

E-MRS Spring Meeting 2013 Symposium D - Advanced Inorganic Materials and Structures for Photovoltaics, 27-31 May 2013, Strasbourg, France

## Industrial bifacial silicon solar cells with up-converter and PbS quantum dots

A. C. Pan\*, I. Zanesco and A. Moehlecke

*Solar Energy Technology Nucleus (NT-Solar), Pontifical Catholic University of Rio Grande do Sul, Av. Ipiranga, 6681, Porto Alegre, Cep: 90619-900, RS – Brazil, \* E-mail address: [aline.pan@pucrs.br](mailto:aline.pan@pucrs.br)*

---

### Abstract

Up-converters use radiation normally transmitted by the solar cell and converts it to radiation, which can be converted to electric energy. Therefore, an up-converter should be placed on the rear side of a bifacial cell. This has the advantage that no impairment of the radiation impinging on the solar cell takes place. The number of photons that may be converted is limited by the absorption range of the up-converter and the efficiency of the up-conversion. High transmittance is required in the absorption range of the up-converter and the use of photoluminescence materials enhances the up-conversion phenomena. The photoluminescence material should absorb over a wide spectral range and emit in the absorption range of the up-converter. This paper presents the evaluation of the optical properties of the up-converter combined with PbS quantum dots and the reduction of the reflection losses in industrial bifacial silicon solar cells with up-converter/quantum dots incorporated. The up-converter materials are in the powder form, and the PbS quantum dots are available in the liquid form, so that an agent is needed, which at the same time should give a good optical coupling to the solar cell. Silicone gel with up-converter and quantum dots was laminated to the rear face of the bifacial cell by using an industrial technique based on frontsheet/EVA/backsheet. Combining the effects of up-converter and quantum dots, the reflection losses were reduced by 20 %, demonstrating that the absorption and emission characteristics of the up-converter and quantum dots embedded in silicon can be tuned to the desired spectral region.

*Keywords:* Up-converter; Bifacial; Silicon; Solar Cells.

---

### 1. Introduction

The development of structures capable of modifying the incident solar spectrum that can lead in theory to efficiencies exceeding the Shockley-Queisser limit for silicon solar cells [1], such as photon converter, has been the object of study of several researchers [2] [3] [4] [5]. Photon conversion is utilized as a way to minimize

\* Corresponding author. Tel.: +55 51 3320 3535; fax: +55 51 3320 3616.  
*E-mail address:* [aline.pan@pucrs.br](mailto:aline.pan@pucrs.br)

absorption losses in a solar cell. Through down-converter (DC) phenomenon can be reduced thermalization losses [6], while the up-conversion (UC) phenomenon decreases transmission losses [7]. These photon converters can in principle be easily implemented on Si solar cells, by adding a layer on top (for conversion towards lower energies) or at the bottom of the cell (for up-conversion). This is viewed as advantageous as there is no need to modify the semiconductor and the well-established crystalline Si technology can be used as a base [8]. This work focuses on the application of UC in silicon solar cells.

The number of photons that may be converted is limited by the absorption range of the up-converter and the efficiency of the up-conversion. High transmittance is required in the absorption range of the up-converter and the use of photoluminescence material enhances the up-conversion phenomena [9]. The use of photoluminescence materials to enhance the up-conversion phenomena have been suggested to some researchers [10] [11] [12]. The idea is to widen the IR radiation being used through a material that can absorb in a range of wavelengths where the UC that not respond, and re-emit in the wavelengths where it does respond. PbS quantum dots (QDs) have appropriate absorption and emission properties in combination with UC and the solar cell [13]. In order to allow successful implementation of up-converter in solar cells, certain conditions have to meet. For this, a device that does not absorb (to transmit) excitation energies of up-converter and subsequently be able to absorb the energy emitted by them is needed. For instance, a bifacial silicon solar cell (BSSC). BSSC is a device able to turn the electrical energy radiation incident on both sides. Bifacial structures also have a high interest in its suitability for use on thinner substrates, a trend in the photovoltaic industry. Furthermore, these structures present advantages when thinning, as compared to the standard ones, even if they are used in a “monofacial mode” (illumination on just one side) [14].

