

IMPROVEMENT OF SPECTRAL RESPONSE OF SOLAR CELLS BY DEPLOYMENT OF SPECTRAL CONVERTERS CONTAINING SEMICONDUCTOR NANOCRYSTALS

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ABSTRACT: Planar converters containing quantum dots as wavelength-shifting moieties on top of multi-crystalline and amorphous silicon solar cells were studied. The highly efficient quantum dots shift by means of absorption and re-emission, the wavelengths where the spectral response of the solar cell is low to wavelengths where the spectral response is high, in order to improve the conversion efficiency of the solar cell. It was calculated that quantum dots with an emission at 603 nm increase the multi-crystalline solar cell short-circuit current by nearly 10%. Simulation results for planar converters on hydrogenated amorphous silicon solar cells show no beneficial effects, due to the high spectral response at low wavelength. Experimental results on multi-crystalline silicon solar cell however do not confirm these findings.

Keywords: Modelling; Fundamentals; Spectral response

1 INTRODUCTION

Conventional single-junction semiconductor solar cells only effectively convert photons of energy close to the semiconductor band gap E_g as a result of the mismatch between the incident solar spectrum and the spectral absorption properties of the material [1]. Photons with energy E_{ph} smaller than the band gap are not absorbed. Photons with energy E_{ph} larger than the band gap are absorbed, but the excess energy $E_{ph}-E_g$ is not used effectively due to thermalisation of the electrons. Several routes have been proposed to overcome these fundamental spectral losses that can account for as much as 50%. All of these methods or concepts, which are referred to as Third Generation (3G) photovoltaics [2], concentrate on a better exploitation of the solar spectrum, e.g., intermediate band gaps [3], quantum dot concentrators [4] and down- and up-converters [5]. In addition, the recently started European project FULLSPECTRUM aims to better use the full solar spectrum by developing new concepts in the search for a breakthrough in PV technology [6].

Conversion of the incident solar spectrum to monochromatic light would greatly increase the efficiency of solar cells. One simply needs to convert the energy of incident photons such that E_{ph} equals E_g or is slightly larger. This spectral conversion can be in two directions, up- or downward. With spectral down (up) conversion we denote any process that reduces (increases) the photon energy.

Spectral down conversion was suggested in the 1970s to be used in so-called luminescent concentrators that were attached on to a solar cell [7]. In these concentrators, organic dye molecules absorb incident light and re-emit this at a red-shifted wavelength. Internal reflection ensures collection of all the re-emitted light in the underlying solar cells. As the spectral sensitivity of silicon is higher in the red than in the blue, an increase in solar cell efficiency was expected. However, in practice this was not reached as a result of not being able to meet the stringent requirements to the organic dye molecules, such as high quantum efficiency and stability, and the

transparency of collector materials in which the dye molecules were dispersed [7].

Research in this field was revitalized recently through the development of the quantum dot concentrator [4]. Quantum dots (QDs) were proposed for use in luminescent concentrators instead of organic dye molecules. QDs are nanometer-sized semiconductor crystals of which the emission wavelength can be tuned by their size, as a result of quantum confinement [8]. The advantages of QDs with respect to organic dye molecules are their high brightness, stability and quantum efficiency [9]. Quantum dots absorb all the light of a wavelength smaller than the absorption maximum ($\sim E_g$), in contrast to the small-band absorption of dye molecules.

In this paper, we will explore the feasibility of QD use in plastic planar converters on top of solar cells, as a simple and potentially cheap way of employing the principle of spectral down conversion. The effect of small-band emission spectra of QDs on solar cell performance parameters was reported earlier [10] and already showed the potential benefits of QD use. Recently, a 6-% relative increase in conversion efficiency was reported for coating a multi-crystalline silicon solar cell with a converter layer [11]. As QDs have much broader absorption bands than the species used in Ref. [11], the deployment of QDs in planar converters could lead to relative efficiency increases of 20-30%. Also, spectral down conversion employing QDs in a polymer matrix has been demonstrated in a light-emitting diode (LED), where a GaN LED was used as an excitation source (425 nm) for QDs emitting at 590 nm [12].

