ERBIUM-DOPED UP-CONVERTERS ON SILICON SOLAR CELLS: ASSESSMENT OF THE POTENTIAL

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ABSTRACT: Erbium-doped up-converters are expected to lead to an increase in efficiency of silicon solar cells by utilising the low energy region of the solar spectrum. This paper focuses on two host-materials, YF_3 and $BaCl_2$ both doped with Er^{3+} and therefore absorbing at about 1.5µm and $BaCl_2$ co-doped with Er^{3+} and Dy^{3+}, and therefore absorbing at about 1.3µm. The number of photons that can be absorbed by each up-converter has been calculated and is in the range of 0.1 - 0.7 × 10^{20} photons / m^2 s. The front and rear anti-reflection coatings of a silicon solar cell have been adapted to show the maximum gain from the up-converters. Using these results, the efficiency enhancement due to the application of an up-converter to a bifacial cell is calculated for both the standard and the adapted cell design. The result is an enhancement in absolute efficiency between 0.05 - 0.12 % for the standard cell and between 0.07 - 0.16 % for the adapted cell. The efficiency improvement due to the up-converter is calculated as a function of the product of up-converter efficiency and the concentration of the incoming sunlight.
Keywords: Up-conversion, Modelling, Silicon Solar Cells

1 Introduction

Up-conversion is one approach in the frame of the so called Third Generation Photovoltaics first proposed by M.A. Green in the year 2002 [1]. Third Generation Photovoltaics unites different approaches to use the energy incident on a solar cell more effectively. Up-conversion refers to processes whereby two or more photons with energy less than the band gap of silicon are combined to produce a photon with energy higher than the band gap of silicon. Detailed balance calculations have shown that application of an up-converter increases the efficiency limit of silicon solar cells from 31% to 37.4% [2,3]. Since low energy photons are transmitted through silicon solar cells, the up-converter should be placed on the rear (Figure 1). This has the advantage of avoiding complications associated with light coupling into the cell. The up-converter should be electrically isolated from the solar cell to avoid additional recombination via the energy levels of the up-converter.

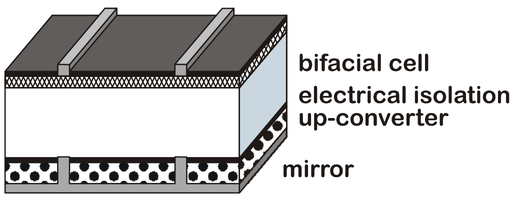

Figure 1: Bifacial cell with the up-converter on the rear side. The up-converter is electrically isolated from the bulk to provide recombination.

The experimental proof of the occurrence of spectral response at 1.5µm of the silicon solar is already done by Shalav *et al.* [4] using $NaYF_4:Er^{3+}$(20%).

Up-conversion has been demonstrated in many systems, mostly consisting of active ions (for example rare earth or transition metals [5,6]) in a host material. For silicon solar cells trivalent Erbium is a good choice for the active ion, because it absorbs at wavelengths lower than that wavelength, which corresponds to the band gap of silicon (1.1µm) and emits within the absorption range of silicon. The width of the absorption range and the up-conversion efficiency both depend strongly on the host-material. We have focused on two host-materials YF_3 and $BaCl_2$ and the two dopant materials trivalent Erbium (Er^{3+}) and trivalent Dysprosium (Dy^{3+}). With an Er^{3+}-dopant Ohwaki and Wang [7] have shown experimentally that $YF_3:Er^{3+}$ has a broader absorption range than $BaCl_2:Er^{3+}$ (Figure 2). This is explained by the different Stark splitting of the energy levels in the Er^{3+} that are excited in the up-conversion process. In both systems the absorption is centred at about 1.5µm. Ohwaki and Wang have also demonstrated that $BaCl_2:Er^{3+}$ is more efficient than $YF_3:Er^{3+}$ due to fewer non-radiative relaxations [7].

Co-doping of $BaCl_2$ with Er^{3+} and Dy^{3+} has been shown to result in absorption at 1.3µm, which does not occur in the single-doped systems [8]. The emission spectrum of the co-doped system shows the characteristics of trivalent Erbium (emission at about 0.44µm, 0.55µm, 0.66µm 0.81µm with the most intense emission at about 0.98µm).

