

Upconverter Silicon Solar Cell Devices for Efficient Utilization of Sub-Band-Gap Photons under Concentrated Solar Radiation

Stefan Fischer¹, Aruna Ivaturi², Benjamin Fröhlich¹, Marc Rüdiger¹, Armin Richter¹, Karl W. Krämer³, Bryce S. Richards^{2,4}, Jan Christoph Goldschmidt^{1,5}

¹Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany; ²Institute of Photonics and Quantum Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland; ³Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland; Department of Materials Science & Engineering; ⁴Nelson Mandela African Institute of Science and Technology, Tengeru, Arusha, Tanzania; ⁵Imperial College, South Kensington Campus, London SW7 2AZ, United Kingdom

Abstract — Upconversion of sub-band-gap photons has the potential to increase the efficiency of solar cells significantly. We realized an upconverter solar cell device, by attaching an upconverter layer of β -NaYF₄ doped with 25% Er³⁺ embedded in the polymer perfluorocyclobutyl to the rear side of a bifacial silicon solar cell. We determined the external quantum efficiency of such upconverter solar cell devices under broad-band, sub-band-gap excitation. Under consideration of spectral mismatch, we calculated the expected increase of the short-circuit current density due to upconversion under the air mass 1.5 global illumination. We determined an enhancement of 2.2 mA/cm² for a spectral excitation band ranging from 1450 nm to 1600 nm and a comparatively low solar concentration of 78 suns. Subsequently, a system of concentrator lens and upconverter solar cell device was characterized with a solar simulator. We determined an increase of the short-circuit current density due to upconversion of sub-band-gap photons of 13.1 mA/cm² under a concentration of 210 suns. This corresponds to a potential relative increase of the solar cell efficiency of 0.19%.

Index Terms — photovoltaic cells, silicon, upconversion, optical frequency conversion, spectral conversion.

I. INTRODUCTION

In silicon solar cells, more than 45% of all photons of the solar spectrum cannot be utilized, because the energy of these photons is below the band gap energy of silicon. These photons carry about 20% of the whole energy of the sun's radiation. As a consequence, transforming these sub-band-gap photons into higher energy photons has the potential to enhance the efficiency of the solar cells considerably. The process to generate high energy photons from a larger number of lower energy photons is called upconversion (UC).

For silicon solar cells, lanthanide doped materials like hexagonal sodium yttrium fluoride (β -NaYF₄) doped with trivalent erbium (Er³⁺), make especially suitable upconverter materials [1]. This upconverter materials feature broad ground state absorption (GSA) spectra around 1523 nm and a dominant upconversion emission around 980 nm, which can be utilized by the silicon solar cells. The energy level structure is sketched in Fig. 1 including the most important UC

processes, which are energy transfer (ET), multi-phonon relaxation (MPR) and spontaneous emission (SPE) [2].

A first experimental approach to enhance the efficiency of a solar cell by upconversion was investigated by Gibart *et al.* in 1996 with a GaAs solar cell [3]. Successful proof-of-concept experiments with silicon solar cells have been performed with the upconverter material β -NaYF₄ with a Er³⁺ doping concentration of 20% [4, 5]. In these experiments the upconverter was attached on the rear side of the solar cell and the upconverter solar cell device was illuminated with monochromatic laser excitation.

For solar cells with larger band gaps other upconverter materials are potentially better suited. The β -NaYF₄ with 18% Yb³⁺ and 2% Er³⁺ are investigated for a-Si:H solar cells and an enhanced external quantum efficiency of the solar cell due to upconversion of photons with wavelengths of around 980 nm was found [6]. Organic compounds represent another group of upconverter materials. Due to triplet-triplet annihilation photons with wavelengths up to approximately 750 nm can be upconverted to shorter wavelengths. It has been shown that such organic upconverters improve the performance of a-Si:H [7] and organic solar cells [8]. At this point we would also like to refer to the overview articles of de Wild *et al.* [9] and Liu *et al.* [10].

To investigate the potential of upconversion for harvesting solar radiation, however, experiments under broad-band excitation or even concentrated sun light are much more meaningful. Typically, the spectral band width of the laser excitation is much smaller than the absorption line of the Er³⁺ transition. In contrast, the solar spectrum, and also the fraction of the spectrum transmitted by bifacial silicon solar cells, is considerably wider than these absorption lines. Under broad-band excitation, in addition to GSA also other upconversion processes, like excited state absorption (ESA), may be in resonance with the excitation and affect the upconversion dynamics. Hence, not only the spectral width but also the spectral intensity distribution of the excitation has to be taken into account.

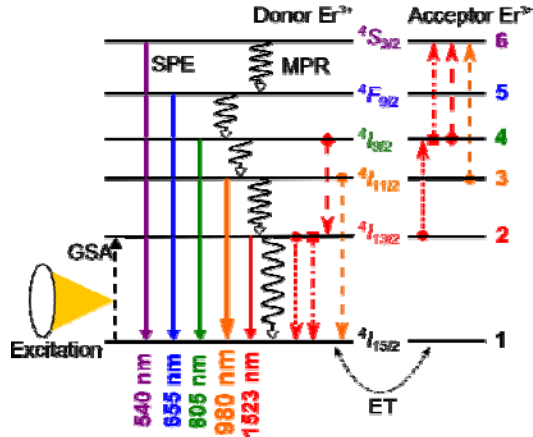


Fig. 1 The most important processes for upconversion in β -NaYF₄ doped with Er³⁺ are shown in this energy level scheme.

