Optoelectronic reciprocity in hot carrier solar cells with ideal energy selective contacts

Andreas Pusch | Milos Dubajic | Michael P. Nielsen | Gavin J. Conibeer | Stephen P. Bremner | Nicholas J. Ekins-Daukes

School of Photovoltaic & Renewable Engineering, UNSW Sydney, Kensington, New South Wales, 2052, Australia

Correspondence
Andreas Pusch, School of Photovoltaic & Renewable Engineering, UNSW Sydney, Kensington, NSW 2052, Australia.
Email: a.pusch@unsw.edu.au

Abstract
Hot carrier solar cells promise theoretical power conversion efficiencies far beyond the single junction limit. However, practical implementations of hot carrier solar cells have lagged far behind those theoretical predictions. Reciprocity relations for electroluminescence from conventional single junction solar cells have been extremely helpful in driving their efficiency ever closer to the theoretical limits. In this work, we discuss how the signatures of a functioning hot carrier device should manifest experimentally when driven in reverse, that is, in electroluminescent mode. Hot carrier properties lead to deviations of the dark I–V from the Shockley diode equation that is typical for conventional single junction solar cells. These deviations are directly linked to an increase in temperature of the carriers and therefore the temperature measured from electroluminescence spectra. We also elucidate how the behaviour of hot carrier solar cells in the dark depends on whether Auger processes play a significant role, revealing a stark contrast between the regime of negligible Auger recombination (carrier conservation model) and dominant Auger recombination (impact ionisation model) for hot carrier solar cells.

KEYWORDS
dark I–V, energy selective contacts, hot carrier solar cells, optoelectronic reciprocity

1 | INTRODUCTION

One of the major limitations for the efficiency with which photovoltaic cells convert sunlight into electricity is the thermalisation of electronic carriers with the crystal lattice of the solar absorber material. Photons with energy higher than the band gap of the absorbing semiconductor lose their excess energy to this thermalisation. It was recognised several decades ago that a solar energy converter in which electrons do not thermalise with the lattice could be coupled with an electronic heat engine that has a conversion efficiency limited by the Carnot efficiency corresponding to the temperature differential between the carriers and the lattice. The solar conversion efficiency of such a device could potentially reach $\approx 85\%$ at full concentration of sunlight if contacts with vanishing energetic bandwidth, but nonetheless high conductivity, could be achieved. Extensive experimental evidence dating back several decades exists, which demonstrates a transient difference between the electronic carrier temperature and the lattice temperature typically lasting a few picoseconds. Several of these early spectroscopic results have been repeated in the context of photovoltaic hot carrier devices using III–V semiconductors and later in various semiconductor nanostructures. InN has unusual vibronic properties that has resulted in transient temperature differences seen over a timespan of a few hundred picoseconds. Graphene photodetectors have been demonstrated whose photoresponse is dominated by hot electron transport and the cooling dynamics of hot carriers in graphene can be tuned by doping and by applying gate voltages. Recently, many different perovskite materials have been investigated for hot carrier properties. Cooling of hot carriers, on the order of tens of picoseconds, was observed with pump-probe experiments and...
attributed to the formation of polarons,\textsuperscript{15} which, while protecting carriers from fast relaxation, also inhibit the energy redistribution between carriers that is crucial for efficient hot carrier solar cells.\textsuperscript{15,16} Theoretical models have been proposed to describe experimental observations by simulating the coupled electron phonon system after photo-excitation stimuli\textsuperscript{17} and consequent transport of excited particles.\textsuperscript{18} Although hot carrier extraction has been experimentally demonstrated in III–V devices,\textsuperscript{19–21} the obtained efficiencies are still far away from improving upon single junction solar cells.

The concept of optoelectronic reciprocity that arises as a consequence of microscopic reversibility and detailed balance has been used in single junction solar cells to infer device properties from electroluminescence measurements, where the device is driven electrically instead of excited with light. It is usually written as\textsuperscript{22}

\[
\phi_{em}(E, V) = EQE(E)\phi_{bh}(E)\left(\frac{e^{\frac{eV}{kT}}}{1 - e^{\frac{eV}{kT}}} - 1\right),
\]

with the photon flux \(\phi_{em}\) dependent on the photon energy \(E\), and the applied voltage \(V\), according to the external quantum efficiency (EQE) of the device, the blackbody spectrum \(\phi_{bh}\) and the temperature of the device \(T\). This formulation is valid for single junction solar cells, unless either the absorptivity or the current collection efficiency—that together determine the external quantum efficiency—change with applied voltage.\textsuperscript{23}