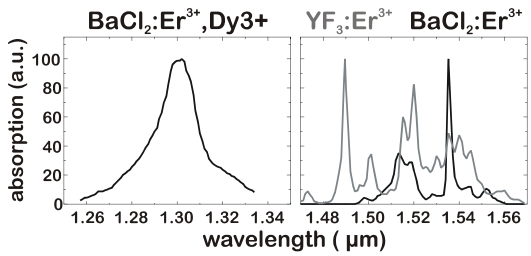

Figure 2: Excitation spectra of the three different up-converters used in this paper. These results were obtained at a fixed emission of 0.55µm (after [7,8]).

This paper evaluates the potential of the three up-converters $YF_3:Er^{3+}$, $BaCl_2:Er^{3+}$ and $BaCl_2:Er^{3+}$, Dy^{3+}. The front and rear reflection coatings of a silicon solar cell have been modelled and adjusted to each up-converter. We have also calculated the optimal electrical properties of a general up-converter. The increase in cell efficiency for the three real up-converters with a cell adjusted to the up-conversion is then calculated and compared with the enhancement due to the up-converter applied on a conventional cell. At only one-sun intensities, we did not expect the efficiency enhancements to outweigh the losses caused by adjusting the cell to the up-converter. Our aim was to determine how the cell design should be changed to optimise the effects of the up-converter. This is especially important in the early stages of this work, since the effects of the up-converter are expected to be very small.

2 PHOTON NUMBERS

As mentioned already, the effectiveness of the up-converter depends on the absorption range and the efficiency of the up-converter. We have calculated the number of photons within the absorption ranges of the chosen up-converters based on the AM15G spectrum. The results are shown in Table I. The calculations were made using the specific absorption behaviour of the three up-converters measured by Ohwaki and Wang [7,8] (Figure 2) and setting the peak absorption to 100%. Even with this optimistic assumption, the number of photons that are available for up-conversion is relatively small. The co-doped system $BaCl_2:Er^{3+}$, Dy^{3+} has the highest number of photons in the absorption range.

It is important to note that the photon numbers in Table I do not take into account the efficiency of the up-converter. Measurements of absolute intensity or efficiency are very challenging, which means most of the experimental data concerning this important property are quoted in arbitrary units. Only a few comparative measurements have been published. One such measurement was done by Ohwaki and Wang [7], who measured an efficiency of the 0.55µm green emission of $BaCl_2:Er^{3+}$ 43 times greater than that of $YF_3:Er^{3+}$. To the authors knowledge, no data is available concerning the relative efficiency of Er^{3+}-Dy^{3+} co-doped and single-doped up-converters.

	Photon numbers ($s^{-1}m^{-2}$)	percentage (%)	current (mA/cm^2)
Upconvertable	13.0×10^{20}	48	20.8
Shiftable to Er^{3+}	6.9×10^{20}	26	11.1
Shiftable to Dy^{3+}	3.3×10^{20}	12	5.2
$YF_3:Er^{3+}$	0.4×10^{20}	1.5	0.6
$BaCl_2:Er^{3+}$	0.1×10^{20}	0.6	0.3
$BaCl_2:Er^{3+}$, Dy^{3+}	0.7×10^{20}	2.4	1.1

Table I: Photon numbers in the wavelength ranges of the various up-converters. In the second column the percentage relative to the number of photons accepted by a silicon solar cell are given. In the last column the corresponding currents are listed.

The number of photons that may be up-converted is limited by the absorption range of the up-converter and the efficiency of up-conversion. If the absorption range of the up-converter can not be increased, one possibility of enhancing the number of photons accepted by the up-converter is to use photoluminescence to shift photons with wavelengths longer than the band gap of silicon and less than the absorption range of the up-converter into this absorption range of the up-converter. For $BaCl_2:Er^{3+}$ 26% additional photons (compared to the number of photons accepted by a silicon solar cell) are available in this intermediate range (Figure 3). The shifting could, for example, be achieved using semiconductor quantum dots, some of which demonstrate a band gap that leads to emission at 1.3 or 1.5µm. Another possibility is luminescent material such as lamp phosphors, which absorb in the IR. The literature on this topic is currently limited due to a perceived lack of application [9].