Up to now, only few experimental investigations of upconversion under broad-band excitation have been performed [11-13] and even fewer such experiments on upconverter solar cell devices [14, 15]. In this work, we will investigate bifacial silicon solar cells with an upconverter attached to the rear side under monochromatic laser and broad-band excitation to determine the external quantum efficiency (EQE) of the devices due to upconversion of sub-band-gap photons. Additionally, we determine the additional short-circuit current due to upconversion from current-voltage (IV)-curves of the upconverter solar cell device under concentrated light of a solar simulator.

II. EXPERIMENTAL DETAILS

A. Device fabrication

We produced bifacial silicon solar cells that were adapted for an upconversion application [16]. The solar cells used in this work feature a double layer front side antireflection coating (ARC) optimized to achieve a low reflection up to ~ 1800 nm (120 nm MgF₂ on top of 110 nm SiN_x), and a rear side single layer ARC optimized for low reflection of sub-band-gap photons and for low reflection of upconverted photons with wavelengths larger than 950 nm (120 nm SiN_x). Thus overall transmittance of sub-band-gap photons was maximized, and the solar cell's efficiency for photons emitted by the upconverter increased. We fabricated both planar and front side textured solar cells on 1 Ω cm, 200 μ m thick, n-type FZ silicon wafers. The size of the solar cells A_{cell} is 2 cm \times 2 cm. Both surfaces were passivated with Al₂O₃ prior to the deposition of the ARC.

The bifacial solar cells were soldered to copper frames, which form the rear contact of the solar cells. The copper frames are then applied on polytetrafluoroethylene (PTFE) blocks with a recess for the upconverter. The PTFE is a good

diffuse reflector and serves as a rear reflector for the upconverted and the incident excitation light.

In this work we used the upconverter powder β -NaYF₄ doped with 25% Er³⁺, which showed a larger upconversion quantum yield than the one with a 20% Er³⁺ doping concentration we used in previous investigations. The β -NaYF₄ doped with 25% Er³⁺ was embedded in the polymer perfluorocyclobutyl (PFCB) with a powder to polymer concentration of 75.7 w/w%. We used a sample with the same concentration of un-doped β -NaYF₄ in the polymer as a reference. The samples have a cylindrical shape with a diameter of 12.6 mm and a thickness of 1 mm [17]. Hence, the upconverter and the reference sample do not cover the complete active area of the solar cell. This will be important for the later discussed determination of the short-circuit current density. The solidified upconverter and reference sample were attached to the solar cells with the index matching liquid (IML) immersion oil (Type 300, Cargille), as depicted in Fig. 2.

B. Measurement setups

For the monochromatic measurements, we used an ECL-210 NIR laser from Santec to illuminate the upconverter solar cell devices with a wavelength of 1508 nm and different laser powers. Due to laser stability a wavelength of 1508 nm was used which shows around 87% of the upconversion luminescence compared to the commonly used 1523 nm excitation wavelength. The laser power and the beam profile were measured to determine the incident irradiance. More details of the setup for monochromatic measurements can be found in Ref. [5].

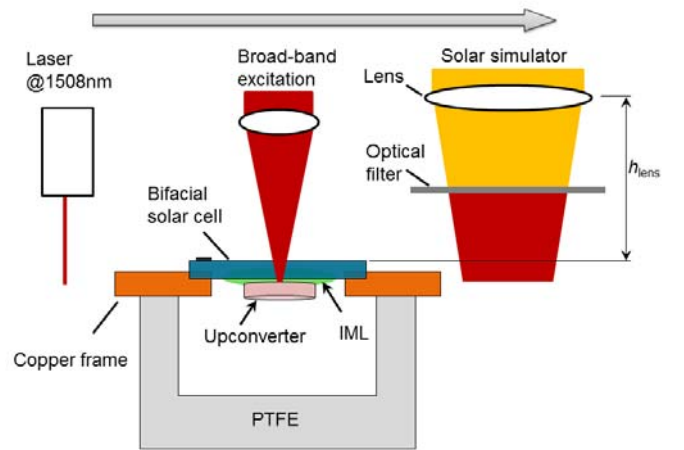


Fig. 2 An upconverter solar cell device, consisting of a bifacial silicon solar cell with an upconverter material embedded in a polymer attached to the rear side of the solar cell, was characterized under monochromatic laser and broad-band excitation. Furthermore, a Fresnel lens was placed in front of the device, and the whole system was characterized with a solar simulator. The additional

short-circuit current density due to upconversion $\Delta j_{\text{SC,UC}}$ was determined for the different concentration levels that could be achieved by adjusting the height of the lens above the measurement chuck h_{lens} .

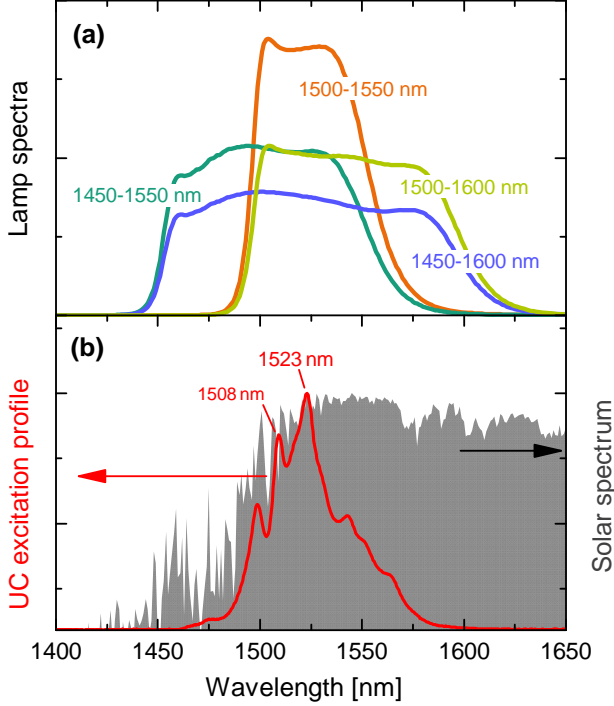


Fig. 3 (a) Normalized excitation spectra as used in the broad-band excitation experiments. (b) The excitation profile of the upconverter for emission of photons at 980 nm (red) overlaps well with the AM1.5G solar spectrum shown in photons per area and time (grey).

