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Evaluation of the effective quantum efficiency of photon conversion layers placed on solar cells

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ABSTRACT

Photon conversion layers are a possible way of improving the efficiency of existing solar cells, even above the Shockley–Queisser limit. The related concepts are often called downshifting, downconversion, and upconversion. Despite the variety of photon conversion systems proposed in the literature, understanding their real impact is often difficult due to joint effects. Here, a new methodology is provided to analyse the efficiency of such conversion layers and to be able to compare the different systems proposed.

1. Introduction

Advanced concepts that can enable high efficiency solar cells include the addition of photon conversion layers (PCL) to the cells to optimize the use of the solar spectrum as an alternative to tandem cells. In this way, reducing the so-called spectral mismatch between the sun and the cell is predicted to increase the efficiency of single gap cells up to 10% (absolute) [1]. There are two attractive ways to implement photon conversion in solar cells, either with upconversion (UC) or with downconversion. Upconversion consists in the conversion of two infrared (IR) photons into one higher energy photon to be absorbed by the cell; and downconversion (DC) consists in converting one ultraviolet (UV) photon into two IR photons to be absorbed by the cell. DC can be useful for most type of solar cells such as Si and CIGS but also for organic or hybrid solar cells where UV radiation harmful for the cells can be suppressed without losing the corresponding energy, thanks to a DC layer on top of the cells. Many approaches have been suggested [2–5], and downconversion has been demonstrated in some cases [6–8]. Cost-effective enhanced encapsulants that are functionalized by photon conversion have been proposed [9] so that the impact on the solar cell fabrication processes can be minimized. While research on DC and UC is wide-spread, attempts to integrate them in real solar cells are scarce [10,11]. This comes from the difficulty to obtain efficient converters that do not absorb the visible spectrum and from the complexity to implement effectively these converters in the solar cell fabrication processes. The sole comparison of the overall cell efficiency or external quantum efficiency (EQE) with and without the PCL is not sufficient to evaluate the contribution of photon converters because of the joint effects of phenomena such as antireflective properties, light scattering, and surface passivation. Thus, comparing a solar cell with and without the PCL placed on top, that acts as an antireflector, may often lead to an increase of cell efficiency and EQE without the presence of efficient photon conversion.

DC systems are generally based on rare earth elements (REE), known for their efficient luminescence and used in industry in fluorescent lamps, fiber optics and lasers. Often a couple of two REE is used, such as Tb, Yb or Pr, Yb, to obtain efficient DC [12,13]. The sole measurement of the energy transfer efficiency (ETE) between the first and second REE, or of the measurement of the total quantum efficiency (QE, the ratio of the number of photons emitted to the photons absorbed) is necessary but not sufficient to estimate the impact on the cells.

Indeed, even with a high QE if the absorption is low only a small amount of photons will be emitted by the PCL and this will lead to a marginal improvement of the solar cell. This can also happen if the PCL has a high QE at a certain wavelength but absorbs too many useful photons at other wavelengths. Reemission to the top/air side can also lead to a degradation of the benefit of a PCL, although [1] is considering this in its simulations. Thus, tools are needed to evaluate the impact of the PCL on the solar cell

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which is the scope of this work. The efficiency of DC systems can be investigated by implementing them in solar cells. In this work we have introduced a new methodology and "effective quantum efficiency" to better evaluate the performance of photon conversion layers implemented on solar cells. We examine the performance of four PCL previously obtained that were promising for photovoltaics applications, $Yb_{0.013}Zn_{0.987}O_{+y}$ [14,15], $Nd_{0.005}Si_{0.095}O_{1.5}$ [16,17], $Nd_{0.029}Sn_{0.071}O_{2-y}$ [18], and $SrNd_{0.02}Ti_{0.98}O_{3-y}$ [10]. The materials were optimized in terms of Yb and Nd concentration and growth conditions as to obtain high photoluminescence (PL) from Yb and Nd.

2. Results and discussion

An important step in the quest for the best DC candidate for solar cells is to be able to find which of the different systems proposed in the literature provides the largest PL. Total QE can be measured with an integration sphere or estimated from PL decay curves [12]. However, accurate measurements are delicate partly due to the frequent lack of calibration standards. PL decay cannot always be used to determine QE e.g. in the case of single rare earth (RE) systems or if one of the two RE does not provide PL. As a first step the PL of different systems can be measured in the same setup and conditions and compared from sample to sample. Fig. 1shows the PL intensity normalized to the film thickness for various systems based on Nd or Yb, namely $Yb_{0.013}Zn_{0.987}O_{+y}$ [14,15], $Nd_{0.005}Si_{0.095}O_{1.5}$ [16,17], $Nd_{0.029}Sn_{0.071}O_{2-y}$ [18], $SrNd_{0.02}Ti_{0.98}O_{3-y}$ [10]. It shows that by far the most luminescent system is Nd–$SrTiO_3$. However, the use of Nd in $SrTiO_3$ has the drawback that there is strong PL around 1100 nm and that the response of crystalline silicon solar cells is not very good for such a high wavelength. This problem could be solved by fabricating Yb–$SrTiO_3$. Furthermore, Fig. 1 does not tell if there is downshifting (DS, one UV photon converted into one IR photon) or downconversion (one UV photon converted into two IR photons), and if the total QE is high enough.

