Improving solar cell efficiencies by down-conversion of high-energy photons

T. Trupke, M. A. Green, and P. Würfel

Articles you may be interested in

Evidence of significant down-conversion in a Si-based solar cell using CuInS2/ZnS core shell quantum dots
Appl. Phys. Lett. **104**, 183902 (2014); 10.1063/1.4875616

Enhancement of silicon solar cell efficiency by upconversion: Optical and electrical characterization
J. Appl. Phys. **108**, 044912 (2010); 10.1063/1.3478742

Influence of some design parameters on the efficiency of solar cells with down-conversion and down shifting of high-energy photons
J. Appl. Phys. **102**, 073102 (2007); 10.1063/1.2785026

Tandem dye-sensitized solar cell for improved power conversion efficiencies
Appl. Phys. Lett. **84**, 3397 (2004); 10.1063/1.1723685

APL Photonics

Improving solar cell efficiencies by down-conversion of high-energy photons

T. Trupke[a] and M. A. Green
Centre for Third Generation Photovoltaics, University of New South Wales, NSW 2052, Australia

P. Würfel
Institut für Angewandte Physik, Universität Karlsruhe, D-76128 Karlsruhe, Germany

One of the major loss mechanisms leading to low energy conversion efficiencies of solar cells is the thermalization of charge carriers generated by the absorption of high-energy photons. These losses can largely be reduced in a solar cell if more than one electron–hole pair can be generated per incident photon. A method to realize multiple electron–hole pair generation per incident photon is proposed in this article. Incident photons with energies larger than twice the band gap of the solar cell are absorbed by a luminescence converter, which transforms them into two or more lower energy photons. The theoretical efficiency limit of this system for nonconcentrated sunlight is determined as a function of the solar cell's band gap using detailed balance calculations. It is shown that a maximum conversion efficiency of 39.63% can be achieved for a 6000 K blackbody spectrum and for a luminescence converter with one intermediate level. This is a substantial improvement over the limiting efficiency of 30.9%, which a solar cell exposed directly to nonconcentrated radiation may have under the same assumption of radiative recombination only. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1492021]

I. INTRODUCTION

The thermalization of charge carriers, which are generated by the absorption of high-energy photons, is one of the major loss mechanisms by which energy is wasted in conventional solar cells. One way to reduce these energy losses in a semiconductor solar cell is carrier multiplication, i.e., the generation of multiple electron–hole pairs per incident photon for photon energies larger than twice the band-gap energy of the solar cell material. Brendel *et al.* have calculated the thermodynamic efficiency limits of solar cells with carrier multiplication in a theoretical approach.[1] Impact ionization has been discussed as a means to achieve multiple electron–hole pair generation per absorbed photon in a real solar cell.[2] However, electron–phonon interaction must be excluded or at least largely suppressed in the solar cell material to achieve an efficiency improvement by impact ionization, an assumption which rules out all present solar cell materials.[3]

We present limiting efficiency calculations according to a detailed balance model for a solar cell system, which is also based on the generation of multiple electron–hole pairs per incident photon but uses a different mechanism, namely the down-conversion of incident high-energy photons into two or more photons of smaller energy.

II. DESCRIPTION OF THE DOWN-CONVERSION SYSTEM

A. Different geometries

A schematic representation of our proposed system of a solar cell in combination with a down-converter is shown in Fig. 1. A luminescence converter that, in an ideal case, converts high-energy photons into two or more lower energy photons is located on the front surface of a conventional single junction solar cell. The luminescence converter is electronically isolated from the solar cell, i.e., the coupling between the converter and the solar cell is purely radiative. The absorption of the two or more low-energy photons emitted by the converter leads to the generation of electron–hole pairs in the solar cell, which means that more than one $e-h$ pair is generated in the solar cell per incident high-energy photon.