We describe a simple method that allows for the calculation of modifications of the AM1.5G spectrum due to QD absorption and emission, which includes different QD sizes and concentrations. The modified spectrum is used as input in solar cell simulation programs suited for either crystalline or amorphous silicon. We will determine the optimum QD size (spectral properties) and concentration on the conversion efficiency for standard baseline solar cells manufactured at ECN (mc-Si) and Utrecht University (a-Si:H). Finally,

preliminary results on experimental verification on mc-Si solar cells will be discussed.

2 METHODOLOGY

2.1 Device configuration

The configuration that is studied is depicted in Fig. 1. A plastic layer containing QDs is applied on top of a solar cell. The size of the QDs is chosen such that their emission maximum is in the red part of the spectrum; they thus will absorb both blue as well as green incident light. We implicitly assume that the solar cell has an optimum spectral response in the red. Depending on the QD concentration also unabsorbed blue and green light enters the solar cell. Of course, highly transparent plastics are to be used.

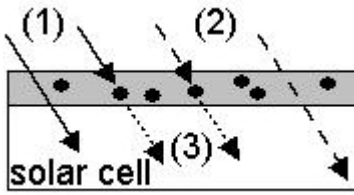


Figure 1: Schematic drawing of the studied configuration. A plastic layer containing QDs is applied on top of a solar cell. Both blue (1) and green (2) light is absorbed by the QD and re-emitted in the red (3), which is subsequently absorbed in the solar cell.

2.2 Solar cell simulation

The standard baseline $n-p-p^+$ mc-Si cell has parameters that are typical of low-cost commercial products, including series resistance, shunt conductance and a second diode [13]. It measures $10 \times 10 \text{ cm}^2$ in area, has a thickness of $300 \mu\text{m}$, and has a shallow diffused emitter of $50 \Omega/\text{sq}$. The front broadband reflectance is 9% across the solar spectrum, as a result of the front surface anti-reflection coating (71-nm thick silicon nitride with a refractive index $n=2.1$). The thickness of the back-surface field (BSF) is $9 \mu\text{m}$ and has a p^+ doping level of $4 \times 10^{18} \text{ cm}^{-3}$. The performance of the solar cell is simulated with the simulation programme PC1D (version 5.8) [14]. The calculated performance parameters (short-circuit current I_{sc} , open-circuit voltage V_{oc} , fill factor FF , and efficiency η) are 31.2 mA/cm^2 , 0.603 V , 0.771 , and 14.5% , respectively.

The standard baseline a-Si:H cell has the usual layer configuration glass/TCO/p-a-SiC:H/i a-Si:H/n a-Si:H/Ag, with layer thicknesses of 1 mm , $1 \mu\text{m}$, 8 nm , 500 nm , 20 nm , and 200 nm , respectively [15]. TCO is a transparent conductive coating, such as SnO_2 . Activation energies for n and p layer are 0.24 eV and 0.46 eV , respectively. Solar cell performance is simulated with the programme ASA (version 3.3) that includes specific features of amorphous semiconductors, such as sloped band edges and mid-gap dangling bond density models [15]. The calculated performance parameters I_{sc} , V_{oc} , FF , and η are 11.9 mA/cm^2 , 0.814 V , 0.675 , and 6.55% , respectively.

2.3 Spectrum conversion

In the configuration shown in Fig. 1, the incident AM1.5G spectrum converted to amount of photons per wavelength $\Phi_s(\lambda)$ will be modified by absorption of photons. First, the amount of absorbed photons $\Phi_a(\lambda)$ is determined from the QD absorption spectrum, which depends on the QD size, their concentration in the

converter layer, and the thickness of this layer. This absorbed amount is subtracted from the AM1.5G spectrum: $\Phi_{sa}(\lambda) = \Phi_s(\lambda) - \Phi_a(\lambda)$.

As the QDs re-emit light at a red-shifted wavelength, the amount of emitted photons $\Phi_e(\lambda)$ is calculated from the QD emission spectrum. To this end, data for quantum efficiency is assumed, as well as the assumption that $\frac{3}{4}$ of the emitted photons is directed towards the underlying solar cell, due to internal reflection in the converter layer [4]. The amount of emitted photons then is added to the already modified AM1.5G spectrum: $\Phi_{sae}(\lambda) = \Phi_{sa}(\lambda) + \Phi_e(\lambda)$. Finally, the resulting spectrum serves as input for the solar cell simulation models.

