UPCONVERSION TO ENHANCE SILICON SOLAR CELL EFFICIENCY - DETAILED EXPERIMENTAL ANALYSIS WITH BOTH COHERENT MONOCHROMATIC IRRADIATION AND WHITE LIGHT ILLUMINATION

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ABSTRACT: Upconversion (UC) of sub-band-gap photons is a promising approach to increase solar cell efficiencies, because it makes these sub-band-gap photons useful as well. We investigate the application of β-NaYF$_4$:20% Er^{3+} to silicon solar cells. We determine the external quantum efficiency of an UC silicon solar cell, both under monochromatic excitation and under white light illumination. We demonstrate that an UC silicon solar cell responds under white light with an average UC efficiency of 1.07 ± 0.13% in the spectral range from 1460 to 1600 nm. Concepts are discussed how the narrow absorption range of the UC material can be overcome.

Keywords: Upconversion, silicon, solar cell, characterisation.

1 INTRODUCTION

Silicon solar cells lose about 20% of the energy incident from the sun because long-wavelength photons below the band-gap are not absorbed. Upconversion (UC) means to generate one high-energy photon out of at least two low-energy photons. A detailed description of the various UC mechanisms can be found in [1]. UC pushes the theoretical efficiency limit for a silicon solar cell illuminated by non-concentrated light from close to 30% [2] up to 40.2% [3].

The highest UC efficiencies in the context of silicon solar cells have so far been achieved with hexagonal NaYF$_4$ doped with trivalent erbium, with a 20% erbium content, in expression β-NaYF$_4$:20% Er^{3+} [4, 5]. Er^{3+} features conveniently spaced energy levels, and the β-NaYF$_4$ host lattice shows low phonon energies which reduce non-radiative losses. The application of upconverters to harvest solar energy means that the upconverter is illuminated in a wide spectral range. In contrast, the analysis of UC was carried out mostly with coherent laser illumination [4-7], therefore not reflecting the later application under illumination with the broad solar spectrum. The only experiments with white light were performed in the visible range of the spectrum on organic materials [8] and are therefore of minor significance for the application on silicon solar cells. In this paper, we investigate the behaviour of Er-based upconverters under, both coherent laser excitation and additionally broad spectrum illumination. Subsequently, we compare these two approaches.

2 MEASUREMENTS WITH COHERENT ILLUMINATION

2.1 Setup and method

A bifacial back-junction back-contact silicon solar cell with an active area of 4.5 mm x 4.5 mm served as the basis for our UC photovoltaic device. Details on this type of solar cell are reported in Ref. [9]. The solar cell has both n- and p-contacts on the rear. Under one sun AM1.5G illumination on the grid free planar side, the solar cell exhibits around 19% efficiency.

The upconverter was attached to the grid-free former front side of the solar cell, avoiding problems with the contacts of the solar cell. The UC photovoltaic device was then illuminated from the former rear side. Having all contact fingers on the new front, however, causes serious shading losses. The geometric coverage of the grid fingers amounts to roughly 60% of the active cell area. This cell design is therefore not suited to reach highest efficiencies, but it is a convenient test device for our experiments.

β-NaYF$_4$:20% Er^{3+} is a microcrystalline powder, with a refractive index of n_{UC}=1.52 [5]. We used zapon varnish as a binding agent that connects the particles of the powder (n_{Zapon}=1.50) [10]. The UC powder was mixed with zapon varnish and dried at room temperature. The obtained sample was 0.9 mm thick with a concentration of the β-NaYF$_4$:20% Er^{3+} of 98% by weight. The sample was optically connected to the silicon solar cell by the refractive index matching liquid Cargille immersion oil Type 300 with $n_{coupling}$=1.52.

For the measurement of the external quantum efficiency (EQE), the solar cell was placed on a gold-coated measurement chuck, which has a cavity for the upconverter. The solar cell UC system was illuminated with an IR-laser ECL-210 from Santec that can be tuned from 1430 to 1630 nm. In this spectral range, the external quantum efficiency of the solar cell upconverter system was measured with an irradiance I of 1090 Wm^{-2}. The excitation beam was chopped at a rate of 9 Hz. Additionally, a continuous bias illumination of 0.04 suns was applied. Without an UC layer, no spectral response could be measured at wavelengths above 1200 nm.

