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Improvement of the solar cell efficiency by the ZnO nanoparticle layer via the down-shifting effect

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ABSTRACT

A down-shifting material can generate one low-energy photon for every one incident high-energy photon. When such a material is placed on the front side of a photovoltaic solar cell, it has the potential to enhance the overall efficiency of the PV device by emitting photons in the spectral range where the solar cell efficiency is higher. This paper examines the application of ZnO nanoparticles as a luminescent down-shifting layer (LDSL) on the Si-based, CIGS and CdTe photovoltaic devices. The experimental results measured on a Si-based photovoltaic cell with a top luminescent down-shifting layer are analyzed.

Theoretical solar cells performances were simulated using the SCAPS program. The elaborated electrical and optical models take into account the photoluminescence of the ZnO nanoparticle top layer. The obtained external quantum efficiency (EQE) and I - V characteristics were analyzed in order to estimate the impact of the photoluminescent down-shifting layer on the final efficiency of the Si, CIGS and CdTe solar cells. Contrary to the EQE curves, the I - V characteristics of the CIGS and CdTe solar cells are strongly affected by the presence of the photoluminescent down-shifting layer on their top.

1. Introduction

1.1. Down-shifting and down-conversion in photovoltaics

Third generation solar cells (SCs) are based on fabrication concepts, which should potentially permit to overcome the Shockley-Queisser limit [1]. It is estimated at 33.7% efficiency for a single p-n junction made of a material having a bandgap of 1.1 eV (like Si). Nevertheless, current single crystalline silicon SCs deliver a conversion efficiency of only 27.6% [2]. The SC's efficiency is limited by the factors such as the optical absorption, surface reflection, carrier transport and carrier collection.

The third generation solar cells [3] are being developed, as they should potentially permit to overcome the Shockley-Queisser limit. The 3rd generation concepts include multijunction solar cells, multiple absorption path solar cells (multiple exciton generation), multiple energy level solar cells (localized levels or intermediate energy bands), hot carrier solar cells,

thermophotovoltaics (TPX), photon up-conversion and down-conversion technologies, etc.

The approach based on the variant of the down-conversion is presented, namely the energy down-shifting (DS), in which high energy photons are converted into lower energy ones (see Fig. 1), better matching the Si-based SC's active layer absorption spectrum, to address the issue of the lower efficiency of these SCs in the UV spectral domain when compared to the visible spectral zone. The UV-wavelength response of a standard Si solar cell is low due to the front surface recombination of the hot photogenerated carriers. This can be improved by the application of a luminescent down-shifting layer (LDSL) placed on the front of a solar cell, without a significant modification in the SC's fabrication process, as it should permit to increase its efficiency with a minimal cost. The structure of the solar cell with a luminescent down-shifting layer placed on its top is presented in Fig. 2.

2. Materials

2.1. ZnO nanoparticle as down-shifting layers in solar cells

The photoluminescent down-shifting uses the optical excitation through intermediate bandgap defect levels in order to convert

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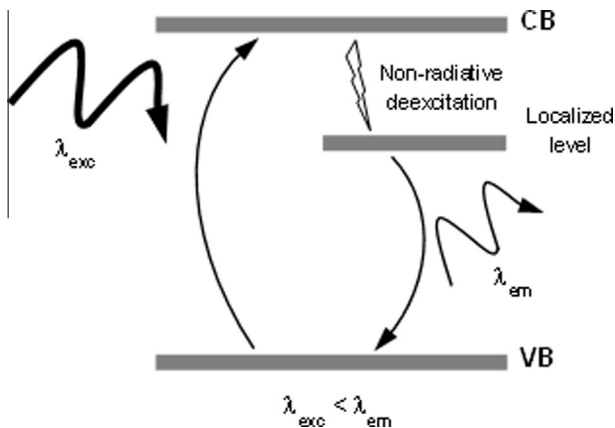


Fig. 1. The mechanism of the down-shifting process; VB is the valence band, CB - the conduction band, λ_{exc} is the excitation wavelength; non-radiative deexcitation to the localized level in the bandgap via the emission of phonons is shown; the radiative emission from the intermediate energy level at the λ_{em} wavelength follows the excitation.

