ENHANCING SILICON SOLAR CELL EFFICIENCY BY MODIFYING THE SOLAR SPECTRUM

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ABSTRACT

Two approaches can be followed to reduce thermalisation and transmission losses in solar cells and thereby better exploit the solar spectrum. Firstly, modification may be done to lower energies, which can be via down-conversion, where one high energy photon is split into two or more low energy photons, or photoluminescence, where photons are shifted into different wavelength regions. Secondly, modification may be done to higher energies using up-conversion, where two or more low energy photons are combined to form one high energy photon. In this paper, the state of the art of these methods and the suitability of materials available today for application to silicon solar cells are presented.

BACKGROUND

Modification of the solar spectrum by spectral converters allows a reduction in losses due to a) transmission of photons with energy lower than the band gap (E<1.12 eV, λ>1.1 µm for silicon) and b) thermalisation of minority carriers generated by photons with energy higher than twice the band gap (E>2.24 eV, λ<0.55 µm for silicon) [1, 2].

Photons with an energy exceeding twice the band gap of the solar cell can be split by a down-converter on the front side of the cell into two (or more) photons, both able to generate electron hole pairs. Using photoluminescence high energy photons can be shifted to lower energies, where the solar cell is more efficient. Down-conversion, which is also called quantum cutting, has so far only been observed in vacuum ultraviolet ranges. Both down conversion and photoluminescence are shown schematically in Figure 1a. In contrast, several photoluminescence converter materials are available and some of them have already been tested in solar cell experiments, including CdSe quantum dots and Si nano-crystals in a dielectric matrix [3, 4]. These systems show promise for application to solar cells with poor blue response.

An up-converter on the rear side of a bifacial solar cell can convert two (or more) transmitted low energy photons to one high energy photon able to generate an electron-hole-pair when re-injected into the solar cell (see Figure 1b). A wide variety of up-converters exist. For application to silicon solar cells the most promising are Erbium-doped materials.

Theoretical calculations [1, 2] show the effect of the application of an up- or down- converter on the cell efficiency limit using a detailed balance model. A shift in the efficiency limit from 30.9% to 36.6% due to the application of an ideal down-converter on the front side and to 37.4% using an up-converter on the rear side of a silicon solar cell under one sun illumination has been calculated. These calculations assume the converters have ideal absorption and emission properties. In previous work, we have calculated the efficiency increase possible for silicon solar cells using existing up-converters [5]. In this paper, we discuss possibilities for each of the spectrum modification methods.

CONVERSION TO LOWER ENERGIES

Down conversion, or quantum-cutting is found in two groups of materials: (i) host-materials doped with rare-earth ions (e.g. Pr^{3+} in fluoridic [6-12] or oxidic hosts [13], Gd^{3+}-doped and/or Eu^{3+}-doped [14-20], Er^{3+}-Tb^{3+}-codoped $LiGdF_4$ [15]), where the down-conversion takes place only within the ion and (ii) band-like down-converters, where an Auger-process takes place within the host-material and
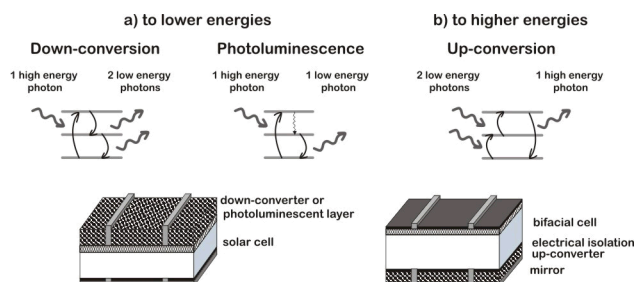

Fig. 1. Spectrum modification: a) to lower energies by down-conversion (one high energy photon is split into two low energy photons) and by photoluminescence (one high energy photon is shifted to lower energies) and b) to higher energies using up-conversion (two low energy photons are combined to one high energy photon). In the lower part of the figure application to the front and rear of a conventional bifacial solar cell is shown.

only the emission occurs within the ions (e.g. Mn-doped phosphates [21, 22], Eu-doped oxides [21, 22, 23], Ag, Cu and/or Zn-doped ZnS [21]). Although quantum efficiencies of up to 190% are proposed theoretically for ionic-like down-converters [20], and experimental quantum efficiencies of up to 240% have been found in band-like down-converters [20], these systems are not suitable for silicon solar cells, since the excitation wavelengths are typically 0.2μm or less.

