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Efficiency enhancement of solar cells by luminescent up-conversion of sunlight

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Abstract

Significant improvements in the efficiency of solar cells by combination with luminescent up- or down-converters have recently been predicted theoretically. Here, we extend the theoretical analysis of the limiting efficiency of the *up-conversion* (UC)-system to realistic Airmass spectra and analyse the spectral robustness of the UC-system. We also present initial experimental results from prototypes involving bifacial silicon solar cells with UC-phosphors attached to the rear surface, and discuss the possibility of realizing efficient UC with low-band-gap solar cells in combination with a light emitting diode.

Keywords: Up-conversion; Silicon solar cells; Limiting efficiency

1. Efficiency improvement by up-conversion (UC)

In conventional single junction solar cells, which are made from a material with band-gap energy E_g, photons with photon energy $\hbar\omega < E_g$ cannot be absorbed and are therefore "lost". In an UC-system these sub-band-gap photons are absorbed in a luminescent layer, which is mechanically attached and optically coupled to the rear surface of a bifacial solar cell [1]. Inside this layer the sub-band-gap photons are partially converted to higher photon energies. The UC photons can then be absorbed inside the solar cell and therefore

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contribute to the generation of additional electron–hole pairs, potentially leading to significantly higher conversion efficiencies.

There are several common mechanisms for UC. The simplest mechanism, which is denoted ground state absorption/excited state absorption (GSA/ESA) [2], is schematically depicted in Fig. 1a. Photon absorption leads to the generation of an excited state inside a luminescent centre via two sequential absorption processes (dotted arrows in Fig. 1a) involving a real meta-stable intermediate state (or, more generally, intermediate band). If the generated excited state relaxes via a radiative transition (vertical solid arrow in Fig. 1a), then an up-converted photon with higher energy is emitted.

In a second, very efficient UC-mechanism the energy required for the emission of an up-converted photon is sequentially transferred to the luminescent centre by nearby ions, which absorb the low energy photons, a process that is called energy transfer up-conversion (ETU) [2]. The ions thus act as sensitizers or antennas for the luminescent centre. In a combination of the previous processes the luminescent centre is first excited into the intermediate state via GSA. Another excited luminescent centre then transfers energy to the initially excited centre, to lift it into a higher excited state (a process denoted GSA/ETU).

The entire UC-system, solar cell plus up-converter, can be represented in an equivalent circuit as shown in Fig. 1b. The actual solar cell itself (denoted C_1) is operated at its maximum power point. The UC material is represented by three individual solar cells, which are series connected. Two low-band-gap solar cells, C_3 and C_4, representing the two intermediate transitions, drive a non-illuminated large band-gap solar cell (C_2) into forward bias. The cell C_2, which represents the radiative transitions, from which the emission of the up-converted photons arise, is thus being used as a light emitting diode (LED). Due to the series connection of C_2, C_3 and C_4 the currents through these cells are equal. Since $C_3 + C_4$ are connected in parallel to C_2, the voltage across $C_3 + C_4$ equals the voltage across C_2. The energy diagram and the equivalent circuit of the up-converter

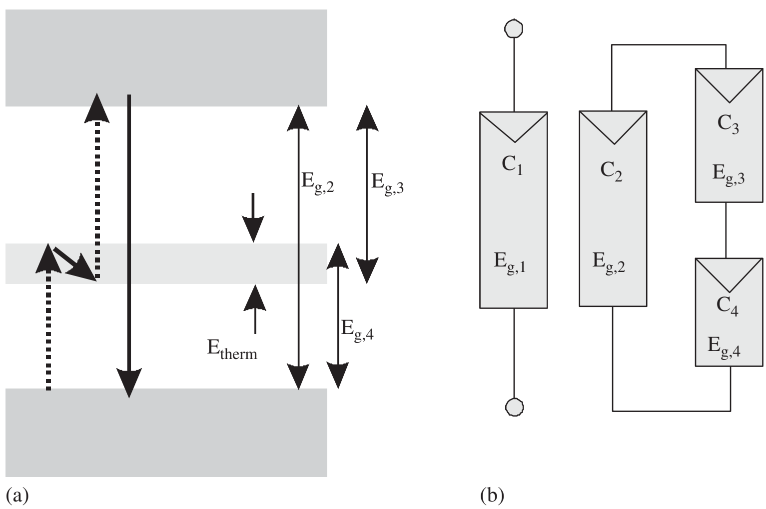


Fig. 1. (a) Schematic energy diagram of an up-conversion material that is based on GSA/ESA. (b) Equivalent circuit of the UC-system.

are thus identical to the energy diagram and equivalent circuit of an ideal impurity photovoltaic (IPV) cell.