The implementation and characterization of UC layers on the rear of BSSC has been reported by several authors [15] [16]. Pan et al. [17] attached some commercial phosphors to the BSSC by dissolving them either in a spin-on oxide or a silicone, and both have been shown to be valid. The incorporation of the UC and QDs in the BSSC into the silicone is more effective than in the oxide. The increase in photocurrent detected in the same wavelength range for a BSSC with the UC in the silicone is ten times higher than oxide. The UCs when embedded in silicone get more clusters form and thus increase the probability of energy transfer mechanisms, which favours UC phenomenon occurs. The Figure 1 [18] shows pictures of the UCs attached by spin-on oxide and silicone obtained by Scanning Electron Microscope. (SEM). When the UC was attached to spin-on oxide is observed great homogeneity, with a small number of clusters in the material (Figure 1 (a)). While for the UC in silicone has a greater amount of clusters created and good distribution thereof. Therefore, the clusters (agglomerations rare earth ( $\text{TR}^{3+}$ ) ion on a small distance) increases the probability of phenomena energy transfer (TE) mainly energy transfer up-conversion (ETU) and cooperative energy transfer (CooR) processes [19]. Furthermore, collecting the photoluminescence (PL) spectra in an emission silicon substrate near strong emissions of ions ( $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$ ) constituents of them UCs contribute to the UC phenomenon more effective. Silicones as used in these experiments may be an alternative for encapsulating photovoltaic modules.

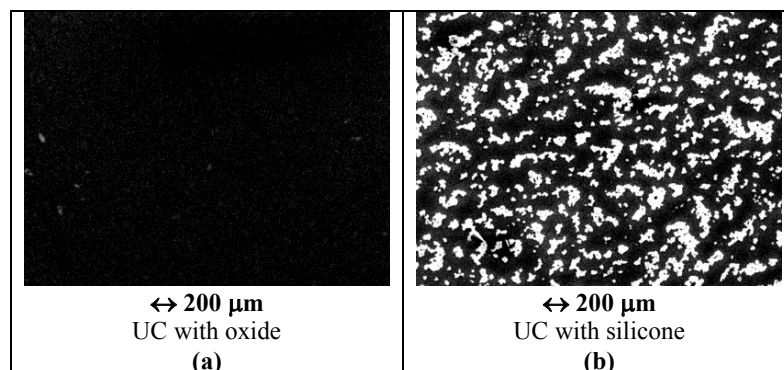


Figure 1. SEM pictures at a magnification of 95 commercial UCs increases attached in spin-on oxide (a) and silicone gel (b) [18].

A photovoltaic module consists of solar cells electrically associated. After being soldered, the cells are encapsulated in order to isolate them from the outside and to protect them from the weather and to provide rigidity to the module. The durability of these modules is more than 30 years and is currently determined by the degradation of the materials used in the encapsulation, that is, the durability of crystalline silicon solar cells is considerably higher.

The performance of the UC and QDs are limited by the absorption range and the efficiency. Both of these properties must be improved before a significant effect of the UC on cell performance will be seen [12]. Therefore, in this paper we first present the manufacturing industrial BSSC process and the integration of these in the UC and QDs, with the objective to demonstrate the viability of this incorporation on PV industry. Second, we characterize the system formed by evaluation of the optical properties of the UC combined with QDs and the reduction of the reflection losses in BSSC with UC/QDs incorporated.