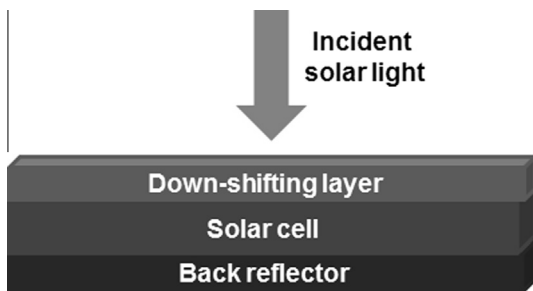


Fig. 2. Schematic diagram of the solar cell with a down-shifting layer placed on its front side.

efficiently high energy photons into lower energy ones. The ideal down-shifting material must possess a large Stokes shift and have a high luminescence quantum yield.

Recently semiconducting nanocrystals [4] and nanoparticles (NPs) [5] found their application as down-shifters for the enhancement of the SC's spectral response. Nanoparticles permit to achieve a high concentration of the intermediate energy levels in the bandgap, necessary for efficient DS and at the same time they can act as an antireflective layer [6]. ZnO turns out to be a very attractive material for DS applications, as it is non-harmful and abundant, benefits from cheap and easy fabrication methods, has a wide bandgap (3.4 eV) and a higher absorption coefficient than other wide bandgap materials such as GaN. Moreover, it has been widely used in photovoltaic devices: ZnO:Al (AZO) layers are applied as transparent contact materials in CIS/CIGS [7], organic [8] and hybrid solar cells [9]. Al-doped ZnO layers have been also used as transparent electrodes in the silicon SCs [10,11] and as a refractive index matching layer (antireflective coating) [12].

This motivated our study of the down-shifting properties of the ZnO_x nanoparticles fabricated via the Low Energy Cluster Beam Deposition (LECBD) method and their application as a LDSL on solar cells. The LECBD setup is presented elsewhere [13]. In our experiments, LDSL containing ZnO_x nanoparticles of less than 5 nm in diameter was deposited [14]. Obtained ZnO_x nanoparticle layers were studied as a function of the oxygen partial pressure (OPP) applied during the nanoparticle fabrication process. It was observed that there exists an optimal oxygen pressure introduced

during the LECBD process, which permits to obtain the highest visible photoluminescence emission from ZnO_x NPs, necessary for an efficient down-shifting [13,14].

The AFM scan made in a tapping mode of the ZnO nanoparticle layer deposited by LECBD method is presented in Fig. 3. Scan size is 5.0 μm × 5.0 μm. The obtained layers were quite homogeneous and relatively flat (with the roughness of about 45 nm), though agglomerates of ZnO_x NPs were present in some places on the layer surface.

Considering presented features of the ZnO_x NPs, one may expect that these particles are efficient down-shifters as they strongly absorb the UV light ($\lambda < 400$ nm), where the Si-based solar cell spectral response (SR) is low, and re-emit photons at longer wavelengths ($\lambda > 425$ nm), where the typical Si-based SC's SR increases. This efficiency enhancement may be even more significant for thin-film solar cells based on chalcopyrites (CuFeS₂) and II–VI compounds (see Fig. 4).

3. Calculations, experiments and discussion

3.1. Simulations of the external quantum efficiency of the standard Si, CIGS and CdTe solar cells

The simulations of the external quantum efficiency (EQE) of an ideal Si (without any reflective layer and without any LDSL), an ideal Copper Indium Gallium Selenide (CuIn_{1-x}Ga_xSe or CIGS with an intrinsic ZnO layer as a contact) and an ideal CdTe (with an ITO contact layer) solar cells were performed using the Solar Cell Capacitance Program (SCAPS) [15]. The results presented in Fig. 4 show apparent EQE deficiencies of 5–8% for the CIGS cell and of even 40% for the CdTe cell in the UV and short visible wavelength range, in comparison to a standard Si cell. For all photovoltaic cell structures this problem may be partially solved by reducing the emitter thickness and the junction depth, but only to a limited extent due to the technological problems [16].

