Particle Conservation in the Hot-carrier Solar Cell

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In conventional p–n junction solar cells, carrier multiplication by impact ionisation, is negligible, owing to the low temperature of the electron–hole pairs. This leads to particle conservation between the net number of absorbed photons and the number of electron–hole pairs withdrawn from the cell. In hot-carrier solar cells, in which electrons are at a high temperature by assuming suppression of electron–phonon scattering, such particle conservation leads to peculiar results. Numerical calculations show that entire current–voltage characteristics with meaningful values of temperature and chemical potential do not exist. If the energy at which electron–hole pairs are extracted is smaller than the average energy of absorbed photons, the temperature of the electrons and holes becomes much larger than the temperature of the sun. When the extraction energy is larger than the average energy of the absorbed photons, an entire current–voltage curve cannot always be obtained. It follows that impact ionisation and Auger recombination cannot be neglected when the thermal energy of the electron–hole pairs is comparable to the bandgap of the absorber. Accounting for these processes results in current–voltage characteristics that are well behaved. Copyright © 2005 John Wiley & Sons, Ltd.

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INTRODUCTION

The theoretical analysis of ideal conventional solar cells1 is based on particle conservation: For each absorbed photon, one electron–hole pair is generated within the device and, for each electron–hole pair that recombines via radiative recombination, a single photon is emitted. However, energy conservation is not applied between the electron–hole pairs that are withdrawn and the absorbed photons because of energy losses by thermalisation of carriers with the lattice. Electron–phonon scattering produces separate Fermi distributions for holes in the valence band and electrons in the conduction band at the lattice temperature with separate Fermi energies for each band. Since the Fermi energy of the conduction band distribution $\varepsilon_{\text{FC}}$ is larger than the Fermi energy for the valence band, $\varepsilon_{\text{FV}}$, the chemical potential of the electron–hole pairs is $\mu_{\text{eh}} = \varepsilon_{\text{FC}} - \varepsilon_{\text{FV}} > 0$. This is an essential result for conventional solar cells, since the maximum electrical energy obtainable per extracted electron–hole pair is equal to their chemical potential.

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In analysing the potential of obtaining high efficiencies by using hot carrier solar cells, Ross and Nozik considered the generation of electron–hole pairs in solids where thermalisation of carriers with the lattice is suppressed. Therefore they applied, in addition to particle conservation, energy conservation between the photons and electron–hole pairs. Electron–electron scattering within a band in this model leads to Fermi distributions for the electrons and the holes which have a higher temperature than the lattice temperature and a negative chemical potential of electron–hole pairs for best performance. Electron–hole pairs are then removed at a single energy $\varepsilon_{\text{ext}}$, where the Fermi distributions in the absorber and the contacts are equal, to achieve the highest possible efficiency for the energy conversion process. For a bandgap of zero, the approach of Ross and Nozik results in conversion efficiencies of $\approx 86\%$ under maximally concentrated blackbody radiation at 6000 K.

Figure 1 presents a schematic of the hot-carrier solar cell consisting of a semiconductor absorber (which can have a band gap of $E_G \geq 0$) between two contacts, each of which transmits electrons at a single energy. Electrons within the absorber are excited from the valence band to the conduction band giving rise to a chemical potential of electron–hole pairs within the absorber of $\mu_{\text{eh}}$. Electrons in the conduction band and holes in the valence band are allowed to scatter with one another, but not with phonons. Some electron–hole pairs make radiative transitions and emit photons whilst the remaining pairs are removed from the absorber via the monoenergetic contacts. The difference in energy between electron and hole removal is termed the extraction energy $\varepsilon_{\text{ext}}$. $\varepsilon_{\text{FR}}$ indicates the Fermi energy of the electrons in the cold distribution in the metal electrode on the right-hand side of the contacts and $\varepsilon_{\text{FL}}$ indicates the Fermi energy of the electrons in the cold distribution on the left-hand side of the contacts. The difference between these two Fermi energies $\varepsilon_{\text{FL}} - \varepsilon_{\text{FR}} = eV$ defines the voltage $V$ of the device (where $e$ is the charge of an electron). As well as the energy conservation condition, a particle conservation condition is applied in the Ross and Nozik approach whereby the number of electrons extracted through the contacts equals the difference between the number of photons absorbed and emitted. By optimising the extraction energy and the bandgap of the absorber the hot-carrier solar cell achieves very high efficiencies for converting sunlight into electricity.