Contrary to down-conversion, the quantum efficiency for photoluminescence cannot exceed one. Nevertheless the gain due to the application of an appropriate luminescent layer can be substantial when the emitter is quite deep or the front passivation is poor, i.e. for solar cells with a limited blue response.

Due to the requirement of high transparency for the regions of the spectrum that are not modified, the most promising photoluminescent systems consist of a dielectric transparent matrix containing quantum dots or nano-crystals in which the shifting takes place. The first experimental attempt to implement this structure was realized by van Sark *et al.* [3] using CdSe quantum dots in a transparent polymeric matrix on a multi-crystalline silicon solar cell, but no improvement due to the modification of the spectrum was evident. Nevertheless, theoretical calculations predict an improvement in short circuit current of nearly 10% relative [24].

A rise in short circuit current of nearly 0.4% absolute was found using nano-structured silicon in a non-stoichiometric silica-layer [4]. Silicon nanostructures in non-stoichiometric dielectric matrices as SiO_x and SiN_x are very promising since they exhibit emission at 0.6-0.8 μm under UV excitation and the host-material can be used as an antireflection-coating and front surface passivation layer. Figure 2 plots the photoluminescence spectra recorded at room temperature for three different dielectric stacks on silicon samples: a thermally annealed PECVD deposited SiN_x, a spin-on glass (SOG) layer containing Si powder extracted from porous silicon, and an annealed silicon oxide film implanted with silicon ions. The peak position depends on the dielectric matrix and on the annealing conditions.

CONVERSION TO HIGHER ENERGIES

Up-converters typically consist of a host-material doped with a rare earth or transition metal ion (a so called active ion). The optical properties of the rare earth ions are only weakly influenced by the host-material because the energy levels involved in the optical transitions are shielded by filled outer shells. In contrast, for transition metal ions, the electrons responsible for the optical transitions are not shielded and the crystal field of the host-material determines the emission and absorption spectra.

Trivalent Erbium is the most suitable rare earth ion for an application to silicon solar cells due to the absorption at 1.5 μm and emission peaks at approximately 0.98 μm,
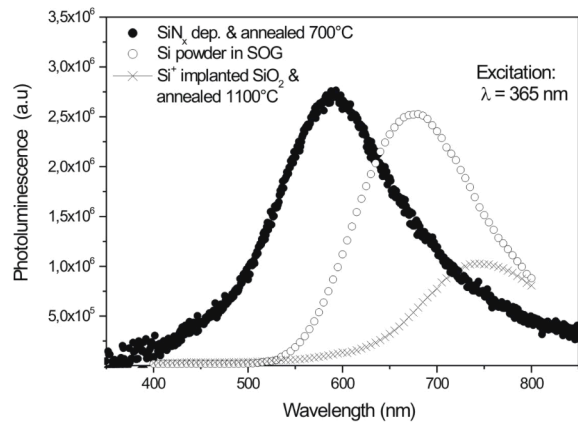

Fig. 2. Room temperature photoluminescence measured in dielectric films deposited on top of silicon samples under excitation at 0.365μm.

0.81 μm, 0.66 μm, 0.55 μm and 0.41 μm. Co-doping with trivalent Dysprosium and Erbium was found to lead to an absorption at 1.3 μm within Dysprosium (see Figure 3) followed by an emission showing the characteristics of the single Er-doped system [25].

The first application of an up-converter to a silicon solar cell was done by Shalav *et al.* [26] using $NaYF_4$ doped with trivalent Erbium. The most efficient phosphor they examined had 20% Er^{3+} doping and gave a maximum external quantum efficiency close to 3.4% with 6 mW 1523 nm laser excitation [27].