The theoretical EQE of the Si-based ideal single junction is very high as it depends only on the recombination velocity at the front electrode. Thus the EQE presented in Fig. 4 suggests that in the case of the Si-based solar cell it may be less interesting to apply a LDSL layer to improve the EQE in the UV and blue spectral region, than in the case of the CIGS and CdTe solar cells, for which a huge increase of the efficiency is expected.

3.2. Simulations of the EQE of the Si, CIGS and CdTe solar cells with a LDSL

In order to determine the influence of the presence of a passive antireflective ZnO bulk layer or of a LDSL on the performances of each type of solar cells, a series of simulations using the SCAPS program was also performed. These simulations were based on the models taking into account the real electric properties of the solar cells. Moreover, ZnO_x NPs luminescence spectrum, measured by the photoluminescence excitation (PLE) method [17] was incorporated into the AM 1.5 G curve to model the performances of real solar cells with a top LDSL. For the simulation purposes, the AM 1.5 G spectrum was replaced by the artificial enlightenment to which the PLE effect was added. The electrical resistivity and optical transmittance of the ZnO_x NPs layer were also taken into account. The first approach was to verify the influence of the modified illumination spectrum on the EQE characteristics of each solar cell. The described models were applied for various types of cells. The results of the EQE characteristics of the Si, CdTe and CIGS cells with a ZnO bulk antireflective layer on their top or with a ZnO_x NPs LDSL on their front are presented in Fig. 5.

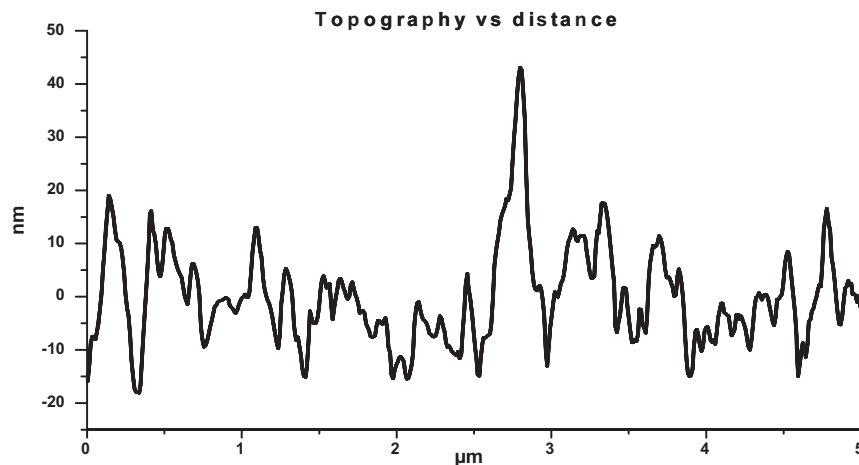
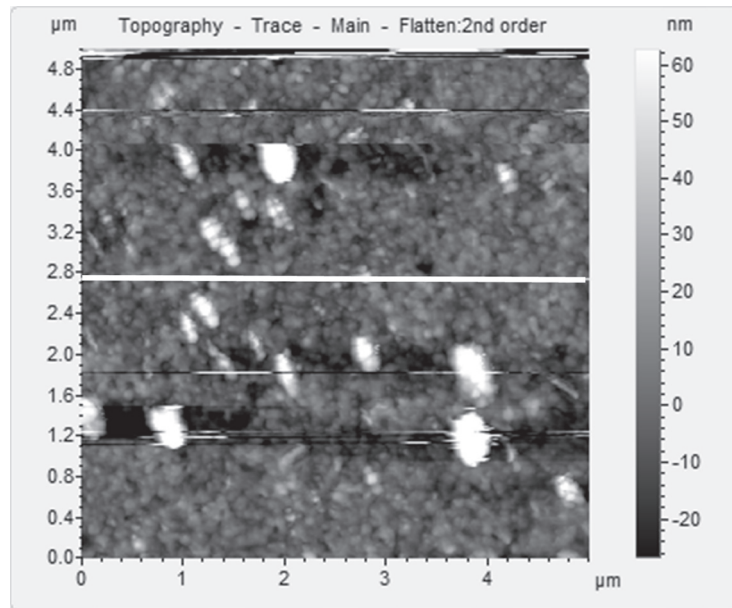