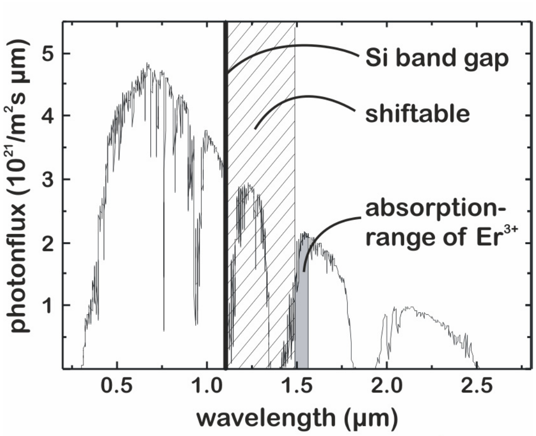

Figure 3: Photon flux of the AM15G solar spectrum. The silicon band gap is indicated by the vertical line. The hatched part assigns the region between the band gap and the absorption range of $BaCl_2:Er^{3+}$.

3 OPTIMUM PROPERTIES OF UP-CONVERTERS

It is interesting to determine the properties of an ideal up-converter. We have modelled the up-converter using a three-level system – the band gap E_{Guc} and an intermediate energy level in the middle. It is assumed that all photons with at least half E_{Guc} will be absorbed by the up-converter and the emission occurs at wavelengths that correspond to E_{Guc}. This model of the up-converter is combined with a cell as described in [10]. The number of transmitted photons with an energy higher than $E_{Guc}/2$ assuming an AM15G spectrum as input, was calculated using SUNRAYS [11]. The number of photons was then halved (2-photon up-conversion was assumed) and used in PC1D simulations to illuminate the rear side of a bifacial cell. This leads to an optimum band gap E_{Guc} of 0.62eV (2µm) for the up-converter and corresponds to an enhancement in the cell efficiency from 18.8% to 22%. The improvement in the cell efficiency is mostly due to the enhanced short circuit current (from 38.3 to 44.4mA/cm^2). As expected, there is only a small change in open circuit voltage 635-639mV. These results are further discussed by C. del Cañizo *et al.* [12].

4 ADJUSTMENT OF THE OPTICAL PROPERTIES

At this time, to the authors knowledge, no up-converters with the optimum energetic properties described in section 3 exist. For existing up-converters it is of interest to determine the possible efficiency enhancements.

To maximise the number of photons that reach the up-converter on the rear side of the cell, the thickness of the antireflection coating on the front side, on the rear side and the refractive index of the up-converter have been optimised. The design of the rear side should not only lead to maximum transmission of the 1.5 or 1.3µm photons, it must also have a high transmittance for the up-converted photons. To find the optimum thicknesses for SiN_x antireflection coating, the following expression for the transmission into the bulk was used:

$$T = T_{FS}\, T_{to\ uc} \cdot T_{uc} \cdot T_{from\ uc}$$

As shown in Figure 4, the total transmission is a function of the transmissions through the front side (T_{FS}), through the rear side into the up-converter ($T_{to\ uc}$) and from the up-converter into the bulk ($T_{from\ uc}$). These terms were calculated on the basis of Crooke [13]. The influence of the up-converter is incorporated in the term T_{uc}. This includes both an emission at 0.98µm and a halving of the number of photons. This is equivalent to assuming two-photon up-conversion.

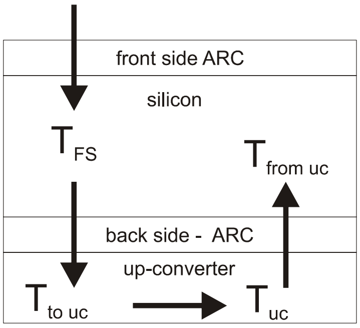

Figure 4: Model of the cell with an up-converter on the rear side. The ARC on the front and the rear has been optimised to maximise the total transmission through the cell into the up-converter and back into the cell.