For the Erbium-doped systems various host-materials exist (for example Fluorides [28, 30-38], Chlorides [29, 30, 31, 39], Oxides [40], Iodides [29, 30] and Bromides [29, 30]). The properties of the host-material influencing the up-conversion process are the phononic properties and the electric field caused by the ions of the host-material surrounding the active ion (crystal field). A high phonon coupling between the host and the doping ion enhances the probability of undesirable non-radiative relaxations. On the other hand, a good coupling is
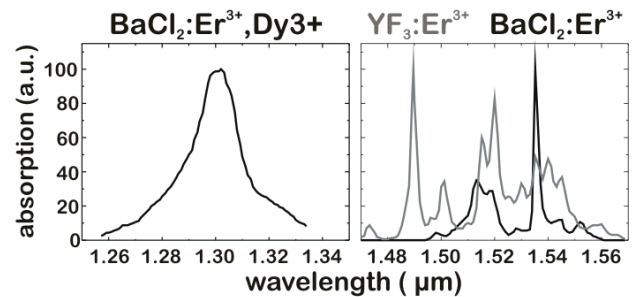

Fig. 3. Infrared absorption spectra of the up-converters $BaCl_2$: Er^{3+}, Dy^{3+}, $BaCl_2$:Er^{3+} and YF_3:Er^{3+} under emission at 0.55 μm. The co-doped up-converter absorbs between 1.26 and 1.33 μm with the absorption maximum at about 1.3 μm. The single doped samples absorb between 1.48 and 1.56 μm. The absorption range of the fluoride is broader than of the chloride.

necessary for energy transfer mechanisms, which are the basis of most of the up-conversion mechanisms. The influence of the crystal field on the doping ion is represented by Stark Splitting and is responsible for the shape of the absorption and emission spectra. Experimentally this was shown by Ohwaki and Wang [29], who found Chlorides as a host-material to be more efficient than Fluorides due to less non-radiative relaxations, while Fluorides show a broader excitation range than for example Chlorides (Figure 3).

Examples of transition metal doped materials showing up-conversion are $MgCl_2:Ti^{2+}$ [41-43], $NaCl:Ti^{2+}$ [43], $Cs_2ZrBr_6:Os^{4+}$ [41], $Cs_2ZrCl_6:Re^{4+}$ [41-43, 46], $YAlO_3:Cr^{3+},Yb^{3+}$ [47, 48] and $Y_3Ga_5O_{12}:Cr^{3+},Yb^{3+}$ [48, 49]. For all these examples, the excitation is at shorter wavelengths than 1.1 µm, which means their application is limited to thin silicon solar cells.

ADAPTION OF SILICON CELL DESIGN FOR ER-DOPED UP-CONVERTERS

In reality, the absorption ranges of existing up-converters are small. Based on the experimental results of Ohwaki and Wang for the absorption properties of $YF_3:Er^{3+}$, $BaCl_2:Er^{3+}$ and $BaCl_2:Er^{3+}, Dy^{3+}$, we have calculated the number of photons available in the wavelength range of existing up-converters. These numbers are shown in Table 1 together with the number of photons located within the absorption range of a silicon solar cell. Even though many additional photons are accessible via ideal two-photon-up-conversion, the expected enhancement of silicon solar cells is small due to the small absorption ranges of the up-converters.

Given the low expected response from the up-converter it could be useful to adapt the optical design of the solar cell to enhance the influence of the up-converter. The optical design of a solar cell is optimized for absorption of the visible part of the spectrum, and therefore a relatively high percentage of infrared photons are reflected. A cell design adjusted to the optical properties of an up-converter should provide a minimum reflection in the infrared part of the spectrum (high transmission, T_{FS}, for the absorption range of the up-converter, see Figure 4), but also a high transmission of this wavelength range through to the rear side of the cell

	Photons available [$s^{-1}m^{-2}$]	Percentage [%]
in Si absorption range	27.2×10^{20}	100
Up-convertable	13.0×10^{20}	48
$YF_3:Er^{3+}$	0.4×10^{20}	1.5
$BaCl_2:Er^{3+}$	0.1×10^{20}	0.6
$BaCl_2:Er^{3+},Dy^{3+}$	0.7×10^{20}	2.4