2. Effect of relaxation of carriers

It has been shown in Ref. [1] that the efficiency of the UC-system is greatly improved for non-concentrated 6000 K blackbody radiation if a relaxation of excited carriers by an energy E_{therm} occurs after one of the intermediate transitions into an energetically lower lying state, from which the recombination into the initial state of that intermediate transition is forbidden by selection rules. This relaxation is indicated in Fig. 1a as the arrow pointing from the upper edge of the intermediate band to the lower edge. The fact, that an additional relaxation, apparently an energy loss mechanism, is beneficial for the overall system performance may be somewhat surprising and shall therefore briefly be elucidated here. The solid curve in Fig. 2 represents the dark IV-characteristics of the cell C_2. The dotted curve represents the IV-characteristic of the series connection of C_3 and C_4, without the above-mentioned relaxation. In that case the current matching condition $I_2 = I_3 = I_4$ is met relatively closely to the open-circuit voltage of $C_{3,4}$, i.e. the forward current through C_2 and thus the up-converted photon current $I_{\text{UC}} = I_2$ are fairly small. The above-mentioned relaxation can be included into the equivalent circuit by allowing the sum of the band-gaps of the cells C_3 and C_4 to be larger than the E_g of the cell C_2 (i.e. $E_{g,3} + E_{g,4} = E_{g,2} + E_{\text{therm}}$) [1]. The corresponding IV-curve of the series connection of C_3 and C_4 for a relaxation energy $E_{\text{therm}} = 50\,\text{meV}$ is shown in Fig. 2 as a dashed line. The short circuit current through C_3 and C_4 is slightly smaller than without the relaxation, which is due to the larger band-gap energies $E_{g,3}$ and $E_{g,4}$. This effect is, however, overcompensated by the larger open-circuit voltage, because the current and voltage

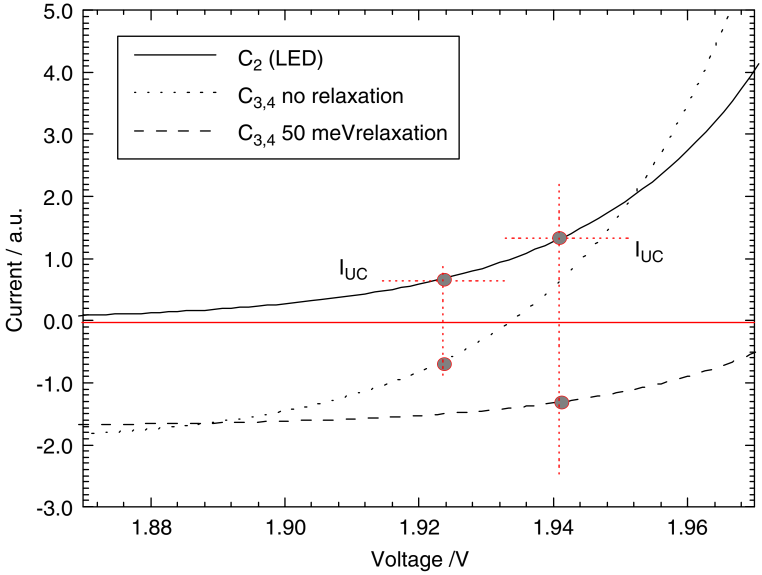


Fig. 2. IV-curves of the cell C_2 (solid line) and of the series connection of C_3 and C_4 inside the up-converter with (dashed) and without (dotted) a relaxation of 50 meV after one of the intermediate transitions.

matching conditions are met at a larger current, corresponding to a better UC efficiency. The relaxation energy in the idealized UC-system is typically on the order 340 meV for AM1.5.

