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# IMPROVING UP-CONVERSION WITH PBS QUANTUM DOTS

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ABSTRACT: This paper evaluates the enhancement of the up-conversion phenomena by combining rare-earth doped phosphors with PbS quantum dots (QDs). We present results on the characterization of two different ways of adhering the up-converter with this fluorescent material to bifacial solar cells: by dissolving the powder in a spin-on oxide and by dissolving it in a silicone gel. The improvement in photocurrent detected for both the oxide and silicone alternatives when including the QDs is 60% better than without them. It is shown that the absorption and emission characteristics of the PbS QDs embedded in oxide and silicone can be tuned into to the desired spectral region. Keywords: quantum dots, up-converter, solar cell.

# 1 INTRODUCTION

The implementation and characterization of upconverters (UCs) layers on the rear of bifacial silicon solar cells (BSSC) has been reported by several authors [1] [<sup>2</sup>]. Pan *et al.* [3] attached some commercial phosphors to the BSSC by dissolving them either in an spin-on oxide or in a silicone. Performance was characterized through External Quantum Efficiency (EQE) measurements, demonstrating a gain in photocurrent in the IR wavelength range. This gain is quite small, firstly because response of the UC process is strongly dependent on light intensity, and also because the wavelength range where it takes place is very narrow, corresponding to a small absorption range of the rareearth dopant.

The use of photoluminescence materials to enhance the UC phenomena has been suggested in a number of times for photovoltaic applications [4] [5]. The idea is to widen the IR light being used through a material that can absorb in a range of wavelengths where the UCs does not respond, and re-emit in the wavelengths where it does respond.

The UC used in the experiments reported is called PTIR545/F, made by the company Phosphor Technology. PTIR545/F is a pink very fine powder that seems to consist, according to EDX measurements, of  $ZnSO_4$  doped with ytterbium (Yb) and a small fraction of erbium (Er).

PbS QDs have appropriate absorption and emission properties for photovoltaic devices of this kind and are readily commercially available. There are several requirements on the QDs that have to be fulfilled for this purpose. Suyver *et al.* [6] reported that the diameter of the QDs should be below 30nm for to reduce light scattering, and for that reason 5.3 nm PbS QDs made by the company *Evident Technology* have been used. These QDs have large EQE and high indices of refraction compared to the phosphors, making them better matched for Si devices [7].The energy transfer will probably ocurr by radiative emission from the QDs followed by absorption by the UC phosphor.

In this paper we combine the UCs with a PbS QDs in a BSSC and characterized the devices through Scanning Electron Microscopy (SEM), measurements photocurrent and photoluminescence. Two different ways of adhering the QDs to the BSCC and UCs have been implemented: by dissolving the QDs and power UCs in a spin-on oxide, and by dissolving it a silicone gel.

# 2 APPLICATION OF THE UP-CONVERTERS AND QUANTUM DOTS IN BIFACIAL SILICON SOLAR CELLS

The process sequence previously developed at our institute [4] for to fabricate of the bifacial silicon solar cell, which is detailed in Figure 1 (a), has been implemented. A final step is added in which the two alternative deposition techniques for the attachment of the UC and QDs to the solar cell are used. The UCs are in powder form and the PbS QDs are in liquid form, so that a binding agent is needed, which at the same time should give a good optical coupling to the solar cell. Pan *et al.* [2] has been described details of these implementations. The schematic structure of the BSSC with UCs and QDs in both deposition techniques are shown in Figure 1 (b) and (c).



**Figure 1:** . Schematic of the manufacturing process of the bifacial solar cells (a), showing the integration of the up-converter and quantum dots in the silicone gel (b) and spin-on oxide (c).

3 CHARACTERIZATION OF UP-CONVERSION PERFORMANCE BY COMBINATION WITH QUANTUM DOTS

It is seen by SEM measurements (not shown here) that the introduction of the QDs in both cases does not alter the properties of the UC, which is good because it is needed that the UC and the QDs do not interfere. In addition, a smaller homogeneity has been observed in samples with QDs, that is to say, greater agglomeration of the active ions in the UC. This factor can also be favourable to the UC phenomenon, because it considerably increases the probabilities of energy transfer mechanisms [8] [9].

The increase in photocurrent detected for a BSSC with UCs and QDs is shown in Figure 2 for both implementation modes, the oxide (a) and the silicone (b). Details on the characterization setup can be found in the reference [10].