In order to compare the different samples a new methodology is put in place. Silicon solar cells as described in [10] are fabricated and the internal quantum efficiency (IQE) is obtained before and after the deposition of the PCL. The IQE is calculated from the measured EQE as described in [10] using:

$$IQE(\nu) = \frac{EQE(\nu)}{1-R(\nu)} \quad (1)$$

where R is the reflectance at the corresponding wavelength ν. The IQE at PL excitation wavelength without the PCL is defined as i_1 and with the PCL i_2. The IQE at PL emission wavelength with the PCL is i_3.The absorbance of the films can be determined by

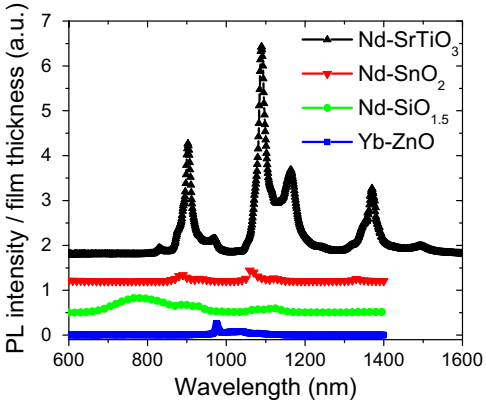

Fig. 1. Comparison of the PL at room temperature in the visible–NIR (325 nm excitation) normalized by the sample thickness for various systems: $SrNd_{0.02}Ti_{0.98}O_{3-y}$, $Nd_{0.029}Sn_{0.071}O_{2-y}$, $Nd_{0.005}Si_{0.095}O_{1.5}$, $Yb_{0.013}Zn_{0.987}O_{+y}$.

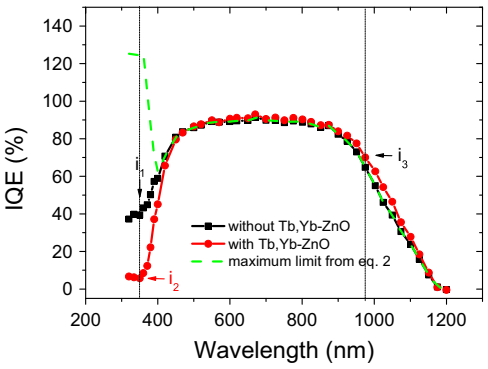

Fig. 2. Evolution of the IQE of a c-Si solar cell without coating and with an 80 nm thick $Tb_{0.04}Yb_{0.01}Zn_{0.95}O_{+y}$ film (deposition described in [14]). i_1, i_2, and i_3 are shown in the figure. The maximum IQE from Eq. (2) in the case of a perfect DC PCL is plotted in dashed line.

spectroscopic ellipsometry for example and it is defined at the excitation wavelength of the PCL as A. The appropriate PL excitation wavelength can be provided by the PL excitation technique (PLE), that is also useful to determine energy transfers between different rare earth elements.

Fig. 2 shows an example of a silicon solar cell without coating and with a Tb,Yb–ZnO PCL. i_1, i_2, and i_3 are indicated in the figure for this example. Tb was combined with Yb in the view of DC, however, this did not lead to PL intensity improvements and PL is similar to Fig. 1. Since this PCL can convert 350 nm photons (PL excitation wavelength) into 975 nm (PL emission wavelength), i_1, i_2 and A are taken at 350 nm, and i_3 at 975 nm. Experimentally, the addition of the PCL leads to a drastic decrease of the IQE at 350 nm which is the excitation wavelength for the PL of this system. This case is an example showing that although the PL signal is clearly visible for this PCL, the layer absorbs many UV photons that are not reemitted. Thus, tests on solar cells are of paramount importance to determine the suitability of a PCL for photovoltaics. Comparisons in cell efficiencies with a solar simulator with and without the PCL will often lead to a better efficiency with the PCL – this is also the case here – due to surface passivation and antireflective properties. Therefore, alternative methods are needed to quantify the performance of the different PCLs. By thermal annealing the doped ZnO PCL, it is possible to obtain a broad PL in the visible region; however, tests on solar cells show that the outcome is similar to Fig. 2, showing that again the amount of PL should be increased.

We now further quantify the interpretation of spectral response (SR) experiments on solar cells. Here the system *PCL+solar cell* is decomposed as an optical filter providing a modified solar spectrum to the solar cell. The maximum possible IQE at excitation wavelength with the PCL, $i_{2,max}$, in the case of DC, can be defined as the sum of the IQE at the excitation wavelength corresponding to the non-absorbed, non-converted photons by the PCL and the IQE at the emission wavelength corresponding to the photons absorbed by the PCL and converted into two photons, i.e.:

$$i_{2,max} = i_1 \times (1-A) + 2 \times i_3 \times A \quad (2)$$

This basic calculation allows to plot in Fig. 2 the maximum IQE that can be obtained with the current solar cell with a perfect DC PCL. In Eq. (2), i_3 is taken as the IQE at PL emission wavelength with the PCL and not without, so that the effect of surface passivation change in the cell with the PCL is taken into account compared to the cell without the PCL.

The ratio of extra electrons due to the conversion η_{ele} is defined as the difference between the IQE at excitation wavelength with the PCL and the IQE at excitation wavelength corresponding to the