Absorption of photons is calculated by using the Lambert-Beer equation: the photon flux density $\Phi(x, \lambda)$ after passing a distance x in a film with absorption coefficient $\alpha(\lambda)$ is written as $\Phi(x, \lambda) = \Phi^0(\lambda) \exp[-\alpha(\lambda)x]$, with $\Phi^0(\lambda)$ the incident photon flux density. The exponential term $\alpha(\lambda)x$ equals $\epsilon_i CD$, with ϵ_i the molar extinction coefficient ($\text{M}^{-1}\text{cm}^{-1}$), C the chromophore concentration (M), and D the thickness of the film (cm). The chromophore (QD) concentration varies from the nM to the mM range. The film thickness typically varies between about $1 \mu\text{m}$ and a few mm, see also [10]. The result of the procedure for a QD emitting at 603 nm is shown in Fig. 2, which also illustrates the effect of QD concentration. QD concentrations were varied from $1 \mu\text{M}$ to 1 mM at a converter thickness D of 1 mm . At a concentration of $1 \mu\text{M}$ an appreciable amount of photons is absorbed in the blue part of the AM1.5G spectrum, while the modified spectrum is increased at the QD emission wavelength. For higher concentrations this effect is clearly much stronger. As the product CD determines the amount of spectral change, optimum values for QD concentration are related to the thickness of the converter.

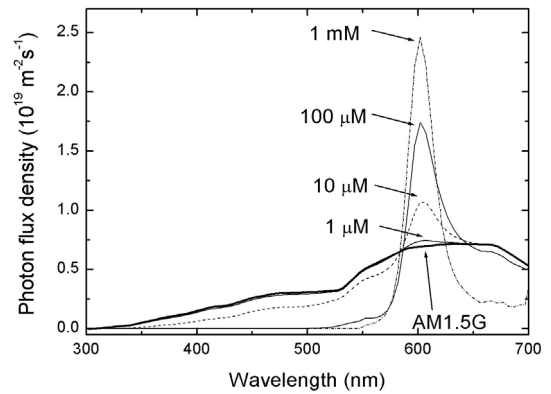


Figure 2: Calculated modified spectra.

2.4 Experimental

Quantum dots (CdSe) of high quantum yield are routinely synthesized in our laboratory following a single-step route using trioctylphosphine and its oxide (TOP/TOPO) and hexadecylamine (HDA) [16]. Typical absorption and emission spectra for the purified QD stock solution in toluene (1.4 mM , quantum yield 40%) are shown in Fig. 3. These spectra have been normalized with respect to the absorption and emission maximum occurring at 594 nm and 603 nm , respectively. The particle diameter is 4.24 nm determined from the relation between absorption maximum and particle diameter reported in literature [16].

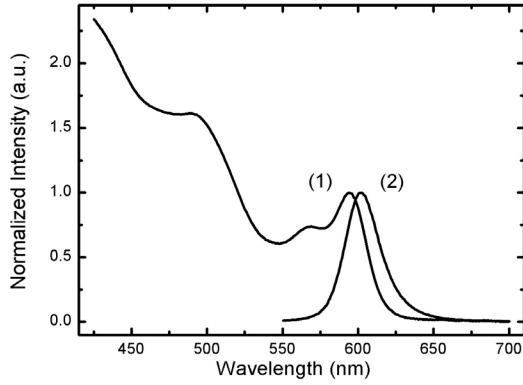


Figure 3: Normalized absorption (1) and emission (2) spectrum of CdSe nanocrystals of 4.24 diameter, capped with TOPO/TOP/HDA.