3. Efficiency limits for AM1.5

In Ref. [1], the limiting efficiency of the UC-system was calculated for an idealized 6000 K-blackbody spectrum. Here, we used the theory outlined in Ref. [1] but replaced the incident 6000 K-spectrum by more realistic terrestrial spectral data (Airmass spectra) [3]. The main assumptions in the theory used are the exclusion of any non-radiative recombination channels within the entire system, of infinite charge carrier-mobilities inside the solar cell and of perfect photon selectivity within the up-converter [1].

For a given E_g of the solar cell C_1 the position of the intermediate level and the relaxation energy inside the UC were varied to give the maximum efficiency (this variation corresponds to the variation of the band-gap energies $E_{g,3}$ and $E_{g,4}$, respectively). The limiting efficiency of the UC-system also depends on the refractive index of the solar cell and of the UC-materials [1]. We used a refractive index $n = 3.6$ for all calculations, a value that is representative of solar cell materials like e.g. silicon and GaAs. Fig. 3 shows the limiting efficiency of a solar cell with an optimized up-converter for the AM1.5 solar spectrum with a total incident power of 982.1 W/m^2, as a function of the solar cell's band-gap. The corresponding numerical data are plotted in Table 1 together with the numerical optimum values for the band-gap energies of the individual cells of the equivalent circuit. The comparison with the Shockley–Queisser-limit, which is valid for conventional single junction solar cells, shows that significant improvements are predicted theoretically by combining such single junction solar cells with optimized up-converters.

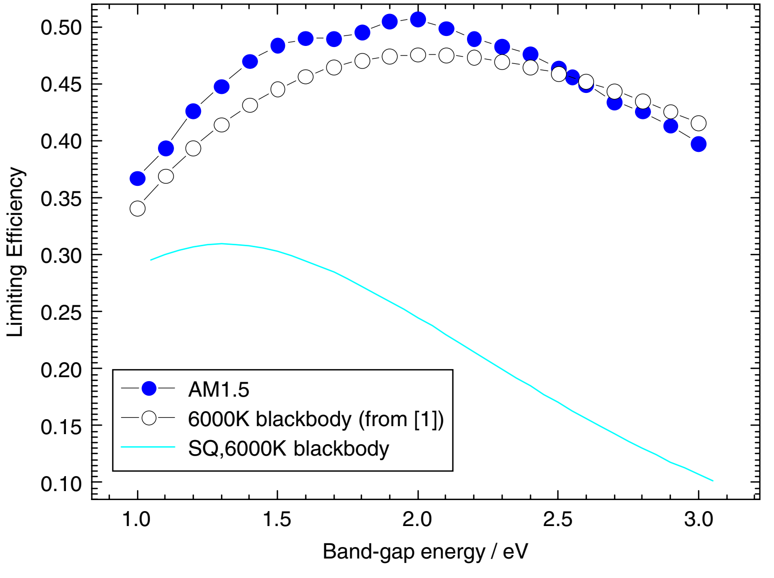


Fig. 3. Limiting efficiency of the up-conversion system for AM1.5 (full circles) and for an incident 6000 K-blackbody spectrum (open circles, data taken from Ref. [1]). The solid line represents the Shockley–Queisser limit for conventional solar cells for a 6000 K-blackbody spectrum.

Table 1
Limiting efficiency of the up-conversion system for AM1.5 for different values of the band gap energy of the solar cell ($E_{g.1}$)

$E_{g,1}$ (eV)	1	1.2	1.4	1.6	1.8	2	2.2	2.4	2.6	2.8	3
Effic. (%)	36.8	42.7	47.0	49.0	49.5	50.7	49.0	47.7	45.0	42.6	39.8
$E_{g,3}$ (eV)	0.54	0.58	0.70	0.74	0.92	0.94	1.02	1.13	1.22	1.34	1.43
$E_{g,4}$ (eV)	0.77	0.94	1.03	1.17	1.29	1.40	1.52	1.62	1.73	1.83	1.93
E_{therm} (eV)	0.31	0.32	0.33	0.31	0.41	0.34	0.34	0.35	0.35	0.37	0.36

The band gap energy $E_{g,3}$, the position of the impurity level (equivalent to $E_{g,4}$) and the relaxation energy E_{therm} are plotted in rows three to five.