Table 1. Number of photons available for the different up-converters. The percentages relative to the number of photons located within the absorption range of a silicon solar cell.
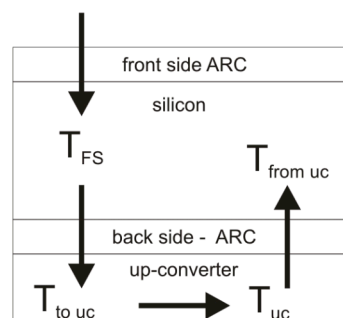

Fig. 4. Model of the bifacial cell with an up-converter on the rear side. The total transmission, T, is the product of the transmission through the front side, T_{FS}, the rear side, T_{RS}, and of the up-converted light back into the cell, $T_{from uc}$. The influence of the up-converter is represented by T_{uc}, which includes a change in wavelength from the excitation wavelengths at 1.5 µm and 1.3 µm to the up-converted light (0.98 µm) and a halving of the photon number. Maximizing T gives optimum thicknesses of the front- and rear anti-reflection coating and an optimum refractive index of the up-converter.

($T_{to uc}$), while the transmission of the light emitted by the up-converter ($T_{from uc}$) into the cell should also be as high as possible. Under the assumption of ideal two-photon-up-conversion, the term T_{uc} causes a change of the wavelength to 0.98 µm and a halving of the number of photons. The total transmission is the product of each single transmission. On the basis of the calculations of Crooke [50], the thicknesses of the anti-reflection coatings for the front and rear side of the cell and the optimum refractive index of the up-converter are calculated and listed in Table 2.

A bifacial cell as described in [50] with conventional optical design and adapted cell designs were used for PC1D-calculations. The results are shown in Table 2. As expected, the adaption of the optical parameters of the cell lead to much higher losses compared to the gain due to the up-converter. There is, however, a substantial increase (approximately 36-40%) in photon current at the wavelength ranges used by the up-converter when the cell

SiN_x	dFS [nm]	n_{opt}	dRS [nm]	Gain [mA/cm²]	Loss [mA/cm²]	increase [%]
$YF_3:Er^{3+}$	191	1.3	142	0.08	5.99	36
$BaCl_2:Er^{3+}$	192	1.3	142	0.04	6.00	37
$BaCl_2:Er^{3+}, Dy^{3+}$	162	1.2	137	0.09	5.35	35

Table 2. Results of the adjustment of the front and rear anti-reflection coating to the properties of the up-converters. The optimum refractive indexes for the up-converter and the resulting transmission are listed. In the last two columns the gain due to the up-converter in the infrared region of the spectrum is compared to the losses due to the adaption to the up-converter in the region accepted by a silicon solar cell.

is adjusted to the up-converter, which leads to an increase in the short circuit current of the solar cell of 35-37% compared to an up-converter applied to a conventional cell. For investigations of the performance of various up-converters it will be useful to have this additional signal.

CONCLUSIONS

In this paper, we presented an overview of materials that can be used to modify the incoming spectrum in order to enhance the efficiency of silicon solar cells. All ways to modify the solar spectrum - down-conversion, photoluminescence and up-conversion - are seen in a broad range of materials. Modification of the spectrum to lower energies using down-converters studied to date seems unlikely to be suitable for application to terrestrial silicon solar cells due to excitation wavelengths lower than the lower band of the solar spectrum. More promising is the application of a photoluminescent layer to silicon solar cells consisting of quantum dots in transparent matrixes. To modify the spectrum to higher energies up-converters based on materials doped with trivalent Erbium or co-doped with trivalent Erbium and trivalent Dysprosium are well suited for application to silicon solar cells due to their absorption and emission properties.

Calculations of the photon numbers accessible using Erbium-doped and Erbium-Dysprosium-co-doped up-converters show that the benefit in solar cell efficiency is limited by the small absorption ranges of the up-converters. An adjustment of the cell design to the optical properties of the up-converter could increase the gain in short circuit current due to the up-converter by 35-37% compared to an up-converter applied to a conventional cell.

ACKNOWLEDGEMENTS

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