Fig. 3. The AFM image and the topography of the ZnO_x nanoparticle layer deposited by the LECBD technique on the top of an Si solar cell.

If the solar cell EQE simulations for each type of cell with a ZnO bulk layer or with the ZnO_x NPs LDSL on their top are compared between them, it may be observed that the presence of the ZnO_x NPs does not change the sensitivity of each photovoltaic cell to the solar light. In the case of the Si solar cells, a passive bulk ZnO layer placed on the top of a cell acts as an optical filter, significantly modifying the absorption in the short and mid-range spectral zones. It is important to note that only in the case of CdS/CdTe and CIGS SCs the ZnO layers are used as the transparent conductive oxide (TCO) emitter contact, since using this type of an electrical contact with even on a non-passivated silicon SC is not beneficial for its final operating performances.

3.3. Practical realization of a crystalline Si solar cell with a ZnO NPs down-shifting top layer

In order to verify the results obtained from the simulations, a series of crystalline Si cells with a 25 cm² area and an emitter layer of 800 nm in thickness and the resistivity of ~35 Ω/square were manufactured. Some of the fabricated cells were passivated with a top SiO₂ layer, on some other only the LDSL of ZnO NPs was deposited on their top using the LECBD technique. The EQE of all

manufactured devices was measured. Fig. 6 presents the results of the EQE measurements on the Si solar cell with a passivating SiO₂ layer and with a ZnO_x NPs LDSL. A real and significant EQE enhancement in two spectral regions (visible and near infrared) was achieved in the case of the Si SCs covered by a ZnO_x NPs layer (Fig. 6).

It can be noticed that the obtained EQE characteristics is modified in three specific spectral regions. For short and medium (from the UV up to 525 nm) wavelengths the EQE slightly decreased due to the absorption of light in the down-shifting layer. From around 525 nm up to 875 nm the ZnO_x luminescence is negligible and only the antireflective effect of the ZnO_x NPs layer improves the EQE, with average value of 2.9%. For low-energy photons from 875 nm up to 1100 nm the luminescence effect is also insignificant, however a proper refractive index of the ZnO_x NPs layer is a way for implementing a layered stack with increasing indexes, which results in a further improvement of EQE, with an average value of 8.5%. Thus, though the EQE improvement due to the luminescent properties of the ZnO_x NPs layer could not be observed, probably due to too low luminescence intensity of the LDSL, the real efficiency enhancement due to the antireflective effect was observed.