A maximum efficiency of 50.69% is calculated for a E_g of 2.0 eV ($E_{g,4} = 0.94$ eV, $E_{g,3} = 1.40$ eV, $E_{therm} = 0.34$ eV). For silicon's E_g (1.12 eV at room temperature) we calculate a limiting efficiency of 40.2%. Compared to the results for a 6000 K blackbody spectrum presented in Ref. [1], the results here show that higher efficiencies can be obtained, in principle, with the AM1.5 spectrum for band-gap energies $E_{g,1} < 2.5$ eV. This is due to the fact that atmospheric absorption reduces the incident light intensity particularly strongly in the spectral range $\hbar\omega < 1.5$ eV, of which a large fraction is not utilized in the system anyway. The comparatively large and discontinuous variations in the optimum value of the relaxation energy are due to the sharp absorption features in the AM1.5 spectrum.

4. Spectral robustness

An important aspect of any photovoltaic device, at least for terrestrial applications, is its spectral robustness, i.e. the variation of the conversion efficiency with variations in the incident spectrum. We calculated the efficiency of the UC-system for different Airmass spectra ranging from AM1 to AM10. As an example Fig. 4 shows the spectral robustness of the UC-system that is optimized for AM1.5.

Because the UC-system incorporates three different energy thresholds we compare its efficiency to the efficiency of a series-connected triple tandem solar cell, i.e. a tandem solar cell with *three* individual solar cells. Fig. 4 shows the spectral robustness of a series-connected triple tandem cell that has been optimized for the AM1.5 spectrum (data taken from Ref. [4]). The comparison of the two curves clearly highlights a major advantage of the UC-system over a series-connected tandem stack. The limiting efficiency of the series connected tandem is marginally higher (51.5%) for AM1.5, the spectrum that it was optimized for, but it reduces significantly to only 32.6% for AM5. In comparison, the efficiency of the UC-system only reduces from 50.7% to 44.0% for the same spectral variation.

The superior spectral robustness of the UC-system is due to the comparatively relaxed current matching constraints. In a series-connected tandem stack the solar cell with the smallest short-circuit current determines the total current within the device and thus the overall system performance. A poor adaptation of one single cell in the stack to the incident spectrum can therefore significantly influence the total system efficiency. In contrast, in the UC-system current matching is only required for the three cells representing the up-converter. The current in the solar cell C_1 may be totally different and is not affected by a potentially poor spectral robustness of the up-converter. For

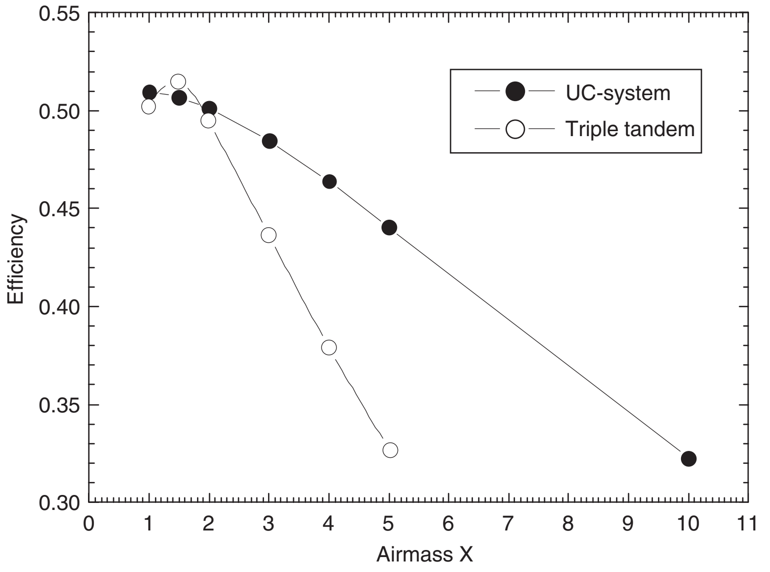


Fig. 4. Spectral robustness of the UC-system (full circles) and of a triple tandem cell (open circles) that is optimized for AM1.5 (data from Ref. [4]).

example in the optimized UC-system from Fig. 3 the current in the solar cell C_1 is $309.8\,\mathrm{A\,m^{-2}}$ at the maximum power point, while the current within the UC is only $173.0\,\mathrm{A\,m^{-2}}$ for AM1.5.

5. Experimental results

In our initial experimental studies the main aim was to demonstrate the UC-concept, i.e. the possibility of achieving enhanced photoresponse at sub-band-gap energies by UC [5].