In a hot carrier solar cell, reciprocity should take a different form because the current can be driven by both temperature and electrochemical potential differentials, making a hot carrier solar cell a hybrid between a photovoltaic and thermoelectric device. For thermo-electrics, reciprocity is encapsulated in the direct relation to the Peltier and Seebeck coefficients, which describe the heat carried by an electric current and the electric field generated by a temperature difference, respectively.\textsuperscript{24} This reciprocity is a direct consequence of the Onsager reciprocal relations.\textsuperscript{25}

Electronic heat engines that are driven backwards act as electronic heat pumps, so we expect the electrical power supplied in reverse operation to heat the electrons in the absorber by pumping heat from the contacts into the absorber region. To elucidate how optoelectronic reciprocity might manifest in hot carrier solar cells, we examine their properties when electronically driven under dark conditions. Dark I–V and electroluminescence are powerful tools for the analysis of any solar cell architecture, yet the properties of hot carrier solar cells in the dark have not been discussed. Here, we build a conceptual model for the I–V characteristics of a hot carrier cell with ideal energy selective contacts. Special regimes in the I–V curve depend on the importance of Auger processes in the description of the hot carrier solar cell but are always associated with an increase in carrier temperature that can be detected as a change in spectral shape of the electroluminescence.

There are two competing models for the hot carrier absorber that consider two extremes regarding the importance of Auger recombination events. Historically, the first is the carrier conservation model, developed by Ross and Nozik, that excludes Auger recombination and impact ionisation processes and allows for a quasi-Fermi level separation (QFLS) in the absorber,\textsuperscript{3} and second is the impact ionisation model, developed by Würfel, that assumes a thermal hot carrier distribution,\textsuperscript{4} that is, no QFLS, corresponding to infinitely fast Auger processes. Note that the carrier conservation model is a better model for hot carrier absorbers with large band gaps, whereas the impact ionisation model is more suitable for low band gap absorbers.\textsuperscript{26,27} We discuss reverse operation of devices described by both of these models. Section 3 concentrates on the impact ionisation model, whereas Section 4 discusses the carrier conservation model.

In order to obtain general trends, we concentrate on a model that can be solved numerically without extensive computational resources. This means that we consider ideal energy selective contacts and electron and hole distributions that are internally fully thermalised. This leads to peculiar consequences in the carrier conservation model, which may partially persist in some operating regimes of actual devices. In a real device, neither of these conditions will be perfectly fulfilled, but the closer a device can approach these limits, the higher its efficiency will be.\textsuperscript{28}

## 2 | General Model

### 2.1 | Ideal energy selective contacts

The goal for hot carrier solar cell contacts is to convert a temperature differential \(\Delta T\) between the carriers in the absorber and the carriers in the contacts to an electrochemical potential difference, or voltage \(V\), between the carriers in the two contacts. In general, a current density \(I\) can be driven by electrochemical potential gradients and/or by temperature gradients\textsuperscript{24}

\[
I = \int_0^\infty g(E)\nu(E)\tau_e \frac{\partial f_0(E)}{\partial E} \left(\frac{\partial \mu}{\partial \chi} + \frac{E - \mu + \mu T}{T} \frac{\partial \chi}{\partial E}\right) dE.
\]

Here, \(g\) denotes the density of electronic states, \(\nu\) is the group velocity of electrons, \(\tau_e\) is their relaxation time and \(f_0\) is the Fermi–Dirac distribution, which depends on the spatially varying electrochemical potential \(\mu\) and temperature \(T\).

To illustrate the transport equation, we can first consider a contact, consisting of a thin semiconductor layer between two metal layers, that only allows carrier transport above a barrier energy, that is, a Schottky or thermionic barrier. Figure 1A depicts how a separation in electrochemical potentials generates a current across the barrier because of the presence of more carriers in the states above the barrier for the carrier population with a higher chemical potential.