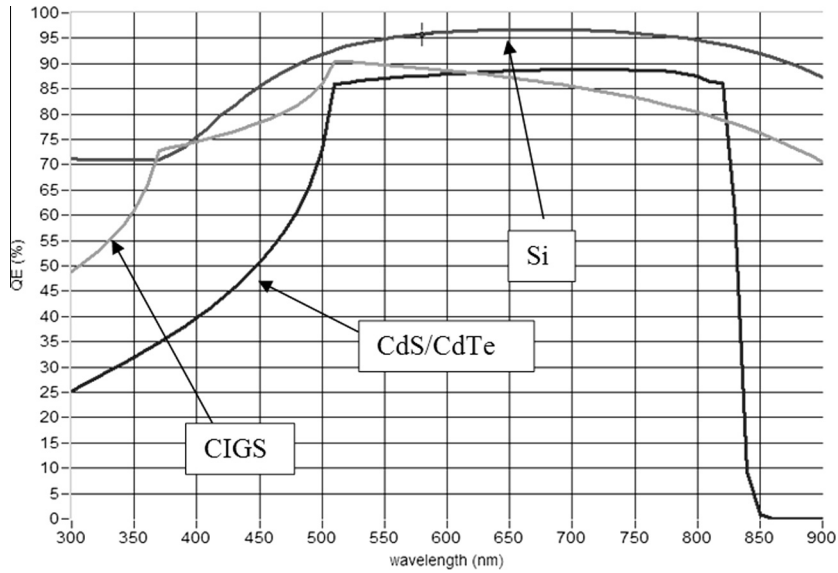


Fig. 4. Numerical SCAPS simulation of external quantum efficiency (marked as QE in the graph) for a standard Si cell (dark grey curve), the CIGS cell (light grey curve) and the CdTe cell (black curve) in function of the incident solar light wavelength.

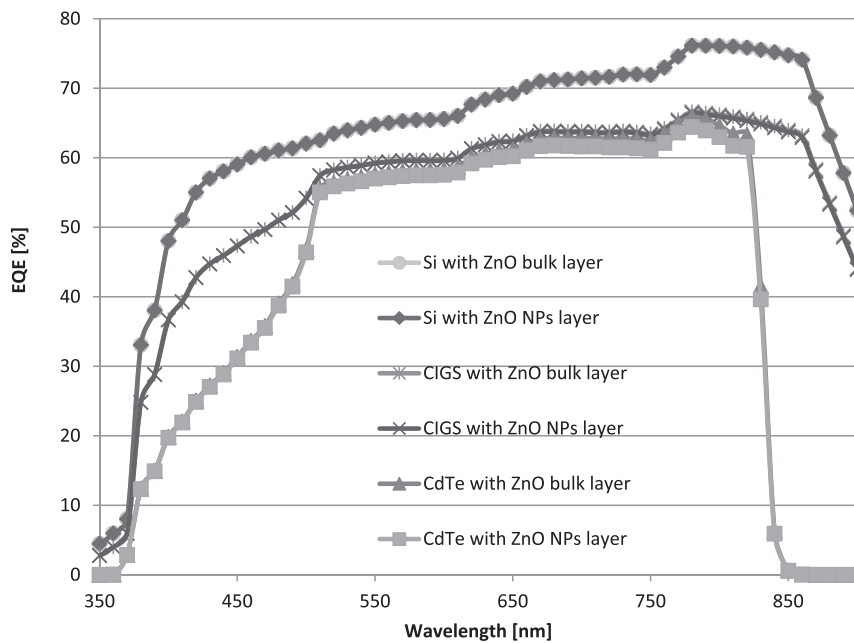


Fig. 5. EQE characteristics simulated using the SCAPS program of the Si, CIGS and CdTe solar cells, covered or by a bulk ZnO passive antireflective layer (marked as “with ZnO bulk layer” in the legend) or by a ZnO_x NPs LDSL (marked as “with ZnO NPs layer” in the legend), taking into account the modification of the solar illumination spectrum by the presence the DS layer in the structure of the cell.

3.4. The improvement of *I-V* characteristics of the solar cells with a ZnO NPs top layer

In order to fully characterize the impact of the LDSL on the final efficiency of the solar cells, their electrical performances should also be calculated. The simulations of the *I-V* characteristics based on the elaborated models taking into account the photoluminescence of the ZnO_x NPs were performed using the SCAPS program. The current–voltage characteristics for three types of cells (Si, CIGS and CdTe) with a ZnO bulk layer or with a constructed model of the ZnO_x NPs layer on their top are shown in Fig. 7.