## 2. Industrial bifacial silicon solar cells

The baseline process used to develop the bifacial silicon solar cells was the following: texture etching, RCA cleaning, boron spin-on deposition, boron diffusion in a quartz tube furnace, silicon oxide growth, resist deposition and oxide etching, RCA cleaning, phosphorus diffusion, phosphorus and borosilicate glass etching, TiO<sub>2</sub> antireflection coating deposition, screen-printing metallization in both sides and edge isolation. Solar cells were developed in 1  $\Omega$ .cm – 20  $\Omega$ .cm n-type solar grade Cz-Si wafers with thickness of 200  $\mu$ m. The boron dopant was spun onto one side of the wafer and the diffusion was carried out in a quartz tube furnace at 1000°C. The n<sup>+</sup> layer was produced by phosphorus diffusion using POCl<sub>3</sub>. A specific passivation was not implemented.

The boron and phosphorus diffusions were independent and experimentally optimized as well as the metal grid firing process. This manufacturing process is similar to that used in the PV industry.

All solar cells were characterized under standard conditions (100 mW/cm<sup>2</sup>, AM1.5G and 25°C) in a solar simulator calibrated with a silicon solar cell previously measured at CalLab - FhG-ISE (Fraunhofer-Institut für Solare Energiesysteme), Germany. Figure 2 presents external quantum efficiency (EQE) of two BSSC developed, BSSC-2 and BSSC-10, for both illumination modes. The p<sup>+</sup> emitter was chosen to receive the incident radiation, and n<sup>+</sup> back surface field (BSF) was laminated to the silicone with UC and QDs incorporated. Our EQE equipment for silicon solar cells is not able to measure the effect of the UC and QDs, because the small additional current than can be provided in the 1400-1600 nm range is smaller than the noise of the measurement.

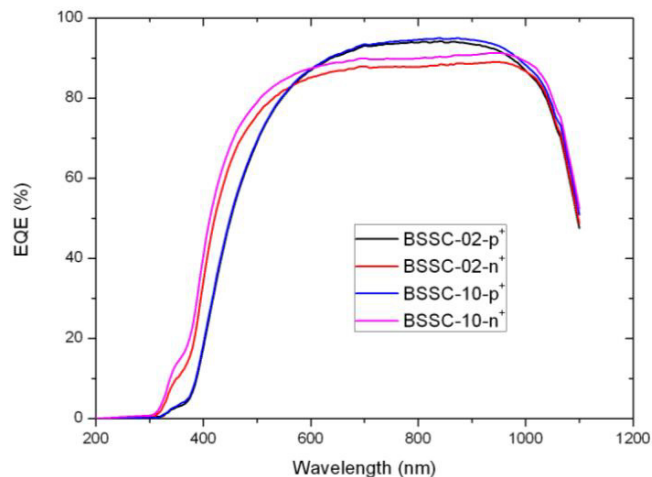


Fig. 2. External quantum efficiency of two BSSC developed in n-type Cz substrates for both illumination modes.

The reflectance of the  $n^+$  BSF is lower than that measured in a  $p^+$  emitter in wavelength range where the BSSC is sensitive. For lower wavelengths, the EQE of the  $n^+$  BSF is higher due to the lower reflectance and also because the BSF is shallower than the emitter.

### 3. Up-converter and PbS quantum dots

The UC used in the experiments is called PTIR545/F, made by the company Phosphor Technology. PTIR545/F is a very fine pink powder that seems to consist, according to energy dispersive X ray (EDX) measurements, of  $ZnSO_4$  doped with ytterbium ( $Yb^{3+}$ ) and erbium ( $Er^{3+}$ ). Possible emissions of  $Er^{3+}$  doped materials under excitation around 1500 nm are shown in Figure 3.

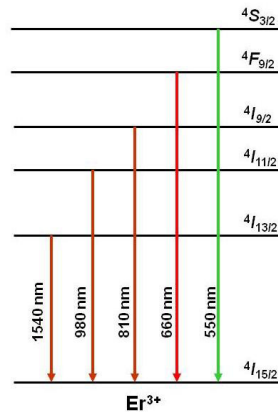


Fig. 3. Emissions of the  $Er^{3+}$  doped materials under excitation around 1500 nm.