Polycrystalline Erbium-doped Sodium–Yttrium–Fluoride ($NaYF_4$: 20% Er^{3+}) phosphors (~5 μm size) were contained in an optically transparent acrylic adhesive and adhered to the rear surface of bifacial buried-contact silicon solar cells. Reflective white paint with a reflectivity >80% in the NIR was used as a reflector on the rear surface of the system.

The spectral response of the buried contact solar cell without the phosphors attached to the rear surface is negligible at wavelengths $\lambda > 1500$ nm. For EQE measurements a 50 W quartz tungsten halogen lamp in combination with a $\frac{1}{4}$ m monochromator was used as tuneable monochromatic light source. For the intensity dependent measurements presented here, the monochromator was tuned to 1520 nm (the wavelength at which the highest EQE due to UC was observed) and the intensity was varied with neutral density filters. The incident light intensity was measured at each wavelength with a calibrated Germanium detector. Absorption measurements of the UC-phosphor where carried out in a Cary 5 G spectrometer with the phosphors incorporated in a transparent plastic pellet.

The EQE of the solar cell is given as the ratio of the electron flux through the external circuit under short circuit conditions divided by the incident photon flux at a given wavelength. The spectral dependence of the EQE of a buried-contact solar cell with the phosphors attached to the rear is shown in Fig. 5. Comparison with the absorption

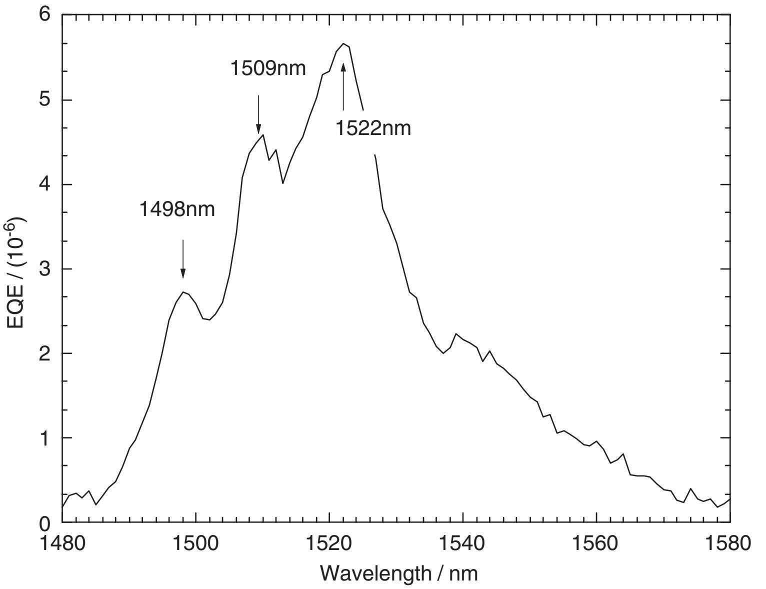


Fig. 5. EQE as a function of excitation wavelength of a bifacial buried contact silicon solar cell with the $NaYF_4$: 20% Er^{3+}-phosphor attached to the rear surface. Without the phosphor the EQE of the cell is negligible in this spectral range.

spectrum of the phosphor shown in Fig. 6 clearly shows that the absorption features of the phosphors also appear in the EQE of the solar cell. The fact that the phosphors and the solar cell only interact radiatively with each other demonstrates, that the enhanced photoresponse of the solar cell originates from UC within the phosphor. We were in fact surprised how well the absorption spectrum of the phosphor, which is measured under low excitation conditions and thus represents the GSA-spectrum matches the EQE of the solar cell, which is representative of the combined GSA/ESA process. We explain this observation by the fact that apparently the ESA spectrum of this phosphor does not have too many prominent spectral features in this spectral range, which would otherwise appear in the EQE spectrum.

A photoluminescence measurement on the phosphor with illumination by a 1550 nm laser diode, revealed that the major fraction of up-converted photons is emitted at wavelength around 980 nm. The conversion from ~1550 to 980 nm mainly causes the enhanced EQE of the solar cell because 980 nm light has an absorption depth of only ~100 μm and is thus strongly absorbed in a wafer-based silicon solar cell. The conversion, we are interested in, is thus from wavelengths in the infrared (IR) spectral range to shorter wavelengths, which are also in the IR, a process that has attracted only little interest in the literature so far. The vast majority of literature on UC is on UC-processes into the visible spectral range.