For the broad-band experiments, the spectrum of a halogen lamp was clipped by several long pass and short pass filters to four different excitation spectra, as shown in Fig. 3(a). The intensity of the broad-band excitation was adjusted by several neutral density filters. The light from the halogen lamp was focused with lenses into an optical fiber. On the other end of the optical fiber lenses were used to focus the light on the sample. The height of the lens system above the upconverter solar cell device was adjusted to obtain the largest short-circuit current due to upconversion of the photons transmitted through the solar cell. The beam profile was determined with a digital camera and a pixel counting method. The excitation spectra from the halogen lamp were recorded with a Jobin Yvon grating monochromator H25 and an InGaAs detector from OptoElectronic Components.

In the third measurement setup, we used a Fresnel lens to focus the light of a standard solar simulator (Wacom, WXS-150S-10, class A) onto the upconverter solar cell device. The Fresnel lens features a focal length of 169 mm and a dimension A_{lens} of $100 \times 100 \text{ mm}^2$. The height of the lens above the upconverter solar cell device h_{lens} can be adjusted with a translation stage. Hence, the concentration of the white

light on the sample is altered. From the geometrical data of our setup, we calculated an illuminated area A_{spot} ranging from $39.3 \pm 8.9 \text{ mm}^2$ at a height h_{lens} of 160 mm to $541.0 \pm 29.9 \text{ mm}^2$ at a height h_{lens} of 135 mm. Herein we assumed that for h_{lens} equal to the focal length, the focus had a spot size of 1 mm. The errors stem from the uncertainty of the height measurement of h_{lens} .

We applied two filters above the solar cell to clip photons that can be utilized by the silicon solar cell. First, a monocrystalline $750 \mu\text{m}$ thick silicon wafer blocks the UV, visible (VIS) and near-infrared (NIR) parts of the lamp spectrum. For a large transmittance of sub-band-gap photons ARCs of 120 nm TiO_2 and 120 nm MgF_2 were deposited on both sides, resulting in a transmittance above 80% in the absorption range of the upconverter. Second, a long pass filter from Edmund Optics with a cut-on wavelength of 1200 nm serves as an additional NIR filter for photons close to the band gap of silicon, which are transmitted through the silicon filter.

We measured the IV-curves of the upconverter solar cell devices with attached upconverter as a function of the height h_{lens} between lens and the front side of the silicon solar cell. Subsequently, we repeated the measurement with the reference sample attached on the rear side of the bifacial silicon solar cell.

C. External quantum efficiency due to upconversion

The same solar cell and the same upconverter sample were used in all measurements. In all three setups, the short circuit current of the solar cell $I_{\text{SC,UC}}$ was recorded with the upconverter attached to the rear of the solar cell. Additionally, the short-circuit current of the solar cell $I_{\text{SC,ref}}$ was recorded, with the un-doped reference sample attached instead of the upconverter sample. Finally, the short-circuit current of a germanium solar cell at the sample position $I_{\text{SC,Ge}}$ was recorded for calibration purposes. The external quantum efficiency EQE_{Ge} of this solar cell is known from calibrated measurements with an uncertainty of 1% absolute. In all these measurements no bias illumination was applied, and care was taken to avoid contributions from scattered light, that could be directly utilized by the solar cell or that could excite the upconverter.

From this data, the external quantum efficiency due to upconversion of sub-band-gap photons EQE_{UC} was determined for the monochromatic laser and the broad-band excitation via

$$EQE_{\text{UC}}(\Phi) = \frac{I_{\text{SC,UC}} - I_{\text{SC,ref}}}{I_{\text{SC,Ge}}} \frac{\int EQE_{\text{Ge}}(\lambda) \Phi_{\lambda}(\lambda) d\lambda}{\int \Phi_{\lambda}(\lambda) d\lambda}. \quad (1)$$

In this equation, the EQE_{Ge} is weighted with the spectral photon flux density of the excitation spectrum $\Phi_{\lambda}(\lambda)$, which is a delta function in case of the monochromatic laser excitation. For the broad-band excitation we used the spectra shown in Fig. 3(a).

D. Spectral mismatch corrections

Fig. 3(b) shows the excitation profile for upconversion emission around 980 nm of the investigated upconverter $\beta\text{-NaYF}_4 : 25\% \text{Er}^{3+}$ in comparison to the solar spectrum. The excitation profile was measured with a photoluminescence setup featuring a double monochromator (Jobin Yvon, H25) with a halogen lamp as excitation source and a monochromator (Jobin Yvon, H25) with an attached Si detector (OptoElectronic Components) for detection of the 980 nm emission. The excitation wavelength was changed in 0.5 nm steps from 1400 nm to 1650 nm. The full width at half maximum of the excitation was approximately 1 nm.