In a different geometry the luminescence converter could also be located on the rear surface of the solar cell. In order to avoid the absorption of the high-energy photons and the subsequent thermalization of $e-h$ pairs inside the solar cell, a bifacial solar cell is needed and additionally the solar cell material must be transparent for high-energy photons in this geometry, a condition that rules out all semiconductor materials used for solar cells, but that can be fulfilled, e.g., by dye molecules in dye-sensitized solar cells. A way to avoid the absorption of high-energy photons in a conventional semiconductor solar cell with infinite bands consists of directing the high-energy part of the solar spectrum toward the down-converter with suitable low-pass-mirrors.

In both geometries a reflector is located on the rear surface of the system. Our calculations reveal that the limiting efficiency is found for the geometry with the converter located on the rear surface. Therefore a detailed description of the theoretical model will be given for that geometry, while we only present the results of our calculations for the geometry with the converter located on the front surface.

[a] Author to whom correspondence should be addressed; electronic mail: thorsten@trupke.de
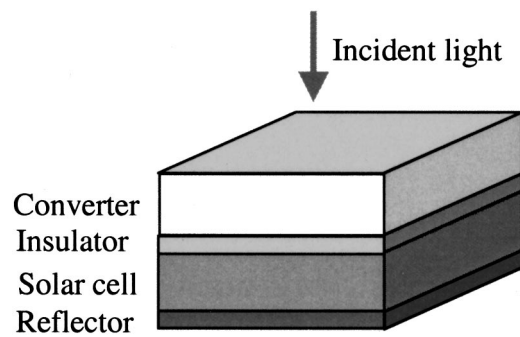
FIG. 1. Schematic diagram of the down-conversion system. The luminescence converter is located on the front surface of a solar cell, which has a band-gap energy E_g. High-energy photons with $\hbar\omega > 2E_g$ are absorbed by the converter and efficiently down converted into two lower energy photons with $\hbar\omega > E_g$, which can both be absorbed by the solar cell. In another geometry the luminescence converter is located on the rear surface of the solar cell. In both cases the solar cell and the converter are electronically isolated from each other and a perfect mirror is located on the rear surface of the system.

B. Description of the down-converter

The down-conversion of incident photons into two or more photons with lower energies can be achieved, in principle, with every three-level system. The absorption of a high-energy photon leads to an electronic transition from the lowest level to the highest excited level. A two-step recombination of the electron to the lowest level via the intermediate level is accompanied by the emission of two lower energy photons, if both steps are radiatively efficient. For solar energy conversion we are rather interested in the down-conversion of a broad spectrum, which can be achieved by a material with a large band gap, which contains states with energies inside the band gap. A luminescence converter modeled as a semiconductor with one intermediate level (IL) of energy E_1 above the valence band edge is shown schematically on the right hand side in Fig. 2. Recently, we have shown[4] that at low light intensities as with nonconcentrated sunlight the major fraction of electron–hole pairs recombines via two intermediate transitions (dotted arrows) rather than by a band-to-band transition from the conduction band to the valence band in such a two-band/one intermediate level system. Contrary, with increasing light intensity the fraction of $e–h$ pairs recombining via band-to-band transitions increases, which makes such a material also suitable for up conversion.[4]

III. THEORY

The theoretical description of the down-conversion system is based on the assumption that no nonradiative recombination takes place anywhere in the device. We will treat the geometry with the luminescence converter located on the rear surface first.

A. Luminescence converter located on the rear surface

An energy diagram for the down-conversion system is shown in Fig. 2. Sunlight is incident from the left side in that representation, if the converter is located on the rear surface.
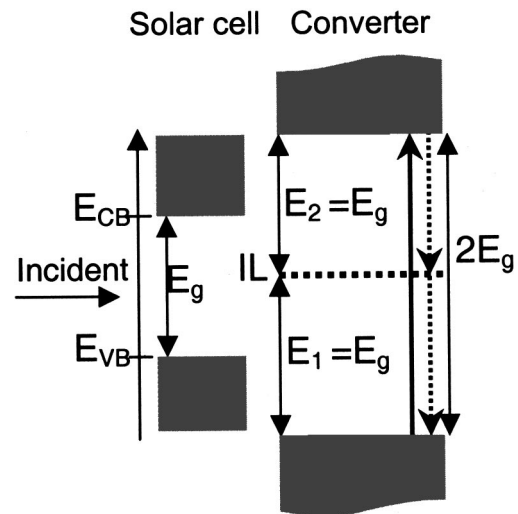