The external quantum efficiency is defined as the ratio of the amount of electrons extracted from the solar cell to the amount of photons incident at a specific wavelength λ_{inc}. To determine the EQE, the short-circuit current of the solar cell due to UC photons $I_{SC,UC}(\lambda_{inc},I)$ was recorded using a lock-in amplifier 7265 from signal recovery. Additionally, the short-circuit current $I_{SC,ref}(\lambda_{inc},I)$ of a germanium reference cell was measured under identical conditions. The external quantum efficiency of the germanium cell $EQE_{ref}(\lambda_{inc})$ is known from different measurements with standard solar cell characterization equipment. By combining the results, the EQE of the UC solar cell system $EQE_{UC}(\lambda_{inc},I)$ can be calculated by

$$EQE_{UC}(\lambda_{inc},I)=EQE_{ref}(\lambda_{inc})\frac{I_{SC,UC}(\lambda_{inc},I)}{I_{SC,ref}(\lambda_{inc},I)}\cdot \qquad (1)$$

The uncertainty of the $EQE_{ref}(\lambda_{inc})$ in the IR spectral region is lower than 3% but is still the dominant error. The statistical errors of the two short-circuit currents $I_{SC,UC}(\lambda_{inc},I)$ and $I_{SC,ref}(\lambda_{inc},I)$ calculated from 25 measurements, each at the same λ_{inc} and I, are typically much lower.

2.2 Results

Figure 1 shows the wavelength dependent $EQE_{UC}(\lambda_{inc},I)$. It peaks at 0.34% at an incident wavelength of 1523 nm. This excitation spectrum features distinctive peaks. They originate in the crystal field splitting of the Er^{3+} energy levels and the spectral overlap of the UC steps between those levels [11]. Also a strong oscillation is visible, which results from interference effects within the silicon solar cell.

Figure 2 shows the $EQE_{UC}(\lambda_{inc},I)$ for different irradiances at an excitation wavelength of 1523 nm. The $EQE_{UC}(\lambda_{inc},I)$ increases with increasing irradiance. From theory, it is expected that the dependence of the UC luminescence on the excitation irradiance I follows a power law with a characteristic exponent $m = 2$ for low irradiance values and two-photon UC [1]. Consequently, the measured current due to UC should show the same behaviour. For the $EQE_{UC}(\lambda_{inc},I)$, which is determined by dividing by the number of incident photons, one expects a power law with an exponent m-1. To determine the characteristic exponent m, we performed a least-square fit of the $EQE_{UC}(\lambda_{inc},I)$ data with the function

$$EQE_{UC}(\lambda_{inc},I)=c_1\times I^{m-1}+c_2 \qquad (2)$$

where c_1 and c_2 are additional fitting parameters. We found a characteristic exponent of $m = 1.89$. Stimulated processes, such as stimulated emission and excitation of higher energy levels, are the reason for the value being slightly lower than 2 [12, 13].

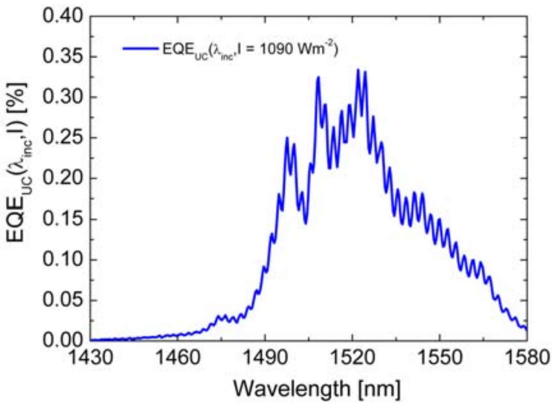

Figure 1: External quantum efficiency of the UC solar cell for different excitation wavelengths at an irradiance of 1090 Wm^{-2}. The $EQE_{UC}(\lambda_{inc},I)$ peaks at 0.34% for an excitation wavelength of 1523 nm.