The solar spectrum provides many photons above wavelengths of ~ 1475 nm, which can be efficiently used by the upconverter, while below ~ 1450 nm less photons impinge on the earth due to absorption by water molecules in the atmosphere. Since, neither the broad-band excitation spectrum nor the spectrum of the solar simulator match precisely the solar spectrum, we applied a spectral mismatch correction on the experimental EQE_{UC} data to determine the EQE_{UC} values that could be expected under illumination with the solar AM1.5G spectrum, if restricted to the same spectral range and the same effective concentration level. [13]

The mismatch correction has two parts: first the irradiance I is transferred for the different excitation spectra to equivalent solar concentration factors of the solar spectrum AM1.5G in suns C . Second, the experimental EQE_{UC} values are transferred to values which can be expected with the spectral distribution of the solar spectrum at this concentration level. The irradiance I is connected to the spectral photon flux density of the excitation $\Phi_\lambda(\lambda)$ by

$$I = \int \Phi_\lambda(\lambda) \frac{hc}{\lambda} d\lambda. \quad (2)$$

with the Planck constant h and the speed of light c . For the broad-band excitation, the solar concentration factor C

$$C = \frac{\int A(\lambda) T_{\text{cell}}(\lambda) \Phi_\lambda(\lambda) d\lambda}{\int A(\lambda) T_{\text{cell}}(\lambda) \Phi_{\lambda, \text{AM1.5G}}(\lambda) d\lambda}. \quad (3)$$

describes how much the solar radiation has to be concentrated to reach the same integrated photon flux density of absorbed photons as for the considered broad-band excitation spectrum. The limits of the integral are the lower and upper wavelength of the respective broad-band excitation spectrum. T_{cell} is the transmittance of the bifacial silicon solar cell.

In principal, the same methodology can be applied to the monochromatic laser measurements. Here, the spectral bandwidth is very narrow, which results in very high equivalent solar concentration factors.

In the case of the solar simulator, the solar concentration factor C was accessible by geometrical considerations. We used the area of the lens A_{lens} and the calculated area of the light spot A_{spot} for the different settings of h_{lens} , as already mentioned above, to calculate the solar concentration C . The transmittances of the filters and the lens have to be considered as well. We used a transmittance of the lens T_{lens} of 0.92, which is basically determined by the reflectance of the glass surfaces, and 0.80 for the transmittance of the filters T_{filter} , which is an average value over the range from 1400 nm to 1700 nm. The solar concentration factor is consequently

$$C = \frac{T_{\text{lens}} T_{\text{filter}}}{c_{\text{mismatch, sun}}} \frac{A_{\text{lens}}}{A_{\text{spot}}}. \quad (4)$$

The spectral mismatch correction factor $c_{\text{mismatch, sun}}$ describes how the geometrical concentration of the solar simulator translates to a concentration of solar radiation. Therefore, the spectral photon flux density of the standard solar spectrum AM1.5G $\Phi_{\lambda, \text{AM1.5G}}(\lambda)$, the absorption spectrum of the upconverter $A(\lambda)$ and the spectral photon flux density of the solar simulator $\Phi_{\lambda, \text{sun}}(\lambda)$ have to be considered. Due to an uncertainty of the area of the light spot A_{spot} we determined an error of around 28% on the largest concentration value C .

To calculate the EQE_{UC} under illumination with the solar spectrum AM1.5G $\Phi_{\lambda, \text{AM1.5G}}(\lambda)$ a spectral mismatch correction was applied on the EQE_{UC} data. We determined the mismatch correction factors c_{mismatch} by

$$c_{\text{mismatch}} = \frac{\int A(\lambda) T_{\text{cell}}(\lambda) \Phi_{\lambda, \text{AM1.5G}}(\lambda) d\lambda}{\int A(\lambda) T_{\text{cell}}(\lambda) \Phi_\lambda(\lambda) d\lambda} \frac{\int T_{\text{cell}}(\lambda) \Phi_\lambda(\lambda) d\lambda}{\int T_{\text{cell}}(\lambda) \Phi_{\lambda, \text{AM1.5G}}(\lambda) d\lambda}. \quad (5)$$

The c_{mismatch} describe how the EQE_{UC} is altered when illuminated with the solar spectrum instead of the respective broad-band excitation spectrum:

$$EQE_{UC, \text{solar}}(C) = c_{\text{mismatch}} EQE_{UC}(C). \quad (6)$$

E. Calculation of expected short-circuit current density

Using the spectral mismatch correction for the EQE_{UC} an expected additional short-circuit current density $\Delta j_{\text{SC, UC}}$ due to upconversion of sub-band-gap photons under the illumination with the AM1.5G solar spectrum can be calculated by

$$\Delta j_{\text{SC, UC}}(C) = e c_{\text{mismatch}} EQE_{UC}(C) C \int_{\lambda_{\text{low}}}^{\lambda_{\text{up}}} \Phi_{\lambda, \text{AM1.5G}}(\lambda) d\lambda. \quad (7)$$

for broad-band excitation and the laser illumination.

In the case of the solar simulator we calculated the short-circuit current density due to upconversion by

$$\Delta j_{\text{SC, UC}} = \frac{(I_{\text{SC, UC}} - I_{\text{SC, ref}})}{A_{\text{spot}}} c_{\text{mismatch, sun}} \quad (8)$$

with the short-circuit currents determined with attached upconverter $I_{SC,UC}$, reference sample $I_{SC,ref}$ and the mismatch correction factor $c_{mismatch,sun}$, as described above. For a spot area A_{spot} larger than the actual solar cell area A_{cell} of 400 mm² we used A_{cell} instead of A_{spot} .