FIG. 2. Schematic energy diagram of a solar cell in combination with a down-converter. If the converter is located on the rear surface of the solar cell, the incident sunlight comes from the left, as shown. The down-converter consists of a material with a band gap $E_{g,\text{converter}}$ that contains impurity levels (IL) with energy E_1 above the valence band edge. Radiative transitions take place between the valence band and the conduction band (solid arrow) or between one of the bands and the impurity level (dotted arrows). In an ideal case the IL lies in the center of the band gap of the converter and both intermediate transition have energy thresholds for the absorption that are equal to the band-gap energy of the solar cell, i.e., $E_1 = E_2 = E_g$. In the geometry with the converter on the rear surface the widths of the bands in the solar cell must be restricted to avoid the absorption of the high-energy photons with $\hbar\omega > 2E_g$, which shall be absorbed and down converted in the luminescence converter.

The solar cell absorbs photons with energies larger than the band-gap-energy E_g. If the luminescence converter is located on the rear surface, photons with energies larger than twice the band gap shall be transmitted by the solar cell and absorbed by the converter. This can be achieved by restricting the widths of the bands of the solar cell material as shown in Fig. 2.

Emission of photons with energies larger than the band gap of the solar cell via the intermediate transitions inside the luminescence converter represents an energy loss. Therefore, in an idealized case, the energy thresholds E_1 and E_2 for the two intermediate transitions both equal the band-gap energy of the solar cell, i.e., $E_1 = E_2 = E_g$. The intermediate level thus lies in the middle of the band gap of the converter.

B. Photon selectivity

Photon selectivity must be assumed in the calculation of the limiting efficiency of our system. Incident photons with energies larger than twice the band-gap energy E_g of the solar cell shall be down converted, which implies that the absorption of these photons via one of the intermediate transitions in the down-converter is forbidden. Photons in the energy interval between E_g and $2E_g$ emitted by the solar cell into the converter are completely absorbed by the two intermediate transitions, while the high-energy photons with energies larger than $2E_g$ that are transmitted by C1 are completely absorbed via band-to-band transitions.
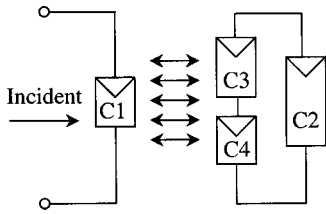
FIG. 3. Equivalent circuit of the system. The luminescence converter is represented by three solar cells C2, C3, and C4 representing the band-to-band transitions and the two types of intermediate transitions, respectively. These three cells are series connected. High energy photons are absorbed by C2, which then biases the cells C3 and C4 into forward direction and causes them to emit electroluminescence.

C. Equivalent circuit

The down-converter is a three-band system. The luminescent emission from such a three-band system has been described theoretically by Luque and Marti.[5] Three types of transitions occur inside the converter, the band-to-band transitions and the two types of intermediate transitions between the valence band and the intermediate state and between the intermediate state and the conduction band, respectively. The theoretical description of the system is based on the assumption that electronic states in the conduction and in the valence band and in the intermediate levels, respectively, are occupied according to individual thermal distributions, which are described by different electrochemical potentials (Fermi energies).

In an ideal case the difference of the electrochemical potentials μ of the two bands in a conventional solar cell, which is a two-band system, is constant throughout the device even under current flow and related to the voltage V of the cell via

$$qV = \mu, \qquad (1)$$

where q is the elementary charge.

As the three types of transitions described above can be regarded as three independent two-band systems with individual electrochemical potential differences, the down-converter can be represented in an equivalent circuit by three solar cells (C2–C4) that are series connected (Fig. 3). Two solar cells (C3 and C4) with small band gaps represent the intermediate transitions, whereas the band-to-band transitions are represented by C2. The converter is radiatively coupled to the solar cell that is denoted C1 in the following.