The CdSe QDs have been dispersed in a polymer/toluene solution. The selected polymer is polylaurylmethacrylate (PLMA), of which it is reported that the quantum efficiency of QDs is retained after dispersion in PLMA [12]. We also found fast (days) luminescence quenching from QDs dispersed in polymethylmethacrylate (PMMA). Various QD/polymer solutions, to which also TOP was added, were coated on top of microscope slides by means of drop (50 μ l) casting at elevated temperature (60 $^{\circ}$ C), and were dried under vacuum. The reduction in volume was about 25 times, while the films remained sticky. Film diameter (dried drop) was about 1 cm. Thickness varied between 100 and 300 μ m, which could be accomplished by adding up to 4 drops of QD/polymer solutions on to already dried drops. An example is shown in Fig. 4.

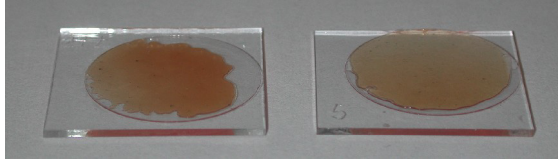


Figure 4: Two PLMA films with incorporated QDs.

The effects on the spectral response of mc-Si solar cells were determined in two ways at the measurement facilities of ECN. First, the glass/polymer samples were placed on top of mc-Si cells, while isopropyl alcohol was used as an index matching intermediate. Thus, the spectral response could be measured. The characteristics of the 5 \times 5 cm² cell were: $I_{sc} = 31.02$ mA/cm², $V_{oc} = 0.605$ V, $FF = 0.764$, $\eta = 14.34\%$. The second way involved direct drop casting of 100 μ l drops on top of a mc-Si solar cell. Thickness was varied by adding up to 3 drops.

3 RESULTS

3.1 Modelling

The optimum centre emission wavelength of QDs in the planar converter on top of a mc-Si solar cell has been found to be around 600 nm [10]. We thus simulated the solar cell performance changes for the QDs emitting at 603 nm for a concentration range from 1 nM to 1 mM. A clear constant increase in short-circuit current of about 6×10^5 %/M is observed up to a concentration of 1 μ M.

Table I. Solar cell performance parameters for the mc-Si solar cell as a function of QD concentration (C_{QD}).

C_{QD} (μ M)	I_{sc} (mA/cm ²)	V_{oc} (V)	FF	P_{max} (mW/cm ²)
0	31.3	0.603	0.771	14.55
1	31.5	0.603	0.770	14.6
10	32.7	0.604	0.768	15.2
100	34.1	0.605	0.766	15.8
1000	33.8	0.605	0.767	15.7

Table II. Solar cell performance parameters for the a-Si:H solar cell as a function of QD concentration (C_{QD}).

C_{QD} (μ M)	I_{sc} (mA/cm ²)	V_{oc} (V)	FF	P_{max} (mW/cm ²)
0	11.9	0.8145	0.675	6.55
10	11.9	0.813	0.675	6.50
100	11.4	0.812	0.671	6.20
1000	10.4	0.810	0.670	5.62
10000	9.27	0.808	0.683	5.11

For higher concentrations the effect levels off, to even decrease at a concentration of 1 mM (not shown). Here, the beneficial effect is counteracted by the increased absorption due to this high concentration. The effect on all solar cell performance parameters is shown in Table I. Clearly, the effects start to occur at 1 μ M. While both short-circuit current and maximum generated power P_{max} follow similar behaviour, the open-circuit voltage and fill factor only slightly decrease.

It should be noted that in practice the results for the highest concentrations (0.1-1 mM) would not be as high as presented here, due to the fact that re-absorption is not taken into account in our simulations. This will lower the amount of emitted photons that enter the solar cell, which will be apparent in a lower peak in the modified spectrum at the QD emission centre wavelength. Nevertheless, a relative increase of near 10% is to our opinion realizable. In addition, as the product of QD concentration and converter thickness CD determines the amount of spectral change, high concentrations can be avoided in converters of larger thickness, as long as CD remains constant.

For the simulation of QDs in the planar converter on top of a-Si:H cells we used QDs of centre emission wavelength of 503 nm, as at this wavelength the strongest effects are expected [10]. The results for the short-circuit current are shown in Table II, for a concentration range from 0.1 μ M to 10 mM. At about a concentration of 10 μ M the effects on short-circuit current start to be noticeable. This concentration is one order of magnitude higher than in the case of mc-Si. Also in contrast to mc-Si, here, the short-circuit current decreases with about 10% for a concentration of 1 mM, in close correspondence to the decrease in spectral intensity (not shown). This apparently has to do with the amount of absorbed photons balanced with the emitted photons in relation to the spectral response.