The performance of the hot-carrier solar cell with particle conservation can be compared with another limiting case where impact ionisation and its inverse process, Auger recombination, are allowed to occur. In this case the number of electron–hole pairs and photons is not conserved, and the resultant occupation of states for the electrons and holes is given by a single Fermi distribution with a chemical potential of the electron–hole pairs equal to zero. Here, absorber temperatures range from 300 K at short-circuit, to 6000 K at open-circuit conditions and the efficiency is independent of extraction energy. The two models of a hot-carrier solar cell will be distinguished in the following as the particle conservation model and the impact-Auger model.

Owing to the monoenergetic extraction of electrons and holes from an ideal hot-carrier solar cell, the net absorbed energy flux is converted to electrical energy at the Carnot efficiency, irrespective of whether electron–hole pairs are conserved. In the case where the chemical potential of the absorber is negative, the emitted photon flux is less than from a thermal emitter with zero chemical potential at the same temperature.
This means that the overall efficiency of the hot-carrier cell is somewhat smaller under the assumption of non-negligible impact ionisation, particularly for non-concentrated radiation, as can be seen in Figure 2.3

**MATHEMATICAL CONSIDERATIONS**

Because particle conservation is enforced, peculiar results occur for the particle conservation (Ross–Nozik) model when the electron–hole pairs are taken out of the absorber with an extraction energy \( \varepsilon_{ext} \) different from the average energy \( \varepsilon_{abs} \) of the absorbed photons. For example, if \( \varepsilon_{ext} < \varepsilon_{abs} \) then the energy of the remaining carriers within the absorber must increase, corresponding to a higher temperature and leading to a higher average energy \( \varepsilon_{em} \) of the emitted photons. At the same time, the chemical potential becomes more negative to maintain a small emitted photon current. This problem becomes apparent when an attempt is made to determine the current–voltage characteristic of the hot-carrier solar cell.

In the particle conservation model, the extracted current density \( j_Q \) follows from particle conservation

\[
j_Q = e j_{eh} = e (j_{gamma,abs} - j_{gamma,em}) \tag{1}
\]

where the absorbed and emitted photon current densities are given by a generalized Planck law.5,6

\[
j_{gamma}(h\omega) = \int_{E_G}^{\infty} \frac{\Omega}{4\pi^3 h^3 c^2} \cdot \frac{(h\omega)^2}{\exp\left(\frac{h\omega - \mu_{eh}}{kT}\right) - 1} d(h\omega) \tag{2}
\]

For absorbed solar radiation the solid angle is \( \Omega = 6.8 \times 10^{-5} \) for non-concentrated light and \( \Omega = \pi \) for maximally concentrated blackbody radiation. The solid angle of emission is assumed to be \( \Omega = \pi \) in all cases (i.e., the entire hemisphere of \( 2\pi \) after accounting for Lambert’s law). \( E_G \) is the bandgap of the absorber, \( \mu_{eh} \) is the chemical potential of the electron–hole pairs in the absorber. For the absorbed solar radiation \( \mu_{eh} = 0 \). The absorptivity is assumed to be 1 for \( h\omega \geq E_G \). The condition \( \mu_{eh} \leq E_G \) applies for the emitted radiation. The sun’s temperature is \( T_S = 6000 \) K, and the temperature of the electrons and holes in the absorber is \( T_H \).

Energy conservation then requires that the extracted energy current density \( j_{E,ext} \) is given by:

\[
j_{E,ext} = \varepsilon_{ext} j_{eh} = j_{E,abs} - j_{E,em} \tag{3}
\]

Absorbed and emitted energy current densities \( j_{E,abs} \) and \( j_{E,em} \) follow from Equation (2) by multiplying the numerator in the integral by \( h\omega \). For a given charge current \( j_Q \) values for \( \mu_{eh} \) and \( T_H \) can be obtained from Equations (1) and (3).
This formulation assumes that when the electrons and holes are withdrawn at the specific energy $\varepsilon_{\text{ext}}$ no energy is lost due to thermalisation with the lattice at room temperature $T_0 = 300 \text{ K}$. The electrical energy ($\text{eV}$) gained from the extracted energy will then be given by Carnot’s formula generalised to energy sources with a non-zero chemical potential:\(^2,^3\)

\[
\text{eV} = \varepsilon_{\text{ext}} \left( 1 - \frac{T_0}{T_H} \right) + \mu_{\text{eh}} \frac{T_0}{T_H}
\]  