Using this equivalent circuit the down-conversion system can be described in a very illustrative way. The large band-gap solar cell C2 in the converter absorbs incident photons with energies larger than $2E_g$ that are transmitted by the solar cell C1. The photovoltage that builds up in C2 drives

the two cells C3 and C4 into forward bias and causes them both to emit electroluminescent radiation, which is subsequently absorbed by C1.

D. Calculation of limiting efficiencies

The efficiency of the system is calculated as the ratio of the power of the solar cell C1 operated at its maximum power point and the incident power. The maximum power point is determined from the current–voltage ($I–V$) curve of the cell C1, which according to an approach introduced by Shockley and Queisser is calculated as the difference between the absorbed photon current and the emitted photon current.[6]

The photon current density emitted by a solar cell is described by a generalization of Kirchhoff's law[7]

$$\dot{N}(E_l, E_u, T, \mu, \epsilon) = \frac{\epsilon}{4\pi^3\hbar^3 c_0^2} \cdot \int_{E_l}^{E_u} (\hbar\omega)^2$$
$$\cdot \left[\exp\left(\frac{\hbar\omega - \mu}{kT} \right) - 1 \right]^{-1} d\hbar\omega, \qquad (2)$$

with E_l and E_u the lower and the upper energy threshold energy for the transition investigated, T the temperature of the emitter, and μ the electrochemical potential difference corresponding to the transition that is related to the voltage of the solar cell by Eq. (1). Equation (2) is based on the assumption that the absorptance of the cell is unity between the lower and the upper energy threshold and zero outside that energy interval.

The symbol ϵ denotes the étendue $\epsilon = \pi n^2 \sin^2(\Theta_c)$, which depends on the half angle Θ_c into which radiation can be emitted and on the square of the refractive index n. For the emission by a blackbody into the air and into a hemisphere the étendue is given by $\epsilon = \pi$. For the emission from one material with refractive index n into another material with the same refractive index the étendue is $\epsilon_{int} = \pi n^2$. The small solid angle of the solar disk, from which direct sunlight can be received, is described by $\epsilon_S = 6.8 \times 10^{-5}$ for nonconcentrated sunlight.

The photon current absorbed by each solar cell in the equivalent circuit for our system depends on the incident light intensity that is the sum of three contributions. The first contribution, the direct sunlight, is described as a $T_s = 6000$ K blackbody spectrum received from ϵ_s, the second contribution is a nearly hemispherical term described by a $T_Z = 300$ K blackbody spectrum received from $\epsilon_{hemi} = \pi - \epsilon_s$, and the third term is the luminescence received from the other three solar cells in the equivalent circuit. The last contribution links the $I–V$ curve of one solar cell in the system to the emission by the other cells. Thus, for the calculation of the $I–V$ curve of C1, the $I–V$ curve of the other three cells in the equivalent circuit must also be calculated.

E. *I–V* characteristics

The *I–V* characteristics of cells C1–C4 are calculated according to Eqs. (3)–(6)

$$I_1(\mu_1)/q = \dot{N}(E_g, 2E_g, T_s, 0, \epsilon_S) + \dot{N}(E_g, 2E_g, T_z, 0, \epsilon_{\text{hemi}})$$
$$- I_3(\mu_{3,4})/q - I_4(\mu_{3,4})/q$$
$$- \dot{N}(E_g, 2E_g, T_z, \mu_1, \pi), \tag{3}$$

$$I_2(\mu_2)/q = \dot{N}(2E_g, \infty, T_s, 0, \epsilon_S) + \dot{N}(2E_g, \infty, T_z, 0, \epsilon_{\text{hemi}})$$
$$- \dot{N}(2E_g, \infty, T_z, \mu_2, \pi), \tag{4}$$

$$I_3(\mu_{3,4})/q = 1/2 \cdot [\dot{N}(E_g, 2E_g, T_z, \mu_1, \epsilon_{\text{int}})$$
$$- \dot{N}(E_g, 2E_g, T_z, \mu_{3,4}, \epsilon_{\text{int}})], \tag{5}$$

$$I_4(\mu_{3,4})/q = 1/2 \cdot [\dot{N}(E_g, 2E_g, T_z, \mu_1, \epsilon_{\text{int}})$$
$$- \dot{N}(E_g, 2E_g, T_z, \mu_{3,4}, \epsilon_{\text{int}})]. \tag{6}$$

