Novel Optimization Principles and Efficiency Limits for Semiconductor Solar Cells

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Quantum efficiencies of more than merely one electron-hole pair per absorbed photon have recently been demonstrated for solar cells. The theoretical upper limit for solar cell conversion efficiency can thus be raised (from 30%) to 43% if photon absorption and electron-hole excitation follow a specific pathway. This pathway includes photon absorption at specific points in the Brillouin zone, and an inverse Auger effect mechanism for the multiplication of electron-hole pairs. We specify the principles and rules for optimal band structure tailoring.

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The efficiency of conversion for solar photons into electrical energy has been vastly improved in the recent past [1,2] up to a 23.3% efficient silicon solar cell [3]. This achievement is based on strict adherence to fundamental physics rather than on reliance upon technological developments. For example, the seemingly obvious engineering principle of providing cells with a large-area backside contact with supposedly essential low resistance losses has been abandoned in favor of a minimal number of small-area contact dots [4,5] because contacts by necessity force the quasi Fermi levels of electrons and holes to equality, thus leading to enhanced pair recombination and curtailed efficiencies. As a second example, it had been noticed that thinner solar cells display higher open circuit voltages [6] and thus (under constant absorption conditions) also improved efficiencies. This initially quite stunning prediction has recently been demonstrated to be a natural consequence of thermodynamics: Reduced thickness leads to higher volume density of photogenerated pairs, which reduces entropy, hence raising conversion efficiency [7].

In this spirit of principal physics, this Letter tackles the remaining most serious source of energy losses in photovoltaic conversion. The energies of the impinging solar photons are acutely underutilized, because (i) light from the red end of the solar spectrum is wasted, since photons with energies $h\nu$ below the lowest band gap E_G of the solar cell material are not absorbed; and (ii) photons from the blue regime create hot carriers with an excess energy $E_x = h\nu - E_G$ which is disregarded in present day cells, because carriers relax unabatedly toward the edges of their bands; hence E_x is dissipated entirely to photons. Until now, the search for an optimum photovoltaic material was limited to a compromise in matching the scalar parameter E_G to the solar spectrum [8,9]. Yielding to these sacrifices in the blue and red ends of the spectrum, one finds then an optimal E_G around 1.2 eV, close to the gap of silicon [8].

We here propose a totally different optimization and matching. The essential proposal is to utilize the blue-generated excess energy E_x of the electrons and holes for the product of multiple carrier pairs: The whole electronic band structure $E(\mathbf{k})$ must be arranged such that conservation of electronic energy E and momentum $\mathbf{k}$ allow for the use of E_x for effective carrier multiplication by Auger generation instead of being drained off into the phonon bath. Effective Auger generation requires that one of the two photogenerated primary carriers receives the lion's share of the excess energy E_x. Proper optimization ought now to consider the entire vectorial band structure $E(\mathbf{k})$ rather than just the fundamental band gap E_G. Reliance on Auger generated multiple carrier pairs leads us to revised upper efficiency limits for photovoltaic energy conversion.

Our recent quantum efficiency measurements on silicon solar cells [10] have demonstrated that indeed more than one electron-hole pair can be generated by one photon from the blue end of the solar spectrum. The underlying physics is sketched in Fig. 1. The ultraviolet photon excites a transition e_1-h_1 at the first direct band gap at the Γ point of the silicon's band structure. As a result one

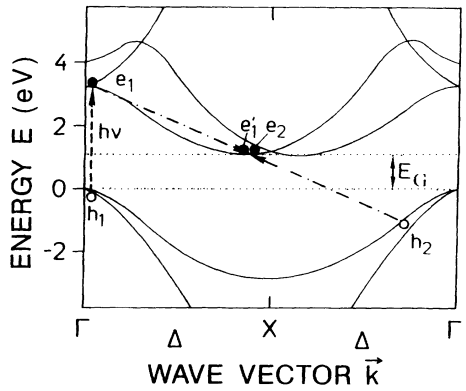

FIG. 1. Carrier multiplication by optically induced Auger generation; example for Δ axis of Si. Light absorption initially generates an electron-hole pair (e_1-h_1) at the Γ point. The hot electron with excess energy $E_x = h\nu - E_G$ undergoes inverse Auger relaxation toward the conduction band minimum near X to become e_1'. Energy E and momentum $\mathbf{k}$ are conserved by the $h_2 \rightarrow e_2$ transition; the end result is the production to two pairs (see also Ref. [10]).