It may be possible to choose, to some extent, the refractive index of the up-converter. We therefore made calculations using the known refractive index of the host material (1.7 for $BaCl_2$ [14] and 1.5 for YF_3 [15]) and determined the optimum refractive index n_{opt} and thickness dRS pair for the rear side ARC. Adjusting the refractive index of the up-converter had only a small effect on the amount of light transmitted: an improvement of between 1.7% and 2.9% was found for the different up-converters. In Table II the results for the adapted front side thickness dFS, the adjusted refractive index n_{opt} and the optimum thickness of the rear side dRS are shown. In the last column the corresponding transmission (including the halving by the up-converter) is listed.

SiN_x	dFS (nm)	n_{opt}	dRS (nm)	T (%)
$YF_3:Er^{3+}$	191	1.3	142	46.8
$BaCl_2:Er^{3+}$	192	1.3	142	46.7
$BaCl_2:Er^{3+}, Dy^{3+}$	162	1.2	137	48.3

Table II: Results of the adjustment of the optical properties of the cell to the up-converter. The percentage of transmission includes the halving of the photon numbers. The related current densities are equivalent to the additional number of electrons neglecting electrical losses.

Table IV shows the gain in current due to the up-converter. As expected, at one-sun illumination, the loss is much higher than the gain from up-converter.

There is, however, a substantial increase (approximately 36-40%) in current at the wavelength ranges used by the up-converter when the cell is adjusted to the up-converter. For investigations of the performance of various up-converters it will be useful to have this additional signal, even if it leads to an overall reduction in the cell efficiency.

SiN_x	gain (mA/cm^2)	loss (mA/cm^2)
$YF_3:Er^{3+}$	0.08	5.99
$BaCl_2:Er^{3+}$	0.04	6.00
$BaCl_2:Er^{3+}, Dy^{3+}$	0.09	5.35

Table IV: Gain and loss in current density due to the adjustment the optical properties to the up-converter.

5 PC1D MODELLING

Using the results obtained in section 4, the maximum current density produced by each up-converter was calculated, converted to wattage at 0.98µm and used in PC1D to illuminate a cell from the rear side (AM15G on the front side). For front and rear antireflection coatings we used both the existing standards and the anti-reflection coatings adapted to the up-converters as discussed above. The cell design is shown in Figure 5. The cell is n-type with a bulk resistance of 30Ωcm. There is a 60 Ω/sq-Phosphorus-emitter and a 90 Ω/sq Boron back surface field (BSF). The surface recombination velocity (SRV) of 20000 cm/s on the emitter and 1500 cm/s on the BSF relates to SiO_2-passivation. Since these values were maintained also for application of SiN_x as ARC, the results of optical adjustment are not fully adapted to the cell used in the PC1D simulations. This could be amended including a SiO_2/SiN_x-stack.

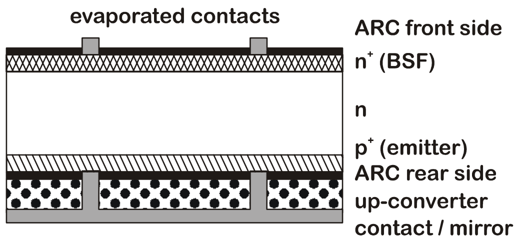

Figure 5: Schematic drawing of the cell the PC1D-simulations are based on. The n-type cell is illuminated with the AM15G-spectrum at the BSF-side. The up-converter is located on the emitter-side of the cell. This is the most efficient arrangement.

Due to the different SRV on the emitter- and BSF-side, the illumination of the BSF with AM15G leads to higher efficiencies than the illumination of the emitter. For monochromatic illumination with 0.98µm this situation is reversed and it is more efficient to illuminate the emitter. Both sides of this cell can therefore be illuminated with the light source for which it is most efficient. The cell results with and without the up-converter are shown in Table V.

For the simulations the internal reflectance was set to 95%, what is not realistic for untextured cells.

In section 4, we showed the current increase due to the up-converter assuming a peak efficiency of 100%. For the results shown in table V, the efficiency of the up-converter can easily be included. In addition, the influence of concentrated sunlight can also be included by multiplying the efficiency of the up-converter with the concentrating factor.