III. RESULTS

A. Monochromatic laser excitation

The results of the monochromatic measurements are shown in Fig. 4. We measured an EQE_{UC} of 1.79% for an irradiance of 1000 Wm⁻² and an incident wavelength of 1508 nm. This translates to a normalized efficiency of 0.179 cm²/W. For comparison, the best values for upconverter silicon solar cell devices presented in literature so far are 0.014 cm²/W by Shalav et al. [4] and 0.030 cm²/W by Fischer et al. [5]. In comparison to Ref. [5], the EQE_{UC} could be enhanced by nearly a factor of 6. However, for the same material as investigated in this work an external upconversion quantum yield of 0.550 cm²/W is reported, which was determined directly by photoluminescence measurements [17].

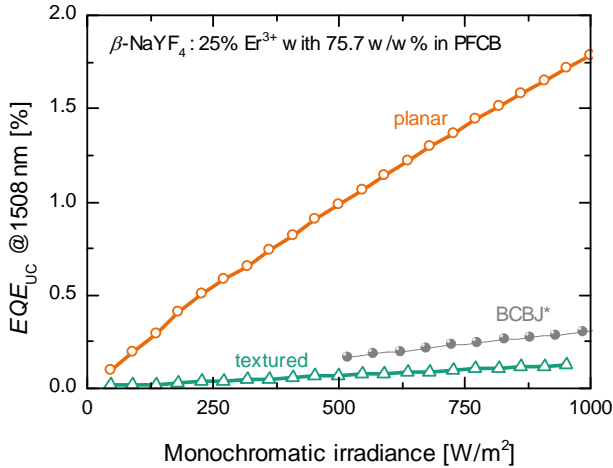


Fig. 4 The EQE_{UC} of a planar bifacial solar cell could be increased by a factor of around 6, compared to the Ref. [5], by optimizing the transmittance of the solar cell and due to a more efficient upconverter. In Ref. [5] a bifacial back-contact back-junction (BCBJ) silicon solar was used. For the front side textured solar cells the effect of the upconverter is fairly low, because of the poor transmittance of sub-band-gap photons through the solar cell.

We found that solar cells textured on the front side with planar rear are not suitable for upconversion applications. In such cells, the transmittance of sub-band-gap photons through the solar cell is fairly poor (~20%) due to a large portion of internal total reflection at the rear side interface. For planar cells the transmittance of sub-band-gap photons was above approximately 80%. Consequently, in the following we will focus on the planar bifacial silicon solar cell.

B. Broad-band excitation

The results of the experiments under broad-band excitation are presented in Fig. 5. We determined an EQE_{UC} of 0.77% for an irradiance of 1063 W/m² with a corresponding normalized efficiency of 0.072 cm²/W for the narrowest considered excitation spectrum, ranging from 1500 nm to 1550 nm. The broader the excitation spectrum the more photons impinge on the upconverter. However, a smaller ratio of these incident photons is absorbed compared to the case of a narrower excitation spectrum around the peak at 1523 nm. In consequence, the EQE_{UC} drops with broader excitation spectra and larger irradiance values are necessary to achieve as large EQE_{UC} values as found for narrower excitation spectra. However, one has to keep in mind that the solar spectrum provides much more photons when broader spectral bands are considered.

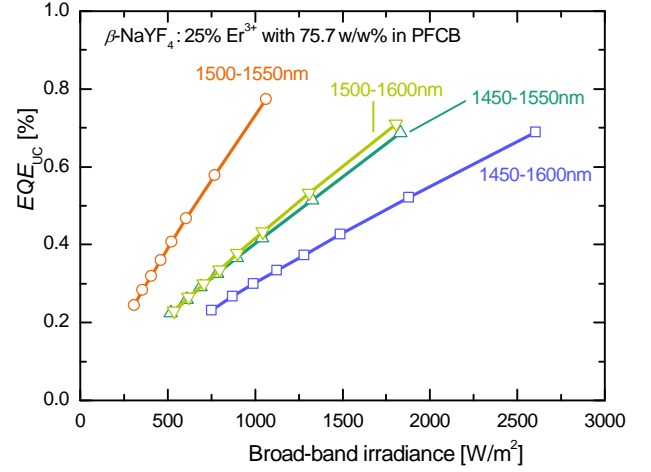


Fig. 5 The external quantum efficiency of the planar solar cell due to upconversion of sub-band-gap photons increases for narrower excitation bands, as a larger ratio of the excitation photons have a wavelength corresponding to the most efficient spectral region of the upconverter.

C. Concentrated light from a solar simulator

The results of the measurement with the solar simulator are shown in Fig. 6. The measured short-circuit current I_{SC} of the upconverter solar cell device increases with the height of the lens above the solar cell. Since the used heights are below the focal length of the lens of 169 mm, a larger h_{lens} translates into a larger concentration of the light from the solar simulator. The I_{SC} with attached reference sample is considerably lower and decreases with the height h_{lens} , possibly due to a smaller fraction of ambient scattered light.