**Figure2:** Increase in photocurrent versus wavelength for a bifacial silicon solar cell with UC embedded in the oxide (a) and in the silicone (b) with and without QDs. The dots correspond to the LED sources have been used, centered in two different wavelengths, and with a half band width of around 50 nm

The improvement in photocurrent detected for a BSSC with commercial UC and PbS-QDs is in all cases 60% better than without them, demonstrating that the absorption and emission characteristics of the QDs embedded in oxide and silicone can be tuned into the desired spectral region. These experimental results are similar to those calculated by Löper *et al.* [11], where they calculated for commercial nanocrystals a fluorescent quantum efficiency of about 50. The photocurrent

extracted from the BSSC is found under excitation from IR LED (1450 to 1550 nm), clearly coinciding with the material of the commercial UC used ( ${}^{4}I_{11/2} \rightarrow {}^{4}I_{15/2}$  Er<sup>3+</sup> ions transition).

To give insight into the phenomena taking place, the configuration of the Yb-Er UC system is represented in Figure 3 (a). The PL spectrum measured for the PTIR545/F-UC in silicone gel with and without QDs is also shown in Figure 3 (b). Laser excitation is at 514.5 nm, but emission in the visible light wavelength (corresponding to transitions from the levels  ${}^{4}I_{9/2}$ ,  ${}^{4}F_{9/2}$ ,  ${}^{4}\text{H}_{11/2}$  of the Er<sup>3+</sup> ion directly to the ground state) cannot be detected. As the detector covers the NIR wavelength range, only transitions in various steps to lower levels  $({}^{4}I_{11/2} \text{ and } {}^{4}I_{13/2})$  will leave a signature in the PL spectrum. These excited states decay to the next lower lying state or directly and radiatively to the ground state. Photons emitted by a transition process from <sup>4</sup>I<sub>11/2</sub> or higher excited levels back to the ground state have more energy than the bandgap for silicon.



**Figure3:** Schematic configuration of the  $Yb^{3+}$ - $Er^{3+}$  UC system (a). Radiative absorption and emission are indicated by solid lines and non-radiative ones by dashed lines. The open circles show the initial state of the center. Photoluminescence spectra of a bifacial silicon solar cell with UC embedded in the silicone with and without QDs (b).

Two NIR infrared emissions are observed in the PL spectrum. The  ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2} Er^{3+}$  ions transition (1540 nm) is clearly observed, and the increase expected from the implementation of QD is achieved. The difference observed in the emission spectrum of PL surely is due to the increase in the absorption of the rare earth ions by the introduction of the QDs. This transition can be possible either because of the resonance between the  $Er^{3+}$  ( ${}^{4}I_{13/2}$ ) and PbS QDs, or more likely because QDs cause scattering of light with results in an increased coupling

into the Er higher energy levels. On the other hand, the shape of this peak agrees with experiments reported by Auzel [12].

The transition from the level  ${}^{4}I_{11/2}$  back to the ground is not seen in the PL neither for the case with QDs nor for the case without them. But this can be explained because to induce the transition  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$  for  $\mathrm{Er}^{3+}$  ions two photons are needed, or a high energy transfer from the  ${}^{4}I_{13/2}$  level, which seems not to be the case for our commercial phosphor. We have not a clear explanation for the peak at 1010 nm seen at the PL, which would need more investigation, but the fact is that the QD have no influence on it.

Based on Figure 2 and Figure 3 (b), we conclude that the application of a layer with UC and QDs to a BSSC can enable such a solar cell to use sub-band gap light indirectly ( $\lambda$ >1100nm) that would otherwise not be absorbed by the silicon. The emission of the PbS-QDs coincides with the ground state absorption of the Er<sup>3+</sup>  $({}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2})$ . Consecutive absorption as well as energy transfer-based UC processes takes place from this first excited state to a second one [12]. However, the PTIR545/F-UC is not so appropriate for solar cells, because of the combination of Yb<sup>3+</sup> and Er<sup>3+</sup>. The UC effect occurs because of the absorption of 980 nmphotons in Yb<sup>3+</sup>, and after the de-excitation of this state, the energy is transferred to the Er<sup>3+</sup>, so that it competes with silicon for the NIR photons with wavelengths of between 900 and 1100 nm [13]. But the PTIR545/F-UC has additional absorption peaks as a result of the  $\mathrm{Er}^{3+}$ (1509, 1522, 1547, 1552 and 1600 nm), and our measurements show that they can contribute to an enhancement of photocurrent. The small broadening of the excitation spectra as compared to other UCS used with BSSC [6] [14] can be to the result of the influence of the phonon energy of the different host materials.

#### 4 CONCLUSION

This study reports on experimental efforts aimed at utilizing the unique optical properties of high-quality QD together with UC for solar cells applications.

Two effective procedures for incorporating PbS into a UC have been developed. We have demonstrated that the combination of an Yb/Er-doped phosphor with PbS-QDs enhances the performance of the up-conversion phenomena.

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