The temperature of the solar cells is set to $T_z = 300$ K in all calculations.

For a material with more than two bands the description of the emitted photon current density by the generalized Kirchhoff law [Eq. (2)] is usually allowed only if the energy ranges for different types of transitions do not overlap. In the optimum conditions for our system, however the two cells C3 and C4 both emit and absorb in exactly the same energy interval between E_g and $2E_g$.

Generally, the description of the emitted photon current density gets more complicated when energy intervals for different transitions overlap. But according to the boundary conditions described below the same current flows through C3 and C4 at steady state. As these cells also have equal lower and upper threshold energies for the absorptance, C3 and C4 can be modeled as identical cells with an identical electrochemical potential difference, which is denoted $\mu_{3,4}$. The photon current densities emitted and absorbed by the down-converter in the energy interval between E_g and $2E_g$ can therefore be modeled as the corresponding photon current densities emitted and absorbed by a single solar cell with the same parameters, being equally shared between C3 and C4, which is taken into account by the factor 1/2 in Eqs. (5) and (6).

The first two terms on the right hand side of Eq. (3) describe generation rates in the cell C1 due to the absorption of that part of the direct and of the hemispherical incident light, which can be absorbed by the solar cell. According to Eqs. (5) and (6) the following two terms in Eq. (3) denote the photon-current densities emitted by the cell C1 into cells C3 and C4 and vice versa. The last term in Eq. (3) describes the photon current density that is emitted by C1 via the front surface into the hemisphere.

F. Boundary conditions

Two boundary conditions must be fulfilled in the calculations: (1) As the down-converter is under open circuit conditions, the same current flows through the three cells C2, C3, and C4. This condition also ascertains a constant occu-
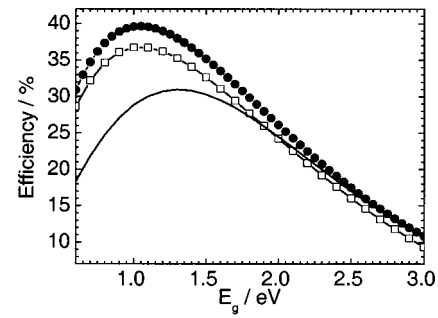

FIG. 4. Efficiency of the system: (solid line) Shockley–Queisser limit for a conventional solar cell (open squares) efficiency of the system with the converter located on the front surface, (solid circles) efficiency of the system with a converter with one impurity located on the rear surface. Nonconcentrated radiation from a 6000 K sun and a refractive index $n = 3.6$ of the solar cell and of the luminescence converter is assumed for all curves.

pancy of the IL as a function of time at steady state. (2) The sum of the voltages of cells C3 and C4 equals the voltage of cell C2.

IV. RESULTS AND DISCUSSION

A. Down-converter on the rear surface

The optimum efficiency of the down-conversion system has been calculated as a function of the band gap of the solar cell C1. The refractive index of the luminescence converter and of the solar cell was $n = 3.6$ in all calculations, a typical value for solar cell materials like Si or GaAs.

The efficiency of the system is shown as a function of the band gap of the solar cell material in Fig. 4 (solid circles). An optimum efficiency of 39.63% is found for a band gap of the solar cell of 1.05 eV. For comparison the Shockley–Queisser limit[6] for a conventional single junction solar cell without a down-converter is plotted as a solid line. A comparison of these two curves shows that a substantial improvement of the efficiency can be achieved with a down-converter on the rear surface of the solar cell for solar cell materials with low band-gap energies. Contrarily at large band-gap energies the calculations for the down-conversion system converge toward the Shockley–Queisser limits because the number of photons in the solar spectrum with energies larger than twice the band-gap energy becomes negligibly small.

