.98 respectively. The obtained value of $J_{ph}$ is almost twice as large as that of a planar solar cell with the same amounts of used materials. Furthermore, the ideal short circuit current density decreases slowly with the incident angle below 60°. We conclude that the investigated SC is a good candidate for the SCs based on semiconductors nanowires.

**Fig. 12** The difference of ideal short circuit current densities ($J_{ph}$) computed for gradient SC with and without Al₂O₃ antireflection coating as a function of the thickness of absorber layer ($t_{cover}$) and the ratio between the array period $p$ and the diameter $D$ of the coated NWs. The 55 data points map has been linear interpolated on a 182 times larger grid

### 6 Conclusion

In this article, we optically simulated a solar cell with core (Si)/shell (CZTS or and CZTSe) vertically-aligned NWs array to optimize the structural morphology. An optimum value of 41 mA/cm² has been found when the NWs are coated by an upper 3 µm-CZTS shell and a lower 6 µm-CZTSe shell. This configuration offers an excellent absorptance of the sunlight and minimizes heat loss. The optimal shell thickness and the ratio of period and NWs diameter are 102 nm and 2.98 respectively. The obtained value of $J_{ph}$ is almost twice as large as that of a planar solar cell with the same amounts of used materials. Furthermore, the ideal short circuit current density decreases slowly with the incident angle below 60°. We conclude that the investigated SC is a good candidate for the SCs based on semiconductors nanowires.

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