To perform a complete analysis of the modification of the solar cell performances due to the presence of the LDSL on the top of each solar cell, the efficiency (η), the fill factor (FF) and the short

circuit current (J_{SC}) were calculated using the *I-V* characteristics. Table 1 presents the summary of the electrical parameters of each type of solar cell.

From the obtained SCAPS simulations of the EQE and *I-V* characteristics and the measurement of the EQE (in the case of the Si solar cell) the benefit originating from the presence of the ZnO_x NPs layer in the solar cells structure was confirmed. In all structures, the efficiency and the current density were improved for the solar cells covered with the ZnO_x NPs LDSL. The smallest increase in the efficiency was obtained for the Si crystalline cell, however for CIGS and CdTe cells the relative efficiency growth of 5.1% and 15.1% was achieved, respectively. Only in the case of CdTe solar cell, a small drop in the FF value was observed, which is typical for CdTe cells, when the increase of the short circuit current

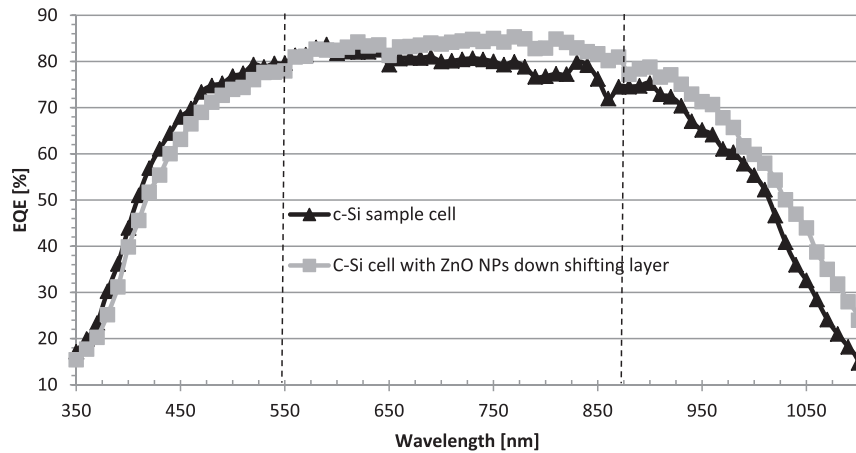


Fig. 6. EQE characteristics of test Si SCs cell without (grey squares) and with (black triangles) down-shifting layer of the ZnO_x NPs placed on the top of a cell.

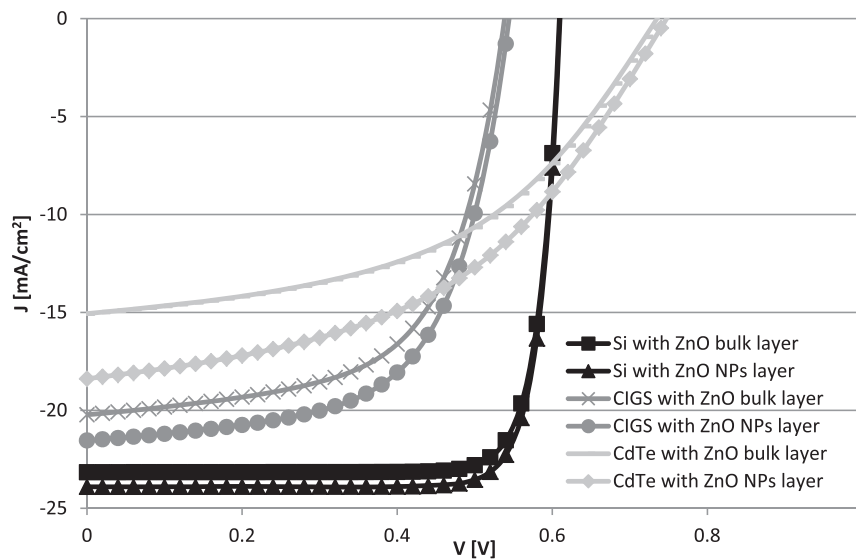


Fig. 7. The simulations of the I - V characteristics obtained using the SCAPS program of the Si, CIGS and CdTe solar cells with ZnO passive antireflective layer (marked as “with ZnO bulk layer” in the legend) or with a ZnO_x NPs down-shifting layer (marked as “with ZnO NPs layer” in the legend) on their top, under AM 1.5 G illumination.