The aim of applying QDs as wavelength shifters is only sensible when an appreciable difference exists in spectral response between the QD centre emission wavelength and the lower wavelengths. As the spectral response of the a-Si:H solar cell is already high at low wavelengths, beneficial effects, if any, will be small.

Only when the QD quantum efficiency equals unity, and when in addition all emitted photons enter the solar cell, an increase in short-circuit current is observed of about 4% for a concentration of 1 mM.

3.2 Experimental verification

The spectral response of the glass/polymer samples on top of the mc-Si solar cell is shown in Fig. 5. Data for the direct drop casted samples (Q) is shown in Fig. 6. The SR curves for wavelengths above about 600 nm are essentially unchanged, which is to be expected. In contrast, the predicted beneficial effects for the blue response are not corroborated. For all samples, the blue response is lowered with respect to the spectral response of the bare mc-Si cell, which seems related to the amount of absorption. This can be quantified (not shown) by relating SR reduction (e.g., at 500 nm) and the product of QD concentration and thickness CD , which determines the absorbance through Lambert Beer's law. Finally, especially for samples that have large thickness and high concentration the inverse absorption spectrum is reflected in the SR curves.

The discrepancy between predicted and observed effects cannot at present be adequately explained. Further work clearly is necessary. Differences between modelling and experiments may originate from the fact that re-absorption is not taken into account in the modelling, while also the quantum efficiency of the QDs used in the experiments is a factor of 2 lower than assumed in the modelling. In addition, if the product of concentration and thickness is too large there is too much absorption, which lowers the beneficial effects. Possibly, this product is too large in the experiments.

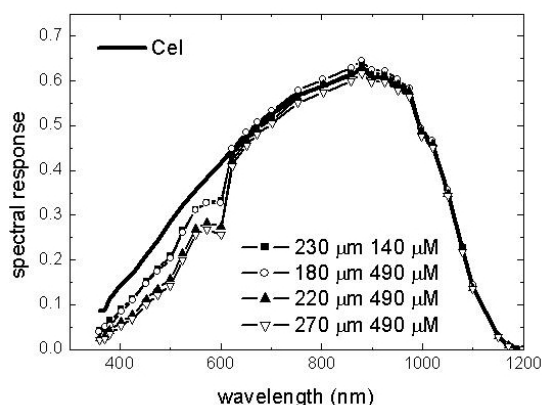


Figure 5: Spectral response for glass/polymer samples.

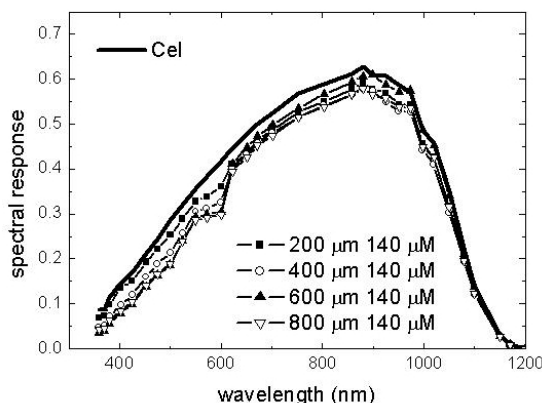


Figure 6: Spectral response for drop casted samples.

4 CONCLUSION

The inclusion of a planar converter that contains wavelength-shifting moieties such as quantum dots should allow for a better use of the solar spectrum. The quantum dots should shift the wavelengths where the spectral response is low to wavelengths where the spectral response is high. Further, losses associated with low quantum efficiency and isotropic emission should be avoided, i.e. striving for near-unity quantum efficiencies and optimising internal reflection.

In this paper we calculated that QDs with a centre emission wavelength of 603 nm included in a planar converter on top of a multi-crystalline solar cell are capable of increasing short-circuit current by nearly 10%. Simulation results for planar converters on hydrogenated amorphous silicon solar cells show no beneficial effects, due to the high spectral response at low wavelength. However, experimental verification for mc-Si cells does not corroborate the predicted results.

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