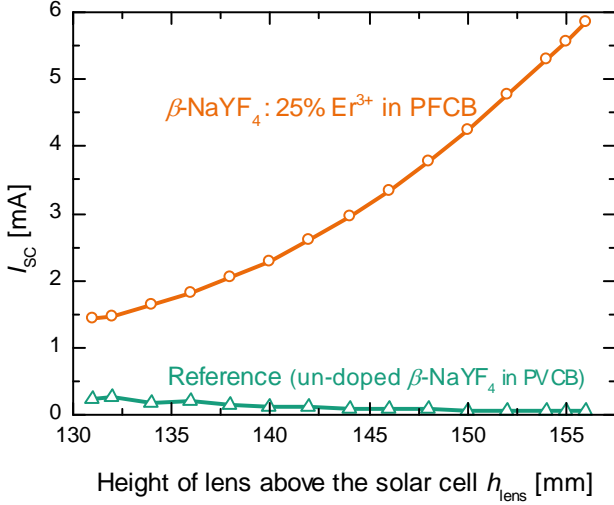


Fig. 6 The short-circuit current I_{SC} as measured with a solar simulator and a Fresnel lens with a height h_{lens} above the planar solar cell. With attached upconverter, I_{SC} increases with increasing height h_{lens} , which translates in a larger concentration. On the other hand, with attached reference sample, the I_{SC} decreases with h_{lens} .

D. Comparison of the different illumination conditions

The estimated additional short-circuit current density due to upconversion of sub-band-gap photons $\Delta j_{SC,UC}$ obtained under the different illumination conditions are depicted in Fig. 7. The larger the spectral bandwidth, the larger is the expected $\Delta j_{SC,UC}$. We determined a $\Delta j_{SC,UC}$ of $2.2 \pm 0.3 \text{ mA/cm}^2$ for a broad-band excitation band ranging from 1450 nm to 1600 nm and a concentration of 78 ± 6 suns.

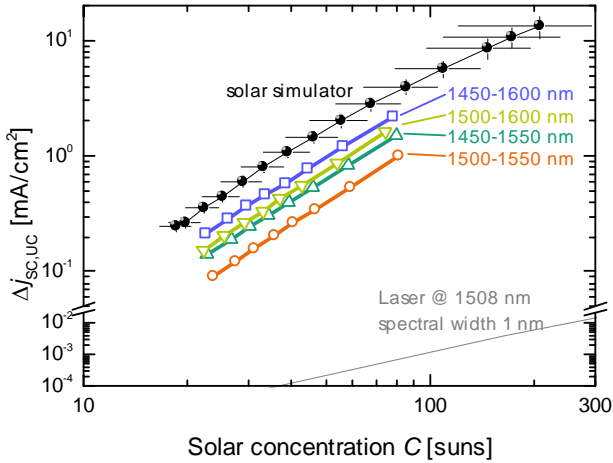


Fig. 7 Comparison of the estimated additional short-circuit current density due to upconversion of sub-band-gap photons $\Delta j_{SC,UC}$ for the various excitation sources in a double log-scale. We found larger $\Delta j_{SC,UC}$ values for broader excitation spectra. Not shown are the errors of around 15% for the $\Delta j_{SC,UC}$ values under broad-band excitation.

Since the spectral width of the laser is very narrow even the large EQE_{UC} values do not compensate for the much lower photon flux density provided by a broader excitation spectrum.

Larger $\Delta j_{SC,UC}$ values are achieved for the solar simulator measurement than the broadest broad-band excitation spectrum. We calculated an additional short-circuit current density of $13.3 \pm 3.0 \text{ mA/cm}^2$ due to upconversion of sub-band-gap photons under a solar concentration of 207 ± 86 suns. This value translates to a relative enhancement of the used silicon solar cell of $0.19 \pm 0.04\%$. The intrinsic j_{SC} of the solar cell is 33.4 mA/cm^2 and a corresponding cell efficiency of 17.6% under 1 sun standard measurement conditions.

IV. DISCUSSION

The key result of this work is that a relatively high increase in short-circuit current density can be expected due to upconversion at low concentration levels of the broad solar radiation. However, since some estimations and approximations have been necessary to calculate the $\Delta j_{SC,UC}$ we would like to point out that the values for the solar simulator are only estimates yet. The main uncertainty stems from the estimation of the concentration and the area of the light spot A_{spot} . Another uncertainty comes from the incomplete coverage of the active solar cell area by the upconverter sample. For example, when A_{spot} is larger than the upconverter sample, some light transmitted by the solar cell does not hit the upconverter directly. Although this light is reflected by the PTFE rear reflector with high probability and can subsequently illuminate the upconverter. This process is less efficient than direct absorption by the upconverter. Hence, with increasing A_{spot} and decreasing concentration C we can expect a stronger decrease of $\Delta j_{SC,UC}$ than we would observe when the full area of the solar cell was covered with an upconverter material.

Nevertheless, the values of $\Delta j_{SC,UC}$ fit into the series of the broad-band data, which show increasing enhancements of $\Delta j_{SC,UC}$ with increasing spectral width of the excitation. The fact that an increase is observed, even for excitation spectra that are considerably larger than the spectral region of efficient upconversion, which is shown by the excitation profile in Fig 3(b), could be explained by excited state absorption, for example, pushing up the quantum yield of the upconverter, as it was suggested in Ref. [14]. This hypothesis could be tested by two-color upconversion quantum yield measurements.

IV. SUMMARY AND CONCLUSION

We investigated upconverter solar cell devices, composed of a bifacial silicon solar cell with the upconverter powder $\beta\text{-NaYF}_4$ doped with 25% Er^{3+} and embedded in perfluorocyclobutyl (PFCB). The upconverter samples are

attached to the rear side of the solar cell. These devices are investigated under monochromatic laser excitation, broad-band excitation and under the concentrated light from a solar simulator. The EQE_{UC} was determined under monochromatic laser excitation and under excitation with four different broad-band spectra. Due to the larger overlap with the absorption spectrum of the upconverter we observed larger EQE_{UC} values for narrower excitation spectra. Under laser excitation, we determined an EQE_{UC} of 1.79% for an irradiance of 1000 Wm^{-2} and an incident wavelength of 1508 nm. This translates to a normalized efficiency of $0.179 \text{ cm}^2/\text{W}$, which constitutes a 6-fold increase compared to previously published values. For the broad-band excitation ranging from 1500 nm to 1550 nm we determined an EQE_{UC} of 0.77% for an irradiance of 1063 W/m^2 with a corresponding normalized efficiency of $0.072 \text{ cm}^2/\text{W}$.