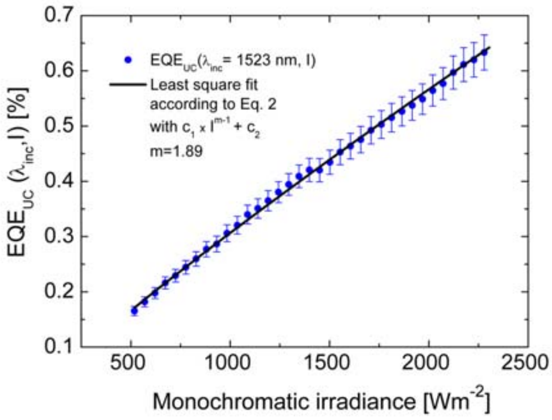

Figure 2: External quantum efficiency of the UC solar cell for different irradiance values at an excitation wavelength of 1523 nm. The $EQE_{UC}(\lambda_{inc},I)$ reaches 0.64% at an irradiance of 2305 Wm^{-2}.

3 MEASUREMENTS UNDER WHITE LIGHT

3.1 Setup and method

Besides the laser excitation, the UC solar cell was measured under concentrated white light illumination as well to determine the additional short-circuit current $I_{SC,UC}$ due to the upconverter. Figure 3 shows a schematic of the experimental setup. Several lenses concentrate the light of a Xe-Lamp onto the solar cell. To increase the relative impact of the UC layer, a 160 µm thick polished silicon wafer blocks most of the light that can be used directly by the Si solar cell, but it transmits IR photons suitable for UC. In this configuration, the benefit of the UC due to a raised short-circuit current I_{SC} is more easily detectable than under full AM1.5 sun illumination. The remaining transmission of the silicon wafer for photons with energies above the band-gap has the function of a bias illumination. Such, the solar cell is operated under sufficient illumination for an efficient use of the upconverted photons.

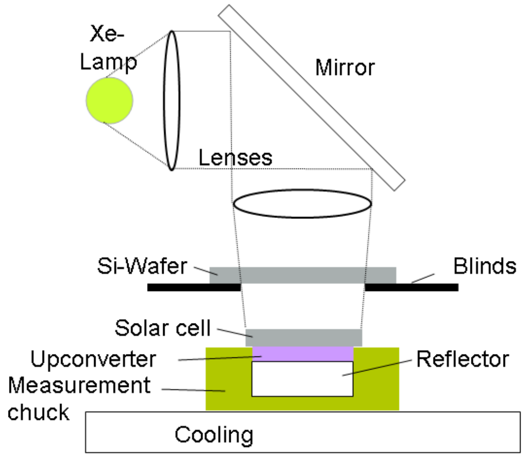

Figure 3: Setup for measurements under concentrated white light illumination. A silicon solar cell serves as long-pass filter to increase the relative impact of the UC.

The measurements were performed with two different lens settings. The resulting bias illumination levels for a silicon solar cell were 0.2 and 0.5 suns, respectively. The solar cell UC system was mounted on the same measurement chuck as described in the previous chapter. The chuck was cooled to keep the solar cell temperature at standard test conditions.

$NaYF_4$:20% Er^{3+} is a good diffuse reflector as well. Therefore, photons with energies above the silicon band-gap could be reflected by the UC powder and be absorbed by the silicon solar cell. This increases the solar cell efficiency without any UC contribution. Therefore, the I_{SC} of the silicon solar cell was measured as well with a diffuse reflector without UC properties. It was made from polytetrafluorethylene (PTFE) and optically coupled to the back of the solar cell. For wavelengths longer than 600 nm, PTFE has a reflectivity exceeding 95% while a 0.9 mm layer of $NaYF_4$:20% Er^{3+} solidified with zapon varnish has a reflectivity below 90%. Accordingly, a short-circuit current measured with upconverter that exceeds the current measured with PTFE back reflector is a clear sign of a positive UC effect.

The relative spectra incident on the solar cell for the two lens settings were determined with a spectrophotometer. The overall intensity was determined with a calibrated back contact Si solar cell designed for concentrated light from which the EQE was known. From these data, the photon fluxes onto the cell area in the active region of the upconverter from 1460 nm to 1600 nm Φ_{cell} were calculated to be $(2.53 \pm 0.03)\mathrm{x}10^{17}\ \mathrm{s}^{-1}$ and $(4.04 \pm 0.09)\mathrm{x}10^{17}\ \mathrm{s}^{-1}$, respectively. Comparing these photon fluxes to the photon flux of the AM1.5 norm spectrum in this spectral range yields effective concentration levels of 458 ± 5, and 732 ± 17 suns, respectively. The stated errors reflect the uncertainty of the average value determined from repeated measurements of the concentration level.