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encounters a favorable condition: The electron e_1 attains a much higher fraction of the excess energy E_x than does the hole h_1. This hot electron e_1 can then undergo the process of Auger generation, i.e., *optically induced impact ionization.* A secondary electron-hole pair e_2-h_2 is created while the primary electron relaxes towards the minimum conduction band edge close to the X point. Excess energy E_x and momentum $\mathbf{k}$ are conserved because the two arrows in Fig. 1 add vectorially to zero. Hence, the net result is the generation of *two* pairs per photon. The minority carriers are then assisted by the cell's structure and perfection to reach their respective output contacts.

The principal prospect for carrier multiplication by optically excited hot carriers was recognized early [11]; however, an experimental proof was missing until recently [10]. As a consequence, all previous theories of efficiency limits for solar cells neglected Auger generation [8,9,12,13]. Only a very recent publication [14] noticed increases of the so-called "ultimate efficiency limit" of Shockley and Queisser [8] if carriers were assumed to be multiplicated. Unfortunately, these recent authors [14] neglected the thermodynamically required [8,9,12,13] radiative recombination process as well as fill factor losses and also used onset energies, which are only appropriate to describe experiments in which the excess energy of the primary carriers is supplied by acceleration in an electrical field instead of *optical* excitation, discussed here.

Figure 2 considers optically induced carrier multiplication by the photons from the blue end of the solar spectrum. The inset shows the geometry which underlies these revised thermodynamical efficiency limits for solar cells. We consider a flat cell which is illuminated by the Sun under an angle Φ_S; for unconcentrated sunlight it holds that $\Phi_S = 0.266°$. The Sun is modeled by a blackbody of temperature $T_S = 5762$ K which emits the areal number

$$n_{\text{phot}}(E) = \frac{f_w (2\pi/c^2 h^3) E^2}{\exp(E/kT_S) - 1} \tag{1}$$

of photons of energy $E = h\nu$ per energy interval and second onto the cell [15], with $f_w = \sin^2\Phi_S = 2.16 \times 10^{-5}$ without concentration. The symbol c stands for the velocity of light and h is Planck's constant.

In the conventional calculation of efficiency limits [8,9,12,13], each of the photons with energies $E = h\nu$ above the gap E_G is assumed to create just one electron-hole pair and to give rise to a maximum areal short circuit current density

$$J_{\text{sc}} = q \int_{E_G}^{\infty} n_{\text{phot}}(E) dE \,, \tag{2}$$

where q stands for the elementary charge. Here we allow for the possibility of carrier multiplication and assume that each photon with an energy $h\nu \geq mE_G$ and $m = (1,2,3,\ldots,m_{\max})$ creates m carrier pairs. Effective carrier multiplication requires optimization of the whole band *structure* (see discussion below) and not only the choice of a best value for the band gap E_G. With the multiplicity m one obtains

$$J_{\text{sc}} = \sum_{m=1}^{m_{\max}-1} mq \int_{mE_G}^{(m+1)E_G} n_{\text{phot}}(E) dE + m_{\max} q \int_{m_{\max}E_G}^{\infty} n_{\text{phot}}(E) dE \tag{3}$$

for a maximum multiplicity $m_{\max} = 1$; the conventional Eq. (2) is recovered. The conversion efficiency $\eta = (J_{\text{sc}} \times V_{\text{oc}} \text{FF})/S$ depends on the short circuit current density J_{sc} of Eq. (3), the open circuit voltage V_{oc}, the fill factor FF, and the solar constant $S = f_w \sigma T_S^4$ with the Stefan-Boltzmann constant σ [16]. For an ideal cell, which follows the Shockley equation and without series resistance losses, the fill factor FF depends on V_{oc} only [16].