We transformed the measured EQE_{UC} values to an expected additional short-circuit current density $\Delta j_{SC,UC}$ due to upconversion of sub-band-gap photons under a given solar concentration. A spectral mismatch correction method was used to account for the spectral differences between the excitation spectra and the solar spectrum, while considering the absorption spectrum of the upconverter. With broad-band excitations, we see larger $\Delta j_{SC,UC}$ values with broader excitation spectra. Accordingly, the measurements performed by concentrating the light of a solar concentrator by a Fresnel lens on the upconverter solar cell device, featuring the broadest excitation spectrum, yield the highest $\Delta j_{SC,UC}$ values. A $\Delta j_{SC,UC}$ of $13.3 \pm 3.0 \text{ mA/cm}^2$ was achieved. This corresponds to a relative efficiency increase of $0.19 \pm 0.04\%$.

REFERENCES

- [1] K. W. Krämer, D. Biner, G. Frei, H. U. Güdel, M. P. Hehlen, and S. R. Lüthi, "Hexagonal sodium yttrium fluoride based green and blue emitting upconversion phosphors," *Chemistry of Materials*, vol. 16, pp. 1244-51, 2004.
- [2] F. Auzel, "Upconversion and anti-stokes processes with f and d ions in solids," *Chemical Review*, vol. 104, pp. 139-73, 2004.
- [3] P. Gibart, F. Auzel, J. C. Guillaume, and K. Zahraman, "Below band-gap IR response of substrate-free GaAs solar cells using two-photon up-conversion," *Japanese Journal of Applied Physics*, vol. 35, pp. 4401-2, 1996.
- [4] A. Shalav, B. S. Richards, and M. A. Green, "Luminescent layers for enhanced silicon solar cell performance: up-conversion," *Solar Energy Materials & Solar Cells*, vol. 91, pp. 829-42, 2007.
- [5] S. Fischer, J. C. Goldschmidt, P. Löper, G. H. Bauer, R. Brüggemann, K. Krämer, D. Biner, M. Hermle, and S. W. Glunz, "Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization," *Journal of Applied Physics*, vol. 108, p. 044912, 2010.
- [6] J. de Wild, J. K. Rath, A. Meijerink, W. G. J. H. M. van Sark, and R. E. I. Schropp, "Enhanced near-infrared response of a-Si:H solar cells with β -NaYF₄:Yb³⁺ (18%), Er³⁺ (2%) upconversion phosphors," *Solar Energy Materials and Solar Cells*, vol. 94, pp. 2395-2398, 2010.
- [7] T. F. Schulze, J. Czolk, Y.-Y. Cheng, B. Fückel, R. W. MacQueen, T. Khoury, M. J. Crossley, B. Stannowski, K. Lips, U. Lemmer, A. Colmann, and T. W. Schmidt, "Efficiency Enhancement of Organic and Thin-Film Silicon Solar Cells with Photochemical Upconversion," *The Journal of Physical Chemistry C*, vol. 116, pp. 22794-22801, 2012.
- [8] A. Nattestad, Y. Y. Cheng, R. W. MacQueen, T. F. Schulze, F. W. Thompson, A. J. Mozer, B. Fückel, T. Khoury, M. J. Crossley, K. Lips, G. G. Wallace, and T. W. Schmidt, "Dye-Sensitized Solar Cell with Integrated Triplet-Triplet Annihilation Upconversion System," *The Journal of Physical Chemistry Letters*, vol. 4, pp. 2073-2078, 2013.
- [9] J. de Wild, A. Meijerink, J. K. Rath, W. G. J. H. M. van Sark, and R. E. I. Schropp, "Upconverter solar cells: materials and applications," *Energy & Environmental Science*, vol. 4, pp. 4835-48, 2011.
- [10] X. Huang, S. Han, W. Huang, and X. Liu, "Enhancing solar cell efficiency: the search for luminescent materials as spectral converters," *Chemical Society Reviews*, vol. 42, pp. 173-201, 2013.
- [11] S. Balushev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda, and G. Wegner, "Up-conversion fluorescence: noncoherent excitation by sunlight," *Physical Review Letters*, vol. 97, p. 143903, 2006.
- [12] S. K. W. MacDougall, A. Ivaturi, J. Marques-Hueso, K. W. Krämer, and B. S. Richards, "Ultra-high photoluminescent quantum yield of b-NaYF₄: 10% Er³⁺ via broadband excitation of upconversion for photovoltaic devices," *Opt. Express*, vol. 20, pp. A879-A887, 2012.
- [13] S. Fischer, B. Fröhlich, H. Steinkemper, K. W. Krämer, and J. C. Goldschmidt, "Absolute Upconversion Quantum Yield of b-NaYF₄ doped with Er³⁺ and External Quantum Efficiency of Upconverter Solar Cell Devices under Broad-Band Excitation considering Spectral Mismatch Corrections," submitted to *Solar Energy Materials & Solar Cells*, 2013.
- [14] J. C. Goldschmidt, S. Fischer, P. Löper, K. W. Krämer, D. Biner, M. Hermle, and S. W. Glunz, "Experimental analysis of upconversion with both coherent monochromatic irradiation and broad spectrum illumination," *Solar Energy Materials and Solar Cells*, vol. 95, pp. 1960-3, 2011.
- [15] J. de Wild, T. F. Duindam, J. K. Rath, A. Meijerink, W. G. J. H. M. Van Sark, and R. E. I. Schropp, "Increased Upconversion Response in a-Si:H Solar Cells With Broad-Band Light," *Photovoltaics, IEEE Journal of*, vol. 3, pp. 17-21, 2013.
- [16] M. Rüdiger, S. Fischer, J. Frank, A. Ivaturi, B. S. Richards, K. W. Krämer, M. Hermle, and J. C. Goldschmidt, "Bifacial n-Type Silicon Solar Cells for Upconversion Applications," vol. in preparation, 2013.
- [17] A. Ivaturi, S. K. W. MacDougall, R. Martin-Rodriguez, M. Quintanilla, J. Marques-Hueso, K. W. Kramer, A. Meijerink, and B. S. Richards, "Optimizing infrared to near infrared upconversion quantum yield of beta-NaYF₄:Er³⁺ in fluoropolymer matrix for photovoltaic devices," *Journal of Applied Physics*, vol. 114, pp. 013505-9, 2013.