To extract the extra current due to the upconverter $I_{SC,UC}$ the average of the short-circuit current measurements with PTFE reflector $I_{SC,PTFE}$ is subtracted from the average of the measurements with upconverter attached to the silicon solar cell $I_{SC,Zap}$

$$I_{SC,UC} = I_{SC,Zap} - I_{SC,PTFE} \,. \tag{3}$$

The concentrated light spot is not fully homogeneous. To determine the uncertainty induced by this inhomogeneity, each measurement was repeated 5 times, with the solar cell removed and remounted for each iteration. For $I_{SC,PTFE}$ and $I_{SC,Zap}$ the uncertainties of the average values as determined from the repeated measurements are listed as uncertainties. The uncertainty of $I_{SC,UC}$ was calculated with Gaussian error propagation from these values. The relative error of $I_{SC,UC}$ is quite high, as although $I_{SC,UC}$ itself is quite small, it is the result of the subtraction of two relatively large values.

3.2 Results and discussion

Table 1 shows the different measured and calculated short-circuit current values. The results are also visualised in Figure 4. Despite all uncertainties, a significant increase of the short-circuit current due to the upconverter was observed. For instance, at 732 suns concentration the short circuit current with white PTFE reflector was 3.26 ± 0.07 mA. This current was increased by 0.69 ± 0.08 mA to 3.95 ± 0.04 mA due to the addition of the UC layer. To our best knowledge, this is the first time that such an increase in short-circuit current due to UC has been measured on a silicon solar cell under broad spectrum illumination.

From the short-circuit current measurements a spectrally integrated external quantum efficiency of the solar cell UC device $EQE_{UC,int}(\Phi_{cell})$ can be calculated via

$$EQE_{UC,\mathrm{int}}(\Phi_{cell}) = \frac{I_{SC,UC}}{q \cdot \Phi_{cell}} \,. \tag{4}$$

In this equation q is the elementary charge.

The $EQE_{UC,int}(\Phi_{cell})$ increases with the concentration from 0.81 ± 0.07% at 458 suns to 1.07 ± 0.13% at 732 suns. This agreement with the theoretical expectation supports the conclusion that the observed effect is due to UC. For further evidence, measurements should be performed with a larger set of concentration levels.

Table I: Summary of the results of the measurements under concentrated white light

Concentration [suns]	458 ± 5	732 ± 17
$I_{SC,PTFE}$ [mA]	1.67 ± 0.02	3.26 ± 0.08
$I_{SC,Zap}$ [mA]	1.99 ± 0.02	3.95 ± 0.04
$I_{SC,UC}$ [mA]	0.33 ± 0.03	0.69 ± 0.08
$\Phi_{cell,UCrange}$ [$10^{17}\ \mathrm{s}^{-1}$]	(2.53 ± 0.03)	(4.04 ± 0.09)
$EQE_{UC,int}$ [%]	0.81 ± 0.07	1.07 ± 0.13
EQE_{UC} [%] monochromatic	0.47± 0.01	0.71± 0.02

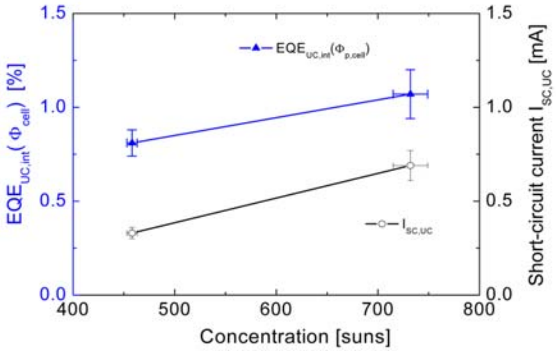

Figure 4: Visualisation of the results under white light illumination. Both the current due to UC $I_{SC,UC}$ and the $EQE_{UC,int}$ increase with the concentration.