Equations (1–4) allow us to calculate the current–voltage characteristic and we are interested in its entire range (i.e., from short-circuit to open-circuit\(^7\)). The current obtained from a hot-carrier solar cell when the voltage is changed from short-circuit to open-circuit can be better seen by rewriting Equation (3) so that the photon currents can be related to the energy currents via the average energies of the absorbed ($h\omega_{\text{abs}}$) and emitted ($h\omega_{\text{em}}$) photons. These average photon energies are given by the absorbed or emitted energy currents divided by the appropriate photon currents:

\[
j_{E,\text{ext}} = \varepsilon_{\text{ext}} j_{\text{eh}} = j_{E,\text{abs}} - j_{E,\text{em}} = h\omega_{\text{abs}} j_{\gamma,\text{abs}} - h\omega_{\text{em}} j_{\gamma,\text{em}}
\]

from which the charge current in Equation (1) can be expressed as

\[
j_Q = e \left( 1 - \frac{\varepsilon_{\text{ext}} - h\omega_{\text{abs}}}{\varepsilon_{\text{ext}} - h\omega_{\text{em}}} \right) j_{\gamma,\text{abs}}
\]

From Equation (6) three different cases can be distinguished:

a) $\varepsilon_{\text{ext}} = h\omega_{\text{abs}}$. This is a singular case, since it requires $h\omega_{\text{abs}} = h\omega_{\text{em}}$ (very exactly in fact).

b) $\varepsilon_{\text{ext}} < h\omega_{\text{abs}}$. This requires $h\omega_{\text{em}} > \varepsilon_{\text{ext}}$. For an increasing current $j_Q$ the average emitted photon energy $h\omega_{\text{em}}$ also increases, indicating that the temperature in the absorber will become greater than $T_S$.

c) $\varepsilon_{\text{ext}} > h\omega_{\text{abs}}$. This requires $h\omega_{\text{em}} < \varepsilon_{\text{ext}}$. For increasing $j_Q$, $h\omega_{\text{em}}$ has to decrease, indicating absorber carrier temperatures below $T_S$. Since $h\omega_{\text{em}} > 0$, the current is limited by the following equation:

\[
j_Q < e \frac{h\omega_{\text{abs}}}{\varepsilon_{\text{ext}}} j_{\gamma,\text{abs}}
\]

indicating that the expected short-circuit current $j_Q = e j_{\gamma,\text{abs}}$ is unattainable.

For all three cases the numerator and denominator in Equation (6) have to be equal under open-circuit conditions to yield zero current. For maximum concentration and open-circuit, the absorber is in equilibrium with the sun resulting in the absorber temperature $T_H$ being equal to the sun’s temperature $T_S$ and $\mu_{\text{eh}} = 0$. The temperature and chemical potential for the hot-carrier solar cell under different conditions of average absorbed photon energy $h\omega_{\text{abs}}$ and extraction energy $\varepsilon_{\text{ext}}$ are shown in Figure 3.

The lines of constant extraction energy shown in Figure 3(a) are labelled relative to the average energy per absorbed photon, and each point on a line corresponds to a different extraction voltage across the hot-carrier cell. The lines converge at $T_H = 6000 \text{ K}$ and $\Delta\mu_{\text{eh}} = 0$, which corresponds to open-circuit conditions. As the voltage is reduced from its open-circuit value, the behaviour of the hot-carrier cell becomes very sensitive to whether the extraction energy is higher or lower than $h\omega_{\text{abs}}$. For extraction energies lower than $h\omega_{\text{abs}}$, the temperature of the hot-carrier cell, after an initial small decrease, increases to values larger than 6000 K, while the chemical potential decreases to large negative values. If the extraction energy is higher than $h\omega_{\text{abs}}$, then the temperature of the hot-carrier cell decreases with decreasing voltage, while the chemical potential passes through a minimum and then tends to the limiting value of the bandgap of the material. Note that, even though the two curves closest to the average energy $h\omega_{\text{abs}}$ differ by only $10^{-10} \text{ eV}$, divergent behaviour with decreasing voltage results from the particle conservation model. The behaviour shown in Figure 3(b) and (c) for a non-zero band gap $E_G$ or for non-concentrated radiation is qualitatively the same as that shown for Figure 3(a).
Under the assumption of particle conservation used in the Ross–Nozik analysis, the hot-carrier solar cell exhibits singular behaviour at the extraction energy equal to the average energy of absorbed photons, with the temperature of the absorber tending to very high temperatures and large negative chemical potentials with decreasing voltage for extraction energies below $\frac{\hbar \omega_{abs}}{C_0}$, and low temperatures and chemical potentials equal to the bandgap for extraction energies above $\frac{\hbar \omega_{abs}}{C_0}$. The reason the assumption of particle conservation gives difficulties for hot-carrier solar cells, despite its success in describing conventional solar cells, is explained in subsequent sections.