PbS QDs have appropriate absorption and emission properties in combination with the UC and the BSSC [13], and are readily commercially available. There are several requirements of the QDs that have to be fulfilled for this purpose. For instance, Suyver et al. [20] reported that the diameter of the QDs should be below 30 nm to reduce light scattering and for that reason a 5.3 nm diameter PbS QDs made by the company Evident Technology were selected and used in this work. The PbS QDs have absorption precisely in the range where neither the BSSC itself nor the UC take advantage of the solar radiation (1200-1500 nm), and the emission takes place in the range where to UC is active, presenting a possible route to improve the UC efficiency.

Pan et al. [9] [17] used these UC in powder form and QDs in liquid form by dissolving them in a silicone gel (Sylgard® 184). This silicone gel showed good optical binding, does not compete with the UC and QDs, as it has a low absorbance at photon wavelengths in which the UC and QDs absorb and emit. Furthermore, since the UCs when embedded in this material get more clusters form and thus increase the probability of energy transfer mechanisms, which favours UC phenomenon occurs.

### 4. Optical properties of the bifacial silicon solar cell with up-converter and quantum dots

BSSC were encapsulated as illustrated in Figure 4 following the standard of PV industry with high transmittance frontsheet (transparent Tedlar®+PET+primer, 25/175 /100  $\mu m$  thick), fast cure EVA (ethylene vinyl acetate) and backsheet (primer+PET+white Tedlar®, 100/125/38  $\mu m$  thick).

Figure 5 (a) shows the reflectance for the two BSSC (BSSC-2 and BSSC-10) before and after encapsulation. BSSC-10 was encapsulated according to the PV industry standard process and BSSC-2 was incorporated the UC and QDs embedded in the silicone gel. The reflectance for the silicone is also presented. The encapsulation increases the reflectance of BSSC due the materials which are used (transparent tedlar and EVA). However, a

reduction in the reflection can be observed at wavelengths where the UC emits. In  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  ( $\approx 1530$  nm),  ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$  ( $\approx 980$  nm),  ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$  ( $\approx 660$  nm) and  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  ( $\approx 550$  nm)  $\text{Er}^{3+}$  ions transition is clearly observed. Thus, the implementation of QD was successful achieved because the absorption was increased. The smaller graph of Figure 5 (b) indicates that at around 1530 nm the reduction in the reflectance is 1.4 %. These decrease observed is due to the increase in the absorption of the rare earth ions (UC) with the introduction of the QDs. This transition can be possible either because of the resonance between the  $\text{Er}^{3+}$  ( ${}^4I_{13/2}$ ) and PbS QDs, or more likely because QDs cause scattering of light which results in an increased coupling into the Er higher energy levels. Transitions from the level  ${}^4I_{11/2}$  (980 nm) and  ${}^4F_{9/2}$  (660 nm) back to the ground diminish the reflectance in 19.1 % and 18.7 % respectively. The most efficient (maximum UC emission) transition is obtained in the 550 nm, and represents a 30.0 % reduction in the reflectance of the solar cell.