The significant improvements of the down-conversion system over the Shockley–Queisser limits for low-band-gap materials indicate that at low light intensities incident high-energy photons are very efficiently down converted into two lower energy photons. This is confirmed by calculations of the integral photon current densities emitted by the three cells representing the down-converter. We find that, e.g., for $E_g = 1.1$ eV and for illumination with a nonconcentrated $T = 6000$ K blackbody spectrum the sum of the integral photon currents emitted via the two intermediate transitions is more than 5000 times larger than the integral photon current due to band-to-band transitions, which can thus be neglected.

The efficiencies calculated for the down-conversion system are below the limiting efficiencies for a solar cell using impact ionization.[3] This is due to the fact that the excess

energy of incident photons above twice the band-gap energy of the solar cell is still lost in the down-conversion system while these losses are completely absent in the case of impact ionization where electron–phonon coupling must be excluded.

A further efficiency improvement can certainly be achieved with a down-converter with more than one intermediate level that can convert incident photons with energies larger than an integer multiple of the band-gap energy of the solar cell into the corresponding integer number of lower band-gap photons. But as has been shown in Ref. 1, the additional benefit for nonconcentrated light is small compared to the increase in efficiency achieved with a down-converter with only one IL.

B. Down-converter on the front surface

The geometry with the luminescence converter on the rear surface of the system requires a bifacial solar cell. In a more elegant geometry, which can, in principle, be applied to any existing solar cell the luminescence converter is located on the front surface of the solar cell. We have calculated the efficiency of that system in a model that is equivalent to the one described above. The main difference is that with the converter on the front surface incident light with energies $\hbar\omega > E_g$ is completely absorbed by the down-converter and the solar cell only receives and absorbs the luminescent radiation emitted by the down-converter.

The resulting efficiencies of the system are shown as open squares in Fig. 4. The curve is significantly below the efficiency curve calculated for a system with the down-converter on the rear surface (solid circles). These lower efficiencies are due to the emission of photons by the down-converter via the front surface. These photons are lost. Contrarily, with the converter on the rear surface the emission by cells C3 and C4 goes completely into cell C1, where it is absorbed.

This additional loss mechanism is responsible for the fact that the efficiency of the down-conversion system with a down-converter on the front surface is below the Shockley–Queisser limit for a conventional solar cell at large band-gap energies (Fig. 4). This is due to the fact that the beneficial effect of the down-converter gets smaller with increasing band gap, while an increasing fraction of the incident photons, which would be completely absorbed in a conventional solar cell, is redirected toward the front surface after absorption and re-emission.

If the down-converter is located at the front surface of the solar cell one might expect that only half of the luminescence emitted by the down-converter contributes to the photocurrent of the solar cell because only this contribution is emitted into the direction of the solar cell. This would in fact be the case for a material with a refractive index $n = 1$, which is emitting hemispherically. However, solar cell materials like silicon or GaAs have a large refractive index of typically $n \approx 3.6$. As mentioned above, the étendue of the luminescence that is emitted via the front surface is $\epsilon = \pi$, while the emission from the down-converter in the direction of the
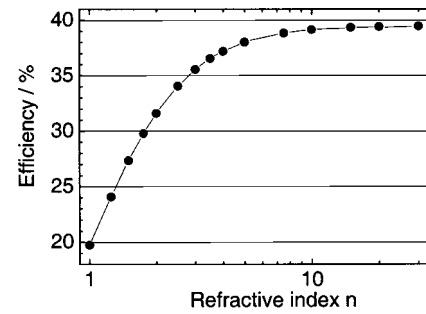

FIG. 5. Efficiency of the system with the converter on the front surface for a band gap of the solar cell of 1.1 eV as a function of the refractive index n. The solar cell and the luminescence converter are assumed to have equal refractive indices.

solar cell is described by $\epsilon_{int} = \pi n^2$, hence a roughly 13 times larger factor for $n = 3.6$.