The lowest curve in Fig. 2 corresponds to the classic limit of Shockley and Queisser [8], which follows from Eq. (3) for $m_{\max} = 1$. All open circuit voltages are calculated from conventional solar cell analysis according to $V_{\text{oc}} = kT_c \ln(J_{\text{sc}}/J_0 + 1)$ [2]. The saturation current density J_0 depends on the detailed loss processes such as recombination via bulk and interface traps, radiative pro-

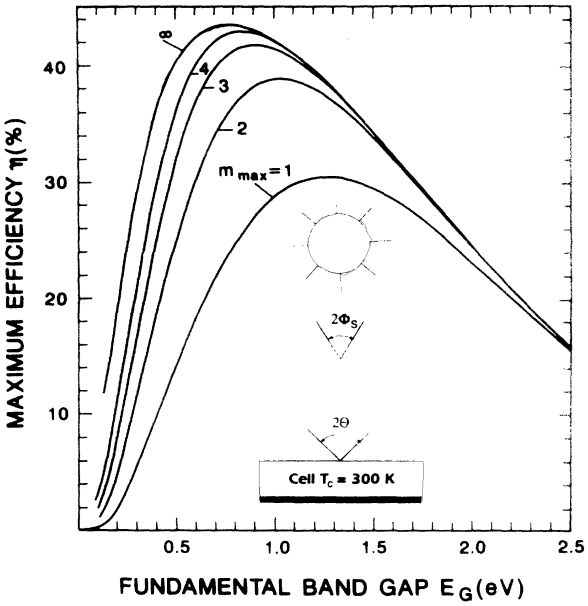

FIG. 2. Maximum efficiency of solar cells under the assumption that their saturation current is limited by radiative recombination only. The lowest curve with a maximum at $\eta = 30.3\%$ for a gap $E_G = 1.26$ eV neglects Auger generation and corresponds to the classic limit of Ref. [8]. The other curves include carrier multiplication with a maximum multiplicity $m_{\max}$ and converge at an optimum efficiency $\eta_{\max}^{\text{opt}} = 43.4\%$ and at an optimum band gap $E_G^{\text{opt}} = 0.757$ eV for the assumed Sun's blackbody illumination under an angle of $\Phi_S = 0.266°$. The cell emits recombination radiation into an angle of $\Theta = 90°$. Even under most optimistic conditions, the limit of 43.4% cannot be exceeded.

cesses, Auger processes, etc. [13,17]. Here was assumed the most favorable case, namely, that J_0 is limited by *radiative* recombination only and given by $J_0 = qQ_c$ where Q_c is the photon flux emitted by the cell [8],

$$Q_c = \sin^2\Theta \int_{E_G}^{\infty} E^2/\{\exp(E/kT_c) - 1\} dE \quad (4)$$

at cell temperature $T_c = 300$ K into the angle Θ. All curves in Fig. 2 are calculated for $\Theta = 90°$ and, in contrast to Ref. [8], we assume here that the cell emits only on one surface.

The series of curves in Fig. 2 converges fast toward a maximum efficiency $\eta_{\max}^{\text{opt}} = 43.4\%$ for an optimum gap $E_G^{\text{opt}} = 0.757$ eV; this $\eta_{\max}^{\text{opt}}$ value is obtained for any quantum efficiency IQE ≥ 8 [i.e., $m_{\max} \geq 8$ in Eq. (3)]. Already 38.7% at $E_G^{\text{opt}} = 1.01$ eV are reached for $m_{\max} = 2$, i.e., when two carrier pairs are created by every photon with energy $h\nu \geq 2E_G$. A value of 41% is exceeded for $m_{\max} = 3.0$. This efficiency is achieved without concentration and is higher than the maximum efficiency of 40.8% which was deduced by de Vos for sunlight with the maximum possible concentration $C_{\max} = 1/f_w = 46\,300$ and IQE = 1 [18]. Physical approaches to obtain high multiplication rates by Auger generation are therefore at least as promising as the technological search for effective concentrators. On the one hand, the semiconductor Si will not reach the uppermost curve in Fig. 2, because Auger *recombination* rather than radiative recombination limits V_{oc} [17]. On the other hand, any efficiency increases above this limiting curve are only possible for nonstandard conditions, such as nonblackbody [17] illumination and emission, reduced emission angles Θ, and for the combined use of concentration and Auger generation [19].