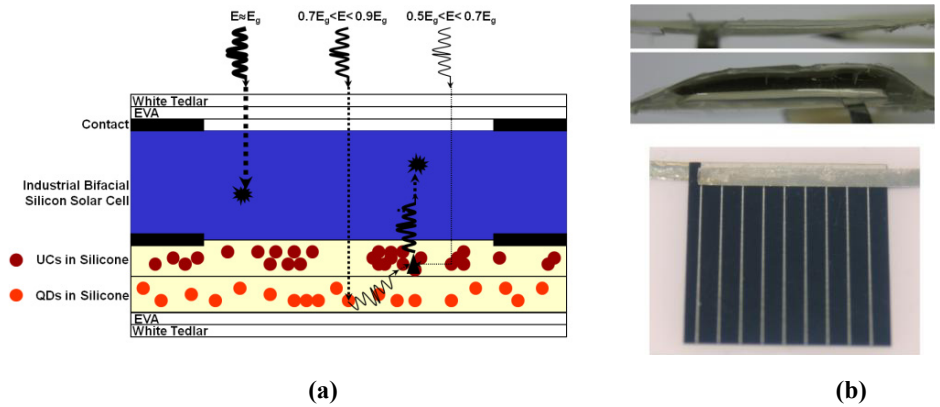


Fig. 4. (a) Encapsulation scheme: industrial BSSC laminated to UC and QDs in silicone. \* represents the generation of an electron-hole pair and  $\blacktriangle$  the UC phenomena. (b) Pictures of the developed encapsulation: cross section with silicone+UC+QDs (above) and frontal view (below)

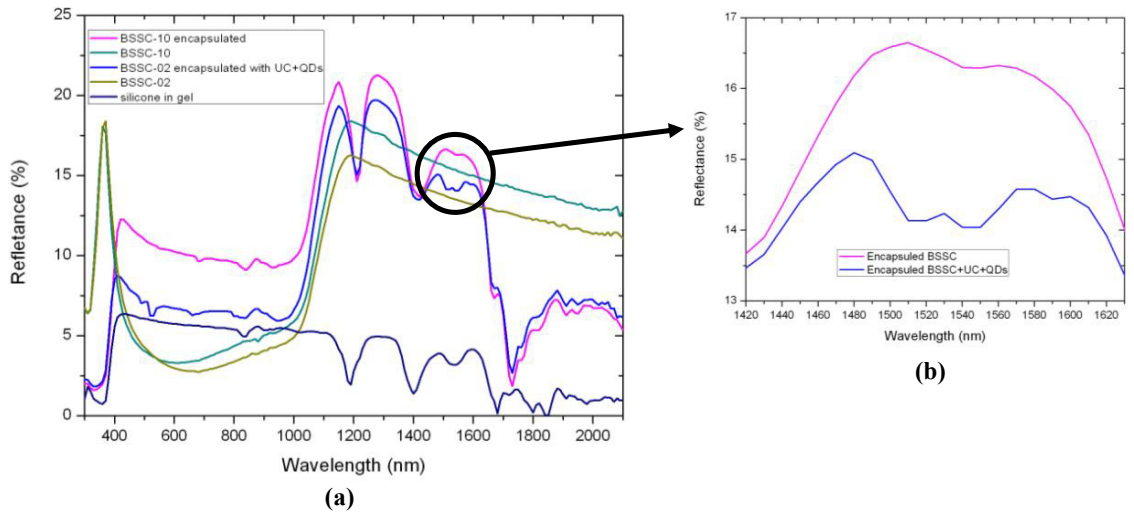


Figure 5. (a) Reflectance of the encapsulated BSSC with and without UC and QDs embedded in the silicone and (b) zoom of the reflectance in the range 1420 nm-1640 nm ( ${}^4I_{13/2}$  ( ${}^4I_{15/2}$ )  $\text{Er}^{3+}$  ion transitions).

Figure 5 (a) shows the reflectance for the two BSSC (BSSC-2 and BSSC-10) before and after encapsulation. BSSC-10 was encapsulated according to the PV industry standard process and BSSC-2 was incorporated the UC and QDs embedded in the silicone gel. The reflectance for the silicone is also presented. The encapsulation increases the reflectance of BSSC due the materials which are used (transparent tedlar and EVA). However, a reduction in the reflection can be observed at wavelengths where the UC emits. In  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  ( $\approx 1530$  nm),  ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$  ( $\approx 980$  nm),  ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$  ( $\approx 660$  nm) and  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  ( $\approx 550$  nm)  $Er^{3+}$  ions transition is clearly observed. Thus, the implementation of QD was successful achieved because the absorption was increased. The smaller graph of Figure 5 (b) indicates that at around 1530 nm the reduction in the reflectance is 1.4 %. These decrease observed is due to the increase in the absorption of the rare earth ions (UC) with the introduction of the QDs. This transition can be possible either because of the resonance between the  $Er^{3+}$  ( ${}^4I_{13/2}$ ) and PbS QDs, or more likely because QDs cause scattering of light which results in an increased coupling into the Er higher energy levels. Transitions from the level  ${}^4I_{11/2}$  (980 nm) and  ${}^4F_{9/2}$  (660 nm) back to the ground diminish the reflectance in 19.1 % and 18.7 % respectively. The most efficient (maximum UC emission) transition is obtained in the 550 nm, and represents a 30.0 % reduction in the reflectance of the solar cell.