As only the fraction of photons, which is emitted into the direction of the solar cell, contributes to the photocurrent of the cell, a large refractive index of the solar cell and of the down-converter is essential for a high conversion efficiency of the system if the converter is located on the front surface. As an example, the efficiency of a solar cell with a down-converter on the front surface is shown as a function of the refractive index n (equal for the solar cell and the luminescence converter) and for a band-gap energy of 1.1 eV in Fig. 5. As expected the efficiency drops below the Shockley–Queisser limit as n approaches one. Contrarily, with increasing refractive index n the photon current emitted via the front surface converges toward zero and the efficiency therefore converges toward 39.63% the limiting value, which is found for the geometry with the converter on the rear surface.

C. Relaxing the assumption $A(\hbar\omega) = 1$

Increasing the refractive index above $n = 3.6$ is certainly not a practical way to bring the efficiency of a real system closer to the limiting efficiencies possible with the luminescence converter located on the rear surface of the solar cell (solid squares in Fig. 4). However, a further improvement can be achieved if we relax the assumption $A(\hbar\omega) = 1$ for the two intermediate transitions, while this condition is maintained for the band-to-band transitions.

One disadvantage of the system with the converter on the front surface as described so far is that not only the high-energy photons but also the lower-energy photons with $E_g < \hbar\omega < 2E_g$, which are not suitable for the down-conversion process, are completely absorbed by the down-converter. The subsequent re-emission of photons results in a randomization of the direction of these photons, which would otherwise be completely absorbed by the solar cell. The fraction of photons, which is emitted into the escape cone of the front surface of the down-converter, is lost. By reducing the absorptance for the intermediate transitions to, e.g., $A(\hbar\omega) = 0.01$ for $E_g < \hbar\omega < 2E_g$, the fraction of incident photons in this energy interval, which is absorbed by the down-converter, is largely reduced.

According to Kirchhoff's law the photon current emitted by the down-converter is linear in the absorptance. The re-

duction of $A(\hbar\omega)$ for the intermediate transitions thus also reduces the ratio of the photon current emitted by the intermediate transitions over the photon current emitted by band-to-band transitions. However, as discussed above this ratio is approximately 5000 if all transitions have total absorption. Therefore, the major fraction of photons is still emitted by the intermediate transitions even if the down-converter is almost transparent in the corresponding energy interval.

The advantage of this modification of the system is that the incident sunlight with photon energies $E_g < \hbar\omega < 2E_g$, which cannot be down converted, is almost completely transmitted by the down-converter and absorbed in the solar cell and thus does not suffer from the additional loss mechanism due to the luminescence converter.

The theoretical description of the system becomes more complicated as we relax the approximation of total absorption for some transitions because the angular dependence of the emitted photon current must be calculated explicitly in order to determine the photon currents that are exchanged between the solar cell and the down-converter. The efficiency improvement can, however, be estimated by calculating the fractions of incident photons with energies $E_g < \hbar\omega < 2E_g$ and with energies $\hbar\omega > 2E_g$ in a $T = 6000$ K blackbody spectrum. According to this calculation the photon current lost due to the emission from the front surface can be reduced by approximately 70% for $E_g = 1.1$ eV if $A(\hbar\omega) = 0.01$ for the intermediate transitions. As the deviations between the efficiency curves for the system with the luminescence converter located on the front and on the rear surface are solely due to this loss mechanism, an upper limit for the efficiency of 38.6% can be estimated for a band gap of 1.1 eV.