No general physical rule predicts an upper limit for the quantum efficiency IQE. However, relaxation of the hot carriers by Auger generation will always compete with emission of phonons. Nevertheless, the probability for carrier multiplication may be high as recently shown by us (see Fig. 3 of Ref. [10]) for particular points of the band structure of Si. As a consequence, we propose to tailor the entire band structure $E(\mathbf{k})$ of semiconductors to support optically induced impact ionization. Figure 3 displays an exemplary $E(\mathbf{k})$ which would be suitable for highly efficient cells with quantum efficiencies IQE ≥ 1. Alloys of Si and Ge may come close to such an $E(\mathbf{k})$ which is tailored according to four demands [20] in a way to make Auger generation effective. Demand 1, the *indirect (direct) band gap rule*, asks for semiconductors with an indirect fundamental gap E_G and a first direct gap $E_{D1} \geq 2E_G$. The direct gap guarantees strong absorption of light with energy $h\nu \geq E_{D1}$, which allows for the creation of two carrier pairs. Demand 2, the *inequality of excess energy rule*, asks that the lion's share of the excess energy $E_x = h\nu - E_G$ is given to one carrier of the primary pair, because E_x of this carrier has to exceed E_G to allow for multiplication. In the ideal case, the highest

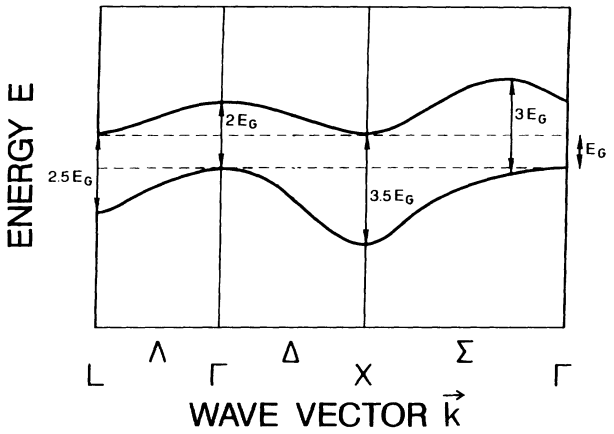

FIG. 3. Band structure $E(\mathbf{k})$ of a fictitious, ideal semiconductor with a high ability to gain from Auger generated carriers. The bands are parallel over large portions in the Brillouin zone. The direct band gaps, starting with a value of $2E_G$, match a wide part of the solar spectrum. The dispersion of bands is chosen such that points with an ability to generate additional carriers by the Auger process coincide with strong optical transitions.

valence band $E_V(\mathbf{k})$ and the lowest conduction band $E_C(\mathbf{k})$ are almost parallel over wide regimes within the Brillouin zone. This demand is fulfilled by *indirect* semiconductors only. Demand 3, the *absorption rule*, asks for strong light absorption at points in $E(\mathbf{k})$, which enables carrier multiplication; consequently, the slope of $E_C(\mathbf{k})$ and $E_V(\mathbf{k})$ should be equal there, $\nabla_k E_C(\mathbf{k}) \approx \nabla_k E_V(\mathbf{k})$ [21]. In addition, the curvature of $E_C(\mathbf{k})$ and $E_V(\mathbf{k})$ should be small at many points to increase the possibilities for Auger generation, which requires conservation of energy E and momentum $\mathbf{k}$; as a consequence, $\nabla_k E_C(\mathbf{k}) \approx \nabla_k E_V(\mathbf{k})$ should hold there. Finally, demand 4, the *continuity rule*, asks for as many direct gaps E_{D1}, E_{D2}, etc., as possible above the fundamental indirect gap E_G, according to $2E_G \leq E_{D1} \leq E_{D2} \leq E_{D3}$ in order to enable Auger generation for many photon energies. The direct gaps should be consecutively pumped with increasing energy $h\nu$ of the photons from the Sun's spectrum.