The short-circuit current of the solar cell at $\lambda = 1520$ nm (with UC-phosphor attached) as a function of the incident light intensity and the corresponding EQE of the cell are shown in Fig. 7 [5]. The data show that the short-circuit current of the cell increases as the square of the incident light intensity. For a process in which two subsequent absorption processes are involved in the generation of one eh-pair, as in the GSA/ ESA process and in

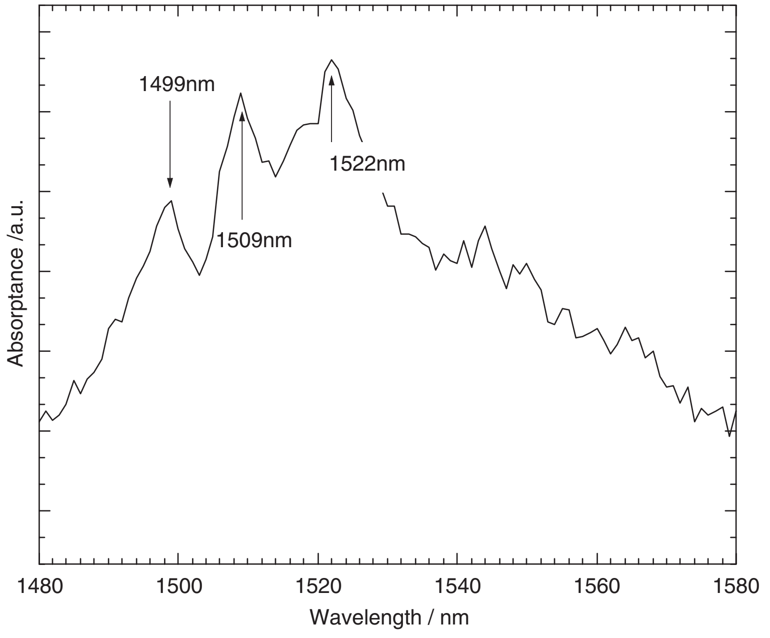


Fig. 6. Absorption spectrum (GSA) of the phosphor $NaYF_4$: 20% Er^{3+} incorporated in a transparent acrylic pellet.

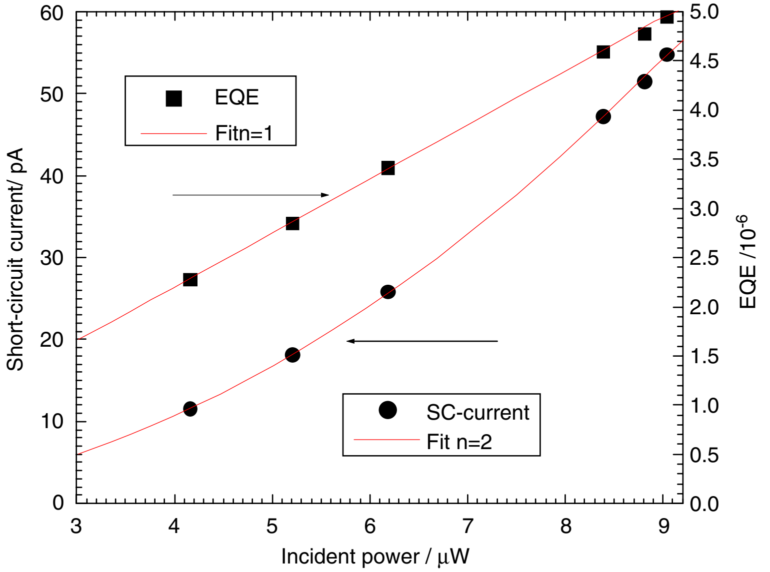


Fig. 7. Short circuit current (circles, left axis) and EQE (squares, right axis) at 1520 nm of a bifacial silicon solar cell with UC-phosphors ($NaYF_4$: 20% Er^{3+}) attached to the rear surface as a function of the incident light intensity.

the ETU process, such a quadratic dependence is expected for moderate excitation conditions [2]. The quadratic increase of the short circuit current with the incident light intensity corresponds to a linear increase of the EQE as a function of light intensity (squares in Fig. 7), the latter again demonstrating the non-linear nature of the two-step UC process.