**CURRENT–VOLTAGE CURVES**

We now present $j_Q-V$ curves for the particle conservation model and for the impact-Auger model, which always has $\mu_{eh}=0$. We use a bandgap of $E_G=0$ which, from Figure 2, produces the highest possible efficiency for maximum concentrated sunlight. With decreasing voltage in Figure 4 the temperature rises and the chemical potential decreases steeply for the particle conservation model where $\varepsilon_{ext} = \hbar \omega_{abs} - 0.01$ eV. The calculation was discontinued at a voltage of 1.00 V, where $T_H$ has reached 70 000 K and $\mu_{eh} = -80$ eV. For the particle conservation model where $\varepsilon_{ext} = \hbar \omega_{abs} + 0.01$ eV, the absorber temperature decreases when the voltage decreases, but no solutions with $\mu_{eh} \leq E_G = 0$ exist for voltages <1.05 V. Allowing infinitesimally small positive values of $\mu_{eh}$ would mean that high levels of stimulated emission would occur, possibly resulting in solutions below this voltage, but this is not included in the present formulation. Therefore, for the particle conservation model of the hot-carrier solar cell it can be concluded that for small (and in practice unavoidable) departures of extraction energy from the average energy of the absorbed photons short-circuit conditions can be obtained only via stimulated emission or with extreme values of the temperature and chemical potential of the electron hole pairs in the absorber.

These results are compared with the impact-Auger model of the hot-carrier solar cell where $\mu_{eh}=0$. For this case complete $j_Q-V$ curves can be obtained without unusual values of device parameters. The reason
why the differences between the $j_{Q-V}$ curves of the two models are hard to discern in Figure 4, is because the limiting efficiencies for these two cases are very similar as obvious from Figure 2. However, in other cases, the differences can be clearly seen, for example in the $j_{Q-V}$, $T-V$, and $\mu_{eh-V}$ curves shown in Figure 5 for an absorber with $E_G = 1 \text{ eV}$ under non-concentrated blackbody radiation. The same conclusion can be drawn for Figure 5, as for Figure 4, indicating that the problems in the numerical analysis are not due to the choice of band gap for the absorber (as both 0 and 1 eV cases are presented). Nor is the difficulty due to the concentration of the sunlight (as both maximally concentrated and non-concentrated sunlight are presented).
PHYSICAL CONSIDERATIONS

It is obvious from the previous results that the restrictions imposed by energy and particle conservation are too severe to allow for physically sensible parameters under short-circuit conditions. In particular, applying the particle conservation condition implies that impact ionisation and Auger recombination are excluded. The significance of these effects can be assessed from Figure 6, showing scattering processes between electrons in idealised semiconductor material of different bandgaps.

In a metal or a semiconductor, the scattering rate $S$ of particle 1 by particle 2 can be described as:

$$
S = M D_1(E_1, k_1) f_1(E_1) D_1(E_1 - \Delta E, k_1 - \Delta k) \\
x [1 - f_1(E_1 - \Delta E)] D_2(E_2, k_2) f_2(E_2) D_2(E_2 + \Delta E, k_2 + \Delta k) [1 - f_2(E_2 + \Delta E)]
$$

Figure 5. $j_Q$–$V$ curve (top) and $T$–$V$ curve (middle) and $\mu_{eh}$–$V$ curve (bottom) for the hot-carrier solar cell under maximally concentrated blackbody radiation for both impact ionization (IA) and particle conservation cases (RN) and where $E_G = 0$ eV, for the following four cases: (a) $\epsilon_{ext} = h\omega_{abs} - 0.01$ eV (IA) (solid line); (b) $\epsilon_{ext} = h\omega_{abs} + 0.01$ eV (IA) (dashed line); (c) $\epsilon_{ext} = h\omega_{abs} - 0.01$ eV (RN) (solid circles); (d) $\epsilon_{ext} = h\omega_{abs} + 0.01$ eV (RN) (open squares). Axes for the insets are the same as for the larger graphs.