The fictitious band structure of Fig. 3 fulfills all four demands and indicates the novel challenge of an *inverse band structure problem* for an ideal photovoltaic material. Rather than starting from a well-defined atomic arrangement in a crystal, for which $E(\mathbf{k})$ has to be found in the familiar manner [22], we are now facing the more complicated task of searching for element combinations and crystal structures that yield a desired $E(\mathbf{k})$.

In conclusion, we propose to utilize the inverse Auger effect to generate extra carrier pairs by high energy solar photons and to optimize the band structure of the material accordingly. Our calculations show that the upper efficiency of solar cells can be substantially increased if one makes effective use of such carrier multiplication.

Novel research challenges in the field of semiconductors arise but seem solvable. For example, the band structure [23] of SiGe contains some features of our fictitious band structure in Fig. 3. Band structures like the one in Fig. 3 promise strong absorption across the direct gaps. Consequently, thin layers suffice to absorb photons with $h\nu \geq 2E_G$. Photons with energies $h\nu$ between E_G and $2E_G$ are absorbed by transitions across the indirect *fundamental* gap E_G. The weak absorbance of such transitions can be offset by effective light trapping [1,2].

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[1] M. A. Green, *High Efficiency Silicon Solar Cells* (Trans Tech, Aedermannsdorf, Switzerland, 1987).
[2] A. W. Blakers, in *Festkörperprobleme/Advances in Solid State Physics*, edited by U. Rössler (Vieweg, Braunschweig, 1990), Vol. 30, p. 403.
[3] M. A. Green, in *Proceedings of the 10th European Photovoltaic Solar Energy Conference*, edited by A. Luque, G. Sala, W. Palz, G. Dos Santos, and P. Helm (Kluwer, Dordrecht, The Netherlands, 1991), p. 250.
[4] R. A. Sinton, Y. Kwark, S. Swirhun, and R. M. Swanson, IEEE Electron. Dev. Lett. **6**, 405 (1985).
[5] A. W. Blakers, A. Wang, A. M. Milne, J. Zhao, and M. A. Green, Appl. Phys. Lett. **55**, 1363 (1989).
[6] H. H. Hovel, in *Solar Cells*, edited by R. K. Willardson and A. C. Beer, Semiconductors and Semimetals Vol. II (Academic, New York, 1975), p. 106.
[7] R. Brendel and H. J. Queisser, Solar Energy Mater. Solar Cells **29**, 397 (1993).
[8] W. Shockley and H. J. Queisser, J. Appl. Phys. **32**, 510 (1961).
[9] G. L. Araujo, in *Physical Limitations to Photovoltaic Energy Conversion*, edited by A. Luque and G. L. Araujo (Adam Hilger, Bristol, 1990), p. 106.
[10] S. Kolodinski, J. H. Werner, T. Wittchen, and H. J. Queisser, Appl. Phys. Lett. **63**, 2405 (1993).
[11] See footnote 12 in Ref. [8].
[12] P. Würfel and W. Ruppel, IEEE Trans. Electron. Dev. **27**, 877 (1980).
[13] T. Tiedje, E. Yablonovitch, G. D. Cody, and B. G. Brooks, IEEE Trans. Electron. Dev. **31**, 711 (1984).
[14] P. T. Landsberg, H. Nussbaumer, and G. Willeke, J. Appl. Phys. **74**, 1451 (1993).
[15] See, for example, A de Vos, *Endoreversible Thermodynamics of Solar Energy Conversion* (Oxford Univ. Press, Oxford, 1992), p. 8.
[16] See, for example, *High Efficiency Silicon Solar Cells* (Ref. [1]), Chap. 6,
[17] M. A. Green, IEEE Trans. Electron. Dev. **31**, 671 (1984).
[18] *Endoreversible Thermodynamics of Solar Energy Conversion* (Ref. [15]), p. 131.
[19] J. H. Werner (unpublished).
[20] S. Kolodinski, J. H. Werner, and H. J. Queisser, Solar Energy Mater. Solar Cells (to be published).
[21] M. L. Cohen and J. R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors* (Springer, Berlin, 1988), p. 32.
[22] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).
[23] U. Schmid, N. E. Christensen, and M. Cardona, Phys. Rev. B **41**, 5919 (1990).