Figure 6 shows the transmittance of an encapsulated BSSC with and without UC and QDs embedded in the silicone. Combining the effects of UC and QDs, the transmission losses were reduced by 17.0 % for wavelengths where the solar cell does not respond (near infrared – 1100 nm to 2100 nm). Precisely at these wavelengths solar cells have high transmission in the excitation wavelength range of the up-converter (about 1500 nm). For the optimization of a conventional cell concept, the transmission at these wavelengths is irrelevant. In fact to enhance the conventional cell performance, the optimization would direct to the opposite - an increased optical path length to lower the transmission at longer wavelengths ( $> 950$  nm). Therefore a compromise must be found between high transmittance at about 1500 nm, while still keeping the overall cell performance high by maintaining a low reflectance in the wavelength range of conventional cell performance. Thus, from the results obtained, it can be concluded that the main purpose of the implementation of UC and QDs in BSSC cells has been established, i.e., low transmission of solar cells at wavelengths where it responds and improved itself considerably to the wavelengths of the near infrared.

Based on Fig. 5 and Fig. 6, 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 radiation indirectly that would otherwise not be absorbed by the silicon.

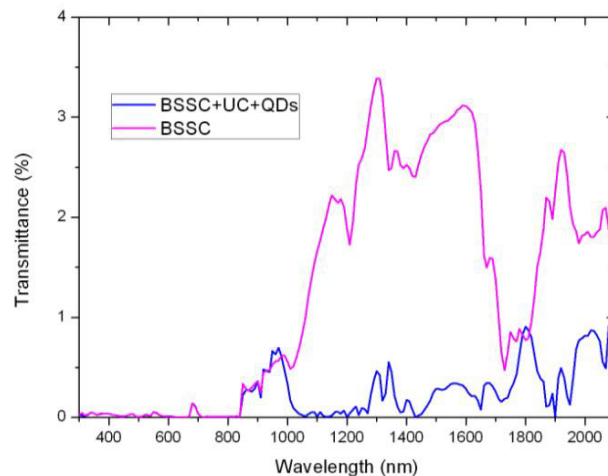


Figure 6. Transmittance of an encapsulated BSSC with and without UC and QDs embedded in the silicone.

## 5. Conclusions

Silicone gel with up-converter and quantum dots was laminated to the rear face of the bifacial cell by using an industrial technique based on frontsheet/EVA/backsheet, and showed the viability of incorporation in the PV industry.

Combining the effects of up-converter and quantum dots, the transmission losses were reduced by 17.0 % and the reflection losses were at 20.0 % of the emissions of the Er<sup>3+</sup> (530 nm, 660 nm, 980 nm and 1530 nm), demonstrating that the absorption and emission characteristics of the up-converter and quantum dots embedded in silicon can be tuned to the desired spectral region.

To our knowledge, this is the first time this phenomenon has been experimentally shown for encapsulated industrial silicon solar cells

## Acknowledgements

This work has been carried out within the framework of the Support Recently Doctor (ARD – 11/1951-2) of the Foundation for Research Support of the State of Rio Grande do Sul (FAPERGS) - Brazil.