Table 1

Comparison of the influence of the ZnO bulk layer and the ZnO_x NPs layer on the electrical parameters of the Si, CdTe and CIGS solar cells.

Cell type	η (%)	FF (%)	J_{sc} (mA/cm ²)
Si cell with a bulk ZnO layer	11.68	82.88	23.16
Si cell with a ZnO_x NPs layer	11.69	82.90	23.90
CIGS cell with a bulk ZnO layer	6.66	61.16	20.22
CIGS cell with a ZnO_x NPs layer	7.00	61.88	21.53
CdTe cell with a bulk ZnO layer	5.33	48.12	15.06
CdTe cell with a ZnO_x NPs layer	6.14	46.30	18.39

occurs [18]. As expected, the open circuit voltage (V_{OC}) in the solar cells with ZnO_x NPs LDSL was only slightly affected by the modified solar light spectrum, as it depends mainly on the bandgap of the solar cell’s active material.

4. Conclusions and perspectives

As it can be concluded from the simulations performed with the SCAPS program, the presence of the luminescent down-shifting layer on the top of a solar cell structure has a little influence on EQE characteristics. The EQE depends mostly on the cell technological parameters such as the emitter thickness and the junction

depth. The slight increase of the experimental EQE values observed in the case of a real Si solar cell covered with a ZnO_x NPs LDSL is mainly caused by the matching of the refractive indexes (antireflective behavior) and not due to the luminescence of the ZnO_x NPs, as the EQE improvement is observed out of the absorption range of the ZnO_x NPs, which is in the UV spectral domain.

Unlike the EQE curves obtained, the simulated I - V characteristics of the solar cells are strongly affected by the presence of the photoluminescent down-shifting layer on their top. The modification of the AM 1.5 G solar emission spectrum by the luminescent emission of the ZnO_x NPs permits to put in evidence the change in the shape of the I - V characteristics, as well as of the solar cell final efficiency and the value of the FF. It turns out that the influence of the luminescent layer on the efficiency of a silicon cell is the smallest and, with imperfect manufacturing technology, may even lead to the drop of the total efficiency. This may be explained by the fact that the Si cells “naturally” have relatively high external quantum efficiency in the short wavelength range. In this case a down-shifting layer placed on the top of the Si cell does not increase significantly the quantity of the photogenerated carriers, while acting as an optical filter, partially absorbing the UV part of the solar spectrum, which decreases the photogenerated current. Additionally ZnO layers are not usually used as the antireflective coating of silicon solar cells, thus further implementation of

ZnO_x NPs layers as a down-shifter in the case of these solar cells is put in question. On the contrary, the efficiency of thin film solar cells based on direct bandgap materials such as CdTe, may be greatly enhanced by the introduction of the down-shifting layer into their structure. Even a slight increment of the quantity of light incident onto the solar cell falling into the spectral absorption domain of the SC's active material increases the quantity of the photogenerated carriers and thus the overall efficiency of the solar cell. Experimental tests on real CIGS and CdTe solar cells with a LDSL top layer will be performed in order to confirm the results obtained from the simulations and to evaluate the influence of the ZnO_x NPs layer on the *I*-*V* characteristics. As far as the solar cell fabrication is concerned, many issues such as proper ohmic emitter contacts, ZnO_x NPs layer uniformity and back reflection reduction must be addressed, however a potential efficiency gain estimated from the numerical simulations is promising enough to encourage laboratory tests.

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