A temperature differential also leads to an imbalance in carrier occupations above the barrier (see Figure 1B) and a resulting flow of electrons. This flow of electrons due to a temperature gradient can be compensated by an electrochemical potential gradient that acts in the opposite direction and an I–V curve with positive electrical power production is traced out. In open circuit, the currents balance (see Figure 1C).
Note that, under open circuit conditions, the net charge current will be zero across such a barrier, but a net energy flow persists as more low energy electrons flow from the higher electrochemical potential to the lower electrochemical potential while more high energy electrons flow from the high temperature region to the low temperature region. This will lead to a reduction in efficiency of the electronic heat engine, which is well known in the context of thermoelectrics. The dimensionless figure of merit $zT$ for a thermoelectric depends on the ratio of heat flows between short circuit and open circuit condition as $zT = Q_{sc}/Q_{oc} - 1$. In a thermoelectric, electronic conduction competes with heat conduction through the lattice, so that there is inevitably a large contribution to the heat flow that is independent of the electrochemical potential and dominates thermal conductivity at open circuit. Therefore, one of the main design criteria for a thermoelectric is to increase the electronic conductivity compared with the thermal conductivity of the lattice. In an ideal hot carrier solar cell, the heated carrier system in the absorber is insulated from the lattice of the absorber, so reducing the open circuit heat flow associated with electronic conduction while reducing the overall conductivity by limiting current to a small energy window can be a viable strategy to increase the efficiency of conversion of the heat gradient to electrical work.

Indeed, an optimal, isentropic conversion of a temperature differential into an electrochemical potential difference, that is, a voltage, can be achieved if conduction is only possible in an infinitely narrow energy window, as illustrated in Figure 1D.

The net current of the infinitely narrow contacts vanishes when

$$\mu_{c1} - \mu_{Ae} = Ec_1 - EC_1 - TC_1/TH_1,$$

which can be rewritten in terms of the voltage $V_{balanced} = \mu_{c1} - \mu_{c2}$ that balances carrier transport as

$$V_{balanced} = \Delta \mu H \frac{T_C}{TH} + Ec_1 - EC_1 - TC_1/TH_1,$$

with the QFLS in the absorber $\Delta \mu H = \mu_{Ae} - \mu_{Ah}$ and $E_c = Ec_1 - Ec_2$. $V_{balanced}$ represents the voltage for isentropic, reversible extraction at the Carnot efficiency, visualised in Figure 2. The $\mu_{ci}$ are the electrochemical potentials of electrons in contact $i$ and $\mu_{Ae}/h$ are the electrochemical potential of electrons and holes in the hot absorber with temperature $TH$, whereas the $Ec_i$ are the energies for the contact $i$ (illustrated in Figure 2).

Note that, for simplicity, we assume here that the temperatures of electrons and holes are equal, which implies either equal density of states or strong electron–hole interactions.

It should be noted that Equation (4) and any equivalent equation, implicitly assumes an ideal energy selective contact and therefore, Carnot efficient conversion of temperature differentials to voltage. Moving to a more realistic partially energy selective contact, a thermionic barrier scheme or extracting from a side valley introduces additional heat flows that complicate analysis and require a new formalism. The use of equations that are valid only for ideal contacts can lead to misleading conclusions when applied to nonideal contacts.
If the contact conductivity $\sigma$ tends towards infinity, representing a delta-function contact, a finite current can be sustained at $V = V_{\text{balanced}}$. Such an infinitely narrow contact with infinite conductivity is termed an ideal energy selective contact. In the language of thermoelectrics, the figure of merit $zT$ of this ideal contact, combined with no heat exchange with the lattice, is infinite as there is no heat conduction at open circuit. In a thermoelectric device, the competition between heat conduction by the lattice with electronic conduction limits $zT$ to finite values even for such an ideal contact.

A real device will require a finite energetic window of conduction as an infinitely narrow window has zero conductivity. The current density for a window of finite energetic width $\Delta E$ can be written as

$$
I = \int_{E_{c1}}^{E_{c2}+\Delta E} \alpha(E) \left( \frac{1}{e^{\frac{E-E_{c1}}{kT}}+1} - \frac{1}{e^{\frac{E-E_{c2}}{kT}}+1} \right) dE,
$$

with the energy-dependent conductivity $\sigma(E) = q\nu(E)g(E)c$, that is, proportional to the number of conductive channels at a particular energy.