The question arises, how the UC efficiencies under white light illumination $EQE_{UC,int}(\Phi_{cell})$ compare to the $EQE_{UC}(\lambda_{inc},I)$ measured with monochromatic laser excitation. The observed photon fluxes in the active region of the upconverter Φ_{cell} of $(2.53 \pm 0.03)\mathrm{x}10^{17}\ \mathrm{s}^{-1}$ and $(4.04 \pm 0.09)\mathrm{x}10^{17}\ \mathrm{s}^{-1}$ correspond to irradiance values of 1629 Wm^{-2} and 2601 Wm^{-2}, respectively, for monochromatic irradiation at 1523 nm. At 1629 Wm^{-2} the $EQE_{UC}(\lambda_{inc=1523\ nm},I)$ was 0.47%. For an irradiance of 2601 Wm^{-2} an extrapolation with the fitted power law according to Eq. 2 yields an $EQE_{UC}(\lambda_{inc=1523\ nm},I)$ of 0.71%. Both monochromatic values are lower than the values determined under white light illumination. This is an interesting result because the monochromatic values were determined at the most efficient wavelength. In contrast, the values under white light constitute an average over the whole active region including wavelengths that showed considerably lower efficiencies in the spectrally resolved measurements, see Figure 1. The bias illumination levels might have contributed to the observed differences. However, the differences are so significant that we assume a positive influence on the efficiency for white light illumination: The transitions between the different energy levels involved in the upconversion process are not centred on exactly the same energy, and each transition itself has a certain width. Therefore, broad spectrum illumination should enhance the probability of an UC process, as photons with the resonant energy for each possible transition are available, as already expected in [14]. Experiments combining more than one tuneable monochromatic excitation source could yield further insight into this issue.

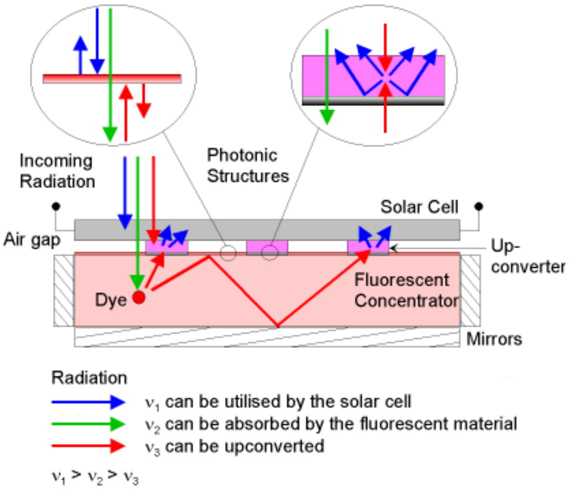

Figure 5: An advanced UC system. By the use of a luminescent material, a larger spectral range is upconverted. Because of the non-linear characteristic of the upconverter, the efficiency increases due to additional geometric concentration. [14]

The positive influence of broad spectrum illumination supports the application of UC in silicon solar cells, because those feature naturally a broad spectrum illumination. Broad spectrum illumination, however, also constitutes a challenge, because the UC region of 1460 nm to 1600 nm is narrow compared to the broad spectral range of sub-Si-band-gap photons. This can be overcome, by combining the upconverter with a second luminescent material [4],[14]. This luminescent material should absorb in a wide spectral range and emit in the absorption range of the upconverter, such extending the utilized spectral range. Additionally, the luminescent material could be incorporated into a fluorescent concentrator to achieve an additional geometric concentration of the light onto the upconverter. This exploits the non-linear characteristic of UC and further increases the UC efficiency [14].

4 CONCLUSIONS AND OUTLOOK

We showed that a silicon solar cell with an attached β-NaYF$_4$:20% Er^{3+} UC material solidified with zapon varnish responds with an $EQE_{UC}(\lambda_{inc},I)$ of 0.34% at an incident wavelength of 1523 nm for an irradiance of 1090 Wm^{-2}. This efficiency increases with irradiance. We demonstrated as well an UC effect under broad spectrum illumination. It results in an extra current due to UC photons of 0.69 ± 0.08 mA under a concentration of 732 ± 17 suns in the active region of the upconverter. Interestingly, the resulting averaged $EQE_{UC,int}(\Phi_{cell})$ over this spectral region of 1.07 ± 0.13% is higher than values determined with monochromatic excitation at comparable irradiances. We therefore assume that broad spectrum illumination enhances the UC efficiency in comparison to monochromatic excitation conditions. A likely explanation is the availability of photons of resonant energies for all involved transitions. We presented the combination of UC with a second luminescent material integrated in a fluorescent concentrator as a possible way to increase the UC efficiency. With such modifications, UC has the potential to significantly enhance silicon solar cell efficiency.

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