The route towards higher EQEs is thus clearly a higher incident light intensity, as also predicted by the limiting efficiency calculations in Ref. [1]. In further recent experiments the solar cell was illuminated by a 5 mW/1550 nm laser diode. For the highest laser power (corresponding to a light intensity of $\sim 2\,\mathrm{kW\,m^{-2}}$) we obtain an EQE of 0.6% at 1550 nm. By variation of the laser power with neutral density filters we find that even at the highest laser power the EQE still increases linearly with the incident light intensity, indicating that significantly larger EQEs are possible in principle. Further experiments employing a more powerful laser source that is tuneable over the spectral range 1500–1580 nm, are currently being carried out in our lab. According to Fig. 5 the choice of a more optimal illumination wavelength (~1520) as opposed to 1550 will already yield a nearly four-fold increase of the EQE.

We are thus confident that by further increasing the incident light intensity, optimising the concentration of the UC-phosphor, improving the rear reflector and by choosing a transparent adhesive host material with a higher refractive index, we will be able to demonstrate UC-efficiencies in the range of several percent in the very near future. Such values are then in a range where real efficiency improvements of the solar cell appear within reach.

In addition we would like to emphasize that in the above-mentioned experiments UC was investigated only with monochromatic illumination. However, the two step excitation of the state from which the emission of the up-converted photon results, can involve different energies. As a result, the UC-efficiency in a two-colour experiment can be orders of magnitude larger than the one-colour UC-efficiency, if the two wavelengths are optimally chosen [2]. In our case, the overall UC-system performance under e.g. AM1.5 illumination could thus benefit from the fact that photons with energies in a continuous spectral range below the E_g of the solar cell material are available for the UC-process.

Co-activation of rare earth doped UC-phosphors with ytterbium has been shown to greatly enhance the UC-efficiency for UC from ~980 nm into the visible spectral range [6]. In this case IR photons at $\lambda \sim 980$ nm photons are absorbed by ytterbium and the absorbed energy is then transferred to nearby rare earth centres (ETU). While not suitable for silicon solar cells such phosphors may be used in the future in combination with solar cells made from materials with larger band gap energies.

6. Physical realization of the equivalent circuit

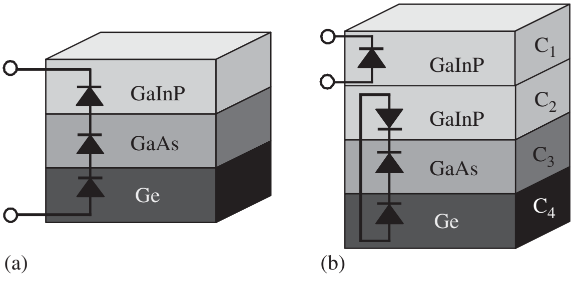
The main appeal of the UC-system is certainly that the efficiency of existing solar cells can potentially be further improved, simply by placing an optimized mixture of UC-phosphors to the rear surface. The experimental efforts presented in Section 5 obviously aim into this direction. However, the equivalent circuit shown in Fig. 1b also suggests another approach for efficient UC, a structure, in which the three cells C_2, C_3 and C_4 are actual physical devices, i.e. two low band-gap solar cells and a large band-gap solar cell that are series connected. UC is achieved by operating the large band-gap solar cell as a LED that is powered by two or more illuminated, series-connected lower band-gap solar cells. While such an approach is certainly technologically more advanced and thus more complicated and expensive, it also has some fundamental advantages:

(1) If the solar cells C_3, C_4 and the LED (C_2) are separate devices, then they may be optimized individually with respect to the band-gaps and to the material properties.
(2) The relaxation after one of the intermediate steps in the UC-process, which is required for efficient UC for non-concentrated light (see Section 2) can easily be achieved by choosing an LED with a band-gap smaller than the sum of the band-gaps of the two solar cells. The relaxation energy can therefore be tuned exactly to the desired optimum value.
(3) The only device, which must be radiatively very efficient, is the LED, because the other two cells in the UC can be operated near their maximum power point, i.e. at voltages at which most carriers are extracted before they ever recombine.
(4) Multi-step-UC involving more than one intermediate level can be realized simply by series connecting more than two low-band-gap solar cells to an LED.