## References

- [1] Shockley W, Queisser H. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *Journal of Applied Physics*. 32-3, 1961, p. 510-519.
- [2] Green M. *Third Generation Photovoltaics: Advanced Solar Energy Conversion*. Springer-Verlag Berlin Heidelberg, 2003.
- [3] Martí A, Luque A. *Next Generation Photovoltaics*. Institute of Physics Publishing Bristol and Philadelphia, 2004.
- [4] Shalav A, Richards B, Green M. Luminescent layers for enhanced silicon solar cell performance: Up-conversion. *Solar Energy Materials & Solar Cells*. 91, 2007, p. 829-842.
- [5] Cañizo C, Tobías I, Pérez-Dedmar J, Pan A C, Luque A. Implementation of a Monte Carlo method to model photon conversion for solar cells. *Thin Solid Films*. 516, 2008, p. 6757-6762.
- [6] Trupke T, Green M, Würfel P. Improving solar cell efficiencies by down-conversion of high-energy photons. *Journal of Applied Physics*. 92-3, 2002, p. 1668-1674.
- [7] Trupke T, Green M, Würfel P. Improving solar cell efficiencies by up-conversion of sub-band-gap light. *Journal of Applied Physics*. 92-7, 2002, p. 4117-4122.
- [8] Shalav A. *Rare-earth doped up-converting phosphors for an enhanced silicon solar cell response*. Ph. D Thesis, UNSW, Sydney, Australia, 2006.
- [9] Pan A C, Cañizo C, Cánovas E, Santos N M, Leitão J P, Luque A. Enhancement of up-conversion efficiency by combining rare earth-doped phosphors with PbS quantum dots. *Solar Energy Materials & Solar Cells*. 94, 2010, p. 1923-1926.
- [10] Fisher S. et al. Material characterization for advanced up-converters systems. In: *Proc. 23<sup>rd</sup> European Photovoltaic Solar Energy Conference and Exhibition*. 2008, Valencia, p. 620-623.
- [11] Kitai A H. Oxide phosphor and dielectric thin films for electroluminescent devices. *Thin Solids Films*. 445, 2003, p. 363-376.
- [12] Strümpel C, Cann M J M, Cañizo C, Tobías I, Fath P. Erbium-doped up-converters on silicon solar cells: assessment of the potential. In: *Proc. 20th European Photovoltaic Solar Energy Conference and Exhibition*. 2005, Barcelona, p. 43-46.
- [13] Geraert V. *ARC Photovoltaics Centre of Excellence Annual Report 2008*. University of New South Wales, 2008.
- [14] Pan A C, Cañizo C, Luque A. Effect of thickness on bifacial silicon solar cells. *IEEE Explore - 2007 Spanish Conference on Electron Devices*. 2007, p. 234-237.
- [15] Richards B S, Shalav A. Enhancing the near infrared spectral response of silicon optoelectronic devices via up-conversion. *IEEE Transition Electron Device*. 54-10, 2007, p. 2679-2684.
- [16] Strümpel C, Cann M J M, Beaucarne G, Shaoui A, Cañizo C, Tobías I. Enhancing silicon solar cell efficiency by modifying the solar spectrum. In: *Proc. IEEE 4<sup>th</sup> World PVSEC*. 2006, Hawaii, p. 87-90.
- [17] Pan A C, Cañizo C, Luque A. Characterization of up-converter layers on bifacial silicon solar cells. *Materials Science and Engineering B*. 159-160, 2009, p. 212-215.
- [18] Pan A C. *Convertidores fotónicos para células solares bifaciais de silício*. PhD Thesis. Madri, 2009.
- [19] Auzel F. Up-conversion and anti-Stokes processes with f and d ions in solids. *Chemical Review*. 104, 2004, p. 139-173.
- [20] Suyver J F et al. Novel materials doped with trivalent lanthanides and transition metal ions showing near-infrared to visible photon upconversion. *Optical Materials*. 27, 2005, p. 1111-1130.