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$$
where \( D \) is the electron density of states, \( f \) is the state occupancy, \( E \) is energy, \( k \) is the wave vector, and \( \Delta E \) and \( \Delta k \) are the energy and wave vector interchanged during the scattering event. The coefficient \( M \) is determined by the matrix element for the given transition. The remaining terms are the product of occupancy terms involving initial state occupancies and final state vacancies and of densities of states terms. The scattering rate will be finite for couplings allowing energy and momentum conservation.

In a metal, the Fermi level lies in the upper conduction band. If the scattering of a high-energy electron well above the Fermi level in this band is considered, the occupancy term contributions to Equation (8) will be strongest for processes involving the scattering of this high-energy electron with an electron from heavily occupied states below the Fermi level, with both final electron states lying in lightly occupied states above the Fermi level. As a consequence, most scattering is restricted to electrons lying approximately within a thermal energy unit, \( kT \), of the metal Fermi level. Identifying the empty states below the Fermi level as holes and the occupied states above the Fermi level as electrons, from one high-energy electron two electrons and one hole are produced by this scattering process which is then recognized as impact ionisation.

In a semiconductor, the conduction band is much more lightly occupied than near the Fermi level within a metal. A high-energy electron within this band can scatter with another electron in the same band, although the low initial state occupancy for the latter results in relatively low scattering rates. There are plenty of occupied low-energy electron states in the valence band, and scattering among these electrons can also occur, as shown in Figure 6(a). Here, the problem is the relatively low density of unoccupied final states in this band, proportional to the hole concentration, resulting again in relatively low scattering rates, at least for the case of a relatively large semiconductor bandgap.

For the case of a small-bandgap semiconductor shown in Figure 6(b), the situation changes dramatically. A high-energy conduction band electron now has sufficient energy to excite a valence band electron across the gap to the conduction band, where there are high densities of unoccupied final states. These inter-band transitions would be expected to result in a large increase in scattering rates once the average kinetic energy of carriers, \( 3/2 kT \), became comparable to the bandgap.

An important consequence of such inter-band scattering is that it results in electron–hole pair creation (impact ionisation). Similarly, the inverse process results in the loss of an electron–hole pair (Auger recombination). The particle conservation model by Ross and Nozik \(^2\) requires scattering of carriers within the same band to reach a common temperature \( T_H \), but excludes inter-band scattering. Inter-band transitions must, however, be taken into account, at least if \( kT_H > E_G \), since inter-band scattering will then be even stronger than...
scattering within the bands. For an electron temperature equal to that of solar radiation (6000 K), $kT_H = 0.5\, \text{eV}$. The explicit exclusion of inter-band scattering by the particle conservation condition invalidates the results\(^2\) for semiconductors with bandgap of up to the order of $kT_H$. In this energy range, the impact-Auger model,\(^4\) based on high rates of inter-band and intra-band scattering, seems to be more reliable.

A feature of both the particle conservation model of Ross and Nozik\(^2\) and the impact-Auger model of Würfel\(^4\) is that they are equilibrium formulations. They rely on large intra-band scattering rates for the temperature to be well defined and additional large inter-band scattering rates in the impact-Auger model for the chemical potential of electron–hole pairs to be zero. Neither model is able to predict what happens if carrier–carrier scattering rates are not large compared with carrier–phonon scattering rates or with carrier extraction rates.

**CONCLUSIONS**

Problems in calculating the current–voltage characteristics of a hot-carrier solar cell by the particle conservation model (Ross–Nozik), have led us to the conclusion that impact ionisation cannot be excluded in a hot-carrier solar cell having a bandgap up to the order of $kT_H$. For example if $T_H = T_S$ (which occurs at open-circuit) then $kT_H = 0.5\, \text{eV}$.

For narrow-bandgap absorbers, inclusion of impact ionisation and its inverse process, Auger recombination, will reduce the Fermi level separation of the electrons and holes and reduce the chemical potential of the electron–hole excitations towards zero. This removes the extreme features of the Ross Nozik model, but also removes its efficiency advantage over the impact-Auger model seen in Figure 2. For absorbers with a large bandgap, particle conservation may still be a justifiable assumption, provided that $E_G \gg kT_H$.

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