D. Photon selectivity

In the theoretical calculations described above we had to assume that high-energy photons are completely used for band-to-band transitions inside the down-converter, i.e., photon selectivity had to be assumed. In a three-band system this can be achieved, e.g., by limiting the widths of the upper and of the lower band. However this restriction of the bands sets an upper threshold energy for the absorptance of the converter and thus reduces the number of high-energy photons that can be down converted, which certainly results in a lower efficiency of the system. A further advantage of reducing the absorptance for the intermediate transitions is that a restriction of the bands of the luminescence converter is no longer necessary to achieve photon selectivity. The low absorptance for the intermediate transitions guarantees that only a minor fraction of high-energy photons is absorbed via one of the intermediate transitions.

V. CONCLUSIONS

The use of a down-converting material in combination with a solar cell to improve the efficiency of conventional solar cells has been discussed. Significant improvements of the efficiency are found for band-gap energies of the solar cell of about 1.1 eV. For $E_g = 1.05$ eV an upper limit of 39.63% is calculated for a luminescence converter with one

intermediate level, which is located on the rear surface of a solar cell. A more practical geometry with a luminescence converter on the front surface has the advantage that it can be applied to any existing solar cell. The efficiency which can be achieved with this geometry is 38.6% for $E_g = 1.1$ eV, a significant improvement over the 30.9% which can be achieved with a conventional solar cell under the same assumption of only radiative recombination. The fact that the maximum efficiency is found for a band gap of around 1.1 eV makes the geometry with the converter on the front surface a promising option to improve the efficiency of silicon solar cells, e.g., high efficiency UNSW PERL cells.

Compared to the impurity photovoltaic effect or the use of impact ionization our approach has the advantage that the efficiency is improved by adding a component to an existing solar cell, which can be optimized independently from the solar cell material itself. The requirements for an efficient luminescence converter located on the front surface of, e.g., a silicon solar cell are a large refractive index, radiatively efficient intermediate transitions, and a large absorptance for photons with energies larger than twice the band-gap energy of silicon in combination with a lower absorptance for the intermediate transitions. No additional constraints are imposed on the solar cell material like, e.g., the exclusion of electron–phonon coupling as in the case of impact ionization or like the need to find a suitable impurity for a particular solar cell material in an IPV solar cell.

For silicon solar cells several III–V compounds (e.g., AlAs or GaP) doped with suitable impurities are materials that could be used as down-converting layers. These compounds have the advantage that high quality layers can be grown with well-established epitaxial methods. Luminescence conversion efficiencies close to 200%, corresponding to the generation of two low energy photons per incident high energy photon, have been demonstrated by Wegh et al.[8] with Eu^{3+}-doped $LiGdF_4$. While the figure 200% is kind of an internal quantum efficiency[9] for direct excitation into the ^6G_j states of the Gd^{3+}, these investigations show that in principle such large down-conversion efficiencies are possible. Further candidates for down-converter materials are therefore other rare earth or metal doped materials. Efficient down-conversion could also be achieved with quantum-well heterostructures in which high-energy photons are absorbed followed by a multiple step recombination involving two or more radiative inter- or intraband transitions as used in cascade lasers.

[1] R. Brendel, J. H. Werner, and H. J. Queisser, Sol. Energy Mater. Sol. Cells **41/42**, 419 (1996).
[2] J. H. Werner, S. Kolodinski, and H. J. Queisser, Phys. Rev. Lett. **72**, 3851 (1994).

[3] P. Würfel, Sol. Energy Mater. Sol. Cells **46**, 43 (1997).
[4] T. Trupke, M. A. Green, and P. Würfel, J. Appl. Phys. (submitted).
[5] A. Luque and A. Marti, Phys. Rev. Lett. **78**, 5014 (1997).
[6] W. Shockley and H. J. Queisser, J. Appl. Phys. **32**, 510 (1961).
[7] T. Trupke, E. Daub, and P. Würfel, Sol. Energy Mater. Sol. Cells **53**,

103 (1998).
[8] R. T. Wegh, H. Donker, K. D. Oskam, and A. Meijerink, Science **283**, 663 (1999).
[9] C. Feldmann, T. Jüstel, C. R. Ronda, and D. U. Wiechert, J. Lumin. **92**, 245 (2001).