An efficient LED is thus required for an efficient up-converter. Very large EQEs were reported e.g. for AlGaInP/GaP LEDs ($>50\%$ [7]) while an extremely high *internal* luminescence quantum efficiency (IQE$>99.7\%$) was reported e.g. for AlGaAs/GaAs double-heterostructures [8]. The crucial point here is that in an efficient UC-system we do not necessarily encounter the problem of light extraction from the high refractive index materials, which normally leads to only moderate EQEs of LEDs even if the IQE is large. The solar cell and the three devices representing the UC could be arranged on top of each other with appropriate refractive index matching. The photons generated in the LED are then not totally reflected on the way to the solar cell, which would be the case if there were an air gap between the two devices. The fact that the most common III–V semiconductors used in PV and also silicon have similarly large refractive indices could be beneficial in this context.

The possibilities offered by growth techniques like metal–organic chemical vapour deposition (MOCVD), which are exploited e.g. for the manufacturing of highly efficient, monolithically grown series-connected tandem stacks could also be used to grow a solar cell and an up-converter on top of each other.

A device schematic for a typical triple tandem cell and for an UC-system are shown in Fig. 8a and b, respectively. The schematics show, that an additional large band-gap



(a) (b)

Fig. 8. Device schematic of a typical series connected 3-cell tandem (a) and of an UC-system (b). In the latter an additional large band-gap cell (C_2) is required (used as the LED). The current is extracted from the top solar cell in (b) and the other three cells must are series connected.

(GaInP just used as an example here) cell is required for the UC-system and, importantly the bottom contact of the cell C_1 and the top contact of C_2 must be accessible from outside, as these contacts are used to extract the current and to be connected to the bottom contact of C_4, respectively. These contacts are certainly the major experimental challenge in the realization of such a device.

While the cells C_1 and C_2 would have the same band-gap energies in an idealized system, one would choose the band-gap of C_2 to be slightly (on the order of kT) larger than the band-gap of C_1 in a real device to make sure that the emission from C_2 is entirely absorbed by C_1. A selective mirror would ideally be located between the cells C_2 and C_3, which reflects the emission of the LED from its rear surface back into the direction of the solar cell C_1.

7. Conclusions

UC is a promising concept for improved solar cell efficiencies. In limiting efficiency calculations, conversion efficiencies up to 50.7% are predicted for non-concentrated sunlight (AM1.5) for a solar cell ($E_g = 2\,eV$) in combination with an optimized up-converter. An efficiency of 40.2% is calculated for silicon's band-gap energy for non-concentrated AM1.5. Importantly, the UC-system is also shown to be superior to a series connected tandem cell with regard to its spectral robustness.

Promising initial experimental results on silicon solar cells in combination with $NaYF_4$:Er^{3+} UC-phosphors, which gave an EQE close to 1% at $\lambda = 1550\,nm$, have been discussed. It should be stressed that these results, which were obtained on a very basic, non-optimized prototype structure, are already orders of magnitude better then results that have been achieved with the impurity photovoltaic (IPV) effect in silicon (EQEs on the order of 10^{-6} were reported e.g. for erbium doped silicon PERL cells [9]).

Significant improvements in the UC-efficiency of phosphors that convert from the IR into the VIS spectral range, e.g. by co-activation with Yb, were achieved in the past as soon as a commercial interest in such phosphors emerged, that justified extensive research programs. Similar further improvements of UC-phosphors that convert from the IR ($\lambda > 1100\,nm$) into the IR ($\lambda < 1100\,nm$), as required for silicon solar cells, might be achieved e.g. by co-activating the phosphor with other rare earth or transition metal ions that absorb in the spectral range below silicon's band-gap. We are confident that with increasing demand for such phosphors, their efficiency can be expected to further improve significantly in the mid term. Given the promising results that we were able to achieve in a non-optimized system with existing UC-phosphors, the prospects for real efficiency improvements of silicon solar cells does not appear to be too remote, in contrast to some other third generation approaches.

The possibility to realize UC in a monolithically grown structure has been discussed and, given its superior spectral robustness, suggested as a potential alternative to series connected tandem solar cells for terrestrial applications.

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