η_{uc}=0	V_{oc} (mV)	J_{sc} (mA/cm^2)	η_{cell} (%)
Standard ARC	642.3	35.9	17.67
adapted to the up-converter			
$YF_3:Er^{3+}$	635.6	30.2	14.73
$BaCl_2:Er^{3+}$	635.6	30.2	14.73
$BaCl_2:Er^{3+}$, Dy^{3+}	636.3	30.8	15.02
η_{uc}=100%	V_{oc} (mV)	J_{sc} (mA/cm^2)	η_{cell} (%)
Standard ARC			
$YF_3:Er^{3+}$	642.5	36.1	17.78
$BaCl_2:Er^{3+}$	642.4	36.0	17.72
$BaCl_2:Er^{3+}$, Dy^{3+}	642.5	36.1	17.79
adapted to the up-converter			
$YF_3:Er^{3+}$	636.0	30.5	14.88
$BaCl_2:Er^{3+}$	635.8	30.3	14.80
$BaCl_2:Er^{3+}$, Dy^{3+}	636.7	31.1	15.19

Table V: Results of the PC1D-simulation with and without application of an up-converter.

To make it more comparable the maximum transmitted current calculated in section 4 corresponds to η_{uc}=100%. From Table V it follows that adapting the optical properties of the cell to the up-converter leads to losses in the cell efficiency of about 2.7-3% for η_{uc}=100%. Although the gain due to the up-converter on the adapted cell is very small (about 0.01-0.05% efficiency), the percentage increase of the effect of the up-converter is 33% to 42%, which corresponds to a relative enhancement of the current found in section 4.

The losses due to the adaptation of the cell to the up-converter are very high at one sun, but at some point the product of the efficiency and the concentration of the sunlight mean that the cell will operate more efficiently if adapted for the up-converter. In Figure 6 the dependence of the cell efficiency on this wattage of the up-converter for the three up-converters is shown. There is a pair of lines for each up-converter. The lines with higher initial cell efficiency correspond to the cell with a standard ARC. The cross-over point of each pair indicates the point at which the cell will operate more efficiently when the antireflection coatings are designed for the up-converter. For $BaCl_2:Er^{3+}$, Dy^{3+} the cross-over point occurs at 6300% which corresponds to 63 suns assuming 100% up-conversion efficiency or 6300 suns assuming 1% up-conversion efficiency. Ideally, the operating concentration and the efficiency of the up-converter should be known. Once this is the case, the anti-reflection coatings may be optimised for the real cell.

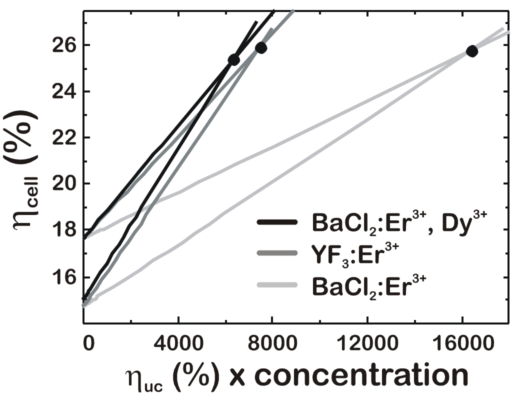

Figure 6: Dependence of the cell efficiency on the product of up-conversion efficiency and concentration of the incoming light for the three up-converters. The upper line of each pair (starting at nearly 18% cell efficiency) corresponds to the cell with standard ARC, the steeper to lines starting at approximately 15% cell efficiency correspond to the cell designs adapted for the up-converter. The junction of the two lines indicates the point at which the performance of the up-converter is sufficiently high that the ARC thicknesses will be dominated by the requirements of the up-converter.

SUMMARY

The efficiency enhancement due to the application of any of the existing up-converters is expected to be very low. The performance of the up-converters is limited by both the absorption range and the efficiency. Both of these properties must be improved before a significant effect of the up-converter on cell performance will be seen. We have shown that an adjustment of the cell design to the up-converter enhances the gain due to the application of an up-converter by about 35%. Adjustment of the cell to the up-converters was found to be necessary under high concentrations.

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