Stefan Fischer studied physics at the University of Heidelberg and the University of Freiburg, Germany. He received his diploma degree from the University of Freiburg in 2009. In 2008 he joined the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany, where he is currently preparing his PhD thesis. His research interests include luminescent materials, light matter interactions, and photon management for solar applications, with a special focus on the characterization of upconverter materials and implementation of upconverters into solar cell devices.

Aruna Ivaturi received her Ph.D (2006) in Experimental Solid State Physics from Indian Institute of Technology Delhi, India. Her thesis focused on the properties of rare-earth nanoparticle layers for 'switchable mirrors'. She then worked at University of Duisburg-Essen, Germany, on synthesis of metal and oxide nanoparticles for gas sensors (2006-07). She was awarded the Alexander von Humboldt Fellowship (2007-09) to carry out self-proposed work on the synthesis of rare-earth oxide nanoparticles via gas phase. Thereafter (2009-10) her work at University of Cambridge, UK, dealt with the growth of metal oxide nanowires for solar cell technology. Since 2011 she has been working with Renewable Energy group at Heriot Watt University.

Benjamin Fröhlich studied physics at the University of Freiburg, Germany. He recently finished his diploma thesis on the “Characterization of upconverter materials for photovoltaics” and is currently working at the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany. His research focus is on luminescent materials and photon management for photovoltaics, especially on the investigation of upconverters and their application to solar cell devices.

Marc Rüdiger received his diploma degree in physics from the University of Freiburg, Germany, in 2007. He completed his Ph.D. thesis which was focused on the analysis and simulation of crystalline silicon solar cells at the Fraunhofer Institute for Solar Energy Systems (ISE), and defended it at the University of Konstanz, Germany, in 2013. Since then, he is working in the group of strategic planning at the Fraunhofer ISE, Freiburg.

Armin Richter received his diploma degree in physics from the University of Hamburg, Germany, in 2008. He joined the Fraunhofer Institute for Solar Energy Systems in 2007, where he is currently working towards his Ph.D. thesis. His research interests include the development and characterization of silicon surface passivation with ALD Al_2O_3 layers, Auger recombination in crystalline silicon, and the development of both sides contacted *n*-type silicon solar cells with front side boron-doped emitter by applying industrial feasible concepts.

Dr. Karl Krämer studied chemistry at the Justus-Liebig University, Giessen, Germany. He received his diploma in 1988 and Dr. rer. nat. in 1991 with Prof. Gerd Meyer. During his PhD he had a leave to the University of Hannover, Germany. Then he took a postdoc position with Prof. Hans Güdel in Bern. Since 2005 he is head of a solid state chemistry group at the Department of Chemistry and Biochemistry, University of Bern, Switzerland. His research is related to the synthesis of anhydrous metal halides, crystal growth, upconversion spectroscopy, Ce^{3+} doped rare earth scintillators, and the investigation of magnetic interactions in low dimensional systems by neutron scattering and magnetic measurements. <http://kraemer.dcb.unibe.ch>

Bryce Richards graduated with a BSc (physics) from Victoria Univ. of Wellington (NZ) in 1994. In 1996, he moved to Sydney, Australia, to complete his Masters and PhD at Univ. New South Wales. Subsequently, he worked as a postdoctoral fellow at the Australian National University before relocating to Scotland in 2006. He was promoted to full professor in 2008 and also founded the Scottish Institute for Solar Energy Research (SISER). His primary research area is spectral conversion for photovoltaics. He is currently on sabbatical in Tanzania undertaking capacity building in solar energy research.

Jan Christoph Goldschmidt received his PhD (Dr. rer. nat.) from the University of Konstanz, Germany for his work at the Fraunhofer Institute for Solar Energy Systems (ISE), Freiburg, Germany, on Novel Solar Cell Concepts (Summa cum laude) in 2009. He is currently head of the Team “Novel solar cell concepts” at Fraunhofer ISE and visiting researcher at Imperial College, London, United Kingdom. Among other things, he is the coordinator of the EU FP7 project “Nanospec – Nanomaterials for harvesting sub-band-gap photons via upconversion to increase solar cell efficiencies”. His research focus is photon management for photovoltaics, including luminescent solar concentrators, spectral splitting, upconversion, and advanced light trapping.