A finite energy width of the contact leads to an exchange of heat between absorber and contact also at open circuit as electrons with lower energies will flow predominantly from contact to absorber, whereas electrons with higher energies flow predominantly from absorber to contact (compare Figure 1C). Narrowing the bandwidth reduces the conductivity as fewer states are available for conduction, so that a compromise has to be found between conductivity and energy width. Practically, attempts at approaching such a contact have been made with resonant tunneling structures.

### 2.2 Energy balance

The energy flux balance equation in a hot carrier solar cell with ideal energy selective contacts is given by

$$
\frac{1}{q} \dot{E}_c = \dot{E}_{\text{em}} - \dot{E}_{\text{abs}} + \dot{Q}_1.
$$

It should be noted that the term on the left hand side describes the energy flow associated with electronic transport across the contact. Each electron–hole pair either injected into (extracted from) the absorber, deposits in (removes from) the absorber an energy $E_c$.

The emitted energy flux is given by

$$
\dot{E}_{\text{em}} = \frac{2\pi}{h^2c^2} \int_0^\infty \left( \frac{\alpha_{\text{abs}}(E)E^2}{e^{\frac{E}{kT}}-1} + \frac{\alpha_{\text{em}}(E)E^2}{e^{\frac{E}{kT}}-1} \right) dE,
$$

where we allow for a non-zero QFLS $\Delta \mu_H$ in the absorber and distinguish between band-to-band absorption—which is influenced by the QFLS—and free carrier absorption. $\alpha_{\text{em}}$ depends implicitly on the carrier density, but the emission does not scale with the QFLS between electrons and holes as it occurs between carriers in the same band.

The absorbed energy flux is given by

$$
\dot{E}_{\text{abs}} = \frac{2\pi}{h^2c^2} \int_0^\infty \alpha(E)E^2 \left( \frac{f}{e^{\frac{E}{kT}}-1} + \frac{1-f}{e^{\frac{-E}{kT}}-1} \right) dE,
$$

with $f$ indicating the fraction of the emission cone of the hot carrier absorber that is taken up by the sun. Dark operation corresponds to $f = 0$, whereas $f = 1$ indicates full concentration and $f = 1/46.260$ corresponds to 1 Sun illumination.
The carrier cooling term \( \dot{Q}_c \) in Equation (4) accounts explicitly for the interaction between electrons and the lattice in the absorber and is discussed in detail in Section 2.4.

In order to understand the energy flux associated with electronic transport, we can separate it into two fundamentally different contributions. One is the free energy that an electron has to acquire to move from the hole contact with Fermi level \( \mu_{\text{c}} \) to the electron contact with Fermi level \( \mu_{\text{e}} \) (see Figure 2), which is equal to the applied bias \( \phi \). In the dark, this free energy flux corresponds to the supplied electrical power density \( P_d = IV \).

The other contribution to the electronic energy flux consists of a heat flux and can be quantified as \( Q_d = (E_v - q\phi)/q \). Because the Fermi level in the electron contact is lower than the contact energy, the electrons injected from the electron contact in the absorber have a higher than average energy, leaving behind a less energetic, or cooled, electron distribution, which is efficiently reheated by the lattice in the contact material (assumed to have strong electron phonon interactions). Therefore, we can assume that the Fermi–Dirac distribution of electrons in the contacts is maintained at the contact temperature. The removal of heat from the contacts leads to an entropy flux out of the contacts of

\[
\dot{S}_c = \dot{Q}_d/T_c. \tag{9}
\]

Under forward bias in the dark, the electronic system in the hot carrier absorber receives the energy flux \( E_v I/q \). This energy flux can again be divided into the free energy flux of each electron–hole pair given by the QFLS \( F_{\text{q}} = \Delta\mu_{\text{h}} I/q \) and a heat flux contribution \( Q_d = (E_v - \Delta\mu_{\text{h}})/q \). The condition for isentropic particle exchange, in which the entropy removed from the contact along with the current is equal to the entropy flux in the absorber generated by the current

\[
\dot{S}_h = Q_d/T_h. \tag{10}
\]
is given by

\[
T_h = T_c \frac{E_v - \Delta\mu_{\text{h}}}{E_v - q\phi}. \tag{11}
\]

Note that this is a rearrangement of Equation (4) for the voltage at which carrier exchange is balanced, proving the isentropic and reversible nature of an ideal energy selective contact.

Thus, although a hot carrier solar cell under illumination contains an electronic particle exchange heat engine\(^{42}\) that converts the temperature difference between carriers in the contacts and in the absorber into electrical power, the same device when driven in the dark functions as an electronic heat pump that uses applied electrical power to heat the electronic system in the absorber.

The presence of a positive QFLS \( \Delta\mu_{\text{h}} \) indicates that some of the power of the heat pump is converted to a positive free energy associated with each electron–hole pair, reducing the temperature that can be achieved. A negative QFLS on the other hand indicates that the creation of an electron–hole pair in the absorber is associated with a decrease in the free energy of the absorber. This increases the carrier temperature that can be achieved with a particular applied bias. In the carrier conservation model, we will encounter both of these behaviours, depending on the operation regime.

In steady state, the hot carrier absorber then emits this heat either as radiation, that is, electroluminescence, or it dissipates the heat to the lattice, where it ultimately diffuses back to the contacts and any substrate that may exist. Note that this model can recover the behaviour of an ideal, conventional light emitting diode if carrier cooling is infinitely fast. Then, the steady state absorber temperature \( T_h \) is fixed to \( T_c \), and the QFLS \( \Delta\mu_{\text{h}} \) is equal to the applied bias.

The conventional light emitting diode can be used as a refrigerator.\(^{43,44}\) Using a hot carrier solar cell as a refrigerator faces the issue of the reverse heat flux \( \dot{Q}_c \) associated with carrier cooling as a major hurdle.

### 2.3 Numerical evaluation

In order to obtain \( I-V \) curves, we need to solve Equation (6) for the current density as function of applied bias. We assume sharp band edges with absorptivity \( \alpha = 0 \) for photon energies below the band gap \( E_g \) and \( \alpha = 1 \) for photon energies above \( E_p \). Without a QFLS (\( \Delta\mu_{\text{h}} = 0 \)), the current density can be calculated directly by inserting Equation (11) into the terms in Equation (6). This is how the results in the section on the impact ionisation model (Section 3) are obtained.

To obtain results for the carrier conservation model (Section 4), we have to introduce a second equation that allows us to fix both \( \Delta\mu_{\text{h}} \) and \( T_h \) as a function of applied bias \( V \) simultaneously. This equation is obtained by assuming that the number of carriers in the absorber can only change due to either absorption and emission processes or via the current flowing through the contacts. This results in the carrier balance equation

\[
I(V) = q(\phi_{\text{em}}(V) - \phi_{\text{abs}}). \tag{12}
\]

where

\[
\phi_{\text{em}}(V) = \frac{2\pi}{\hbar c^2} \int_{E_{\text{em}}}^{\infty} a_{\text{em}}(E) \frac{E^2}{e^{E/\phi_{\text{em}}(V)} - 1} dE, \tag{13}
\]

and

\[
\phi_{\text{abs}} = \frac{2\pi}{\hbar c^2} \int_{0}^{E_p} a_{\text{abs}}(E) \frac{f}{e^{E/\phi_{\text{abs}}(V)} - 1} \frac{1 - f}{e^{E/\phi_{\text{abs}}(V)} - 1} dE. \tag{14}
\]

Free carrier absorption does not influence the number of generated carriers and can be excluded from the carrier balance equations.

For the evaluation of the carrier conservation model, we neglect the free carrier contribution to Equation (7) and assume that the absorptivity originates only from band to band transitions. We also make the Boltzmann approximation to the emitted energy and photon flux, which is justified as long as the difference between band gap and
QFLS in the absorber is much larger than the absorber temperature, that is, \( E_g - \Delta \mu_H > T_H \). The photon flux in Boltzmann approximation reads

\[
\phi_{em} = \frac{2\pi}{h^2 c^2} e^{\frac{E_{em}}{kT}} kT \phi H (E_g^2 + 2kT_e E_g + 2(kT_H)^2),
\]

with the mean energy per emitted photon given by

\[
\langle E_{em} \rangle = \frac{E_g^2 + 3kT_e E_g + 6(kT_H)^2}{E_g^2 + 2kT_e E_g + 2(kT_H)^2}.
\]

By setting \( f = 0 \), we can calculate the dark I–V for hot carrier cells with carrier conservation by considering only the absorption of photons from the thermal photon bath of the ambient.

### 2.4 Carrier cooling

In order to consider carrier cooling, we need to estimate the dependence of the heat transfer rate from carrier system to lattice on the temperature and chemical potential of the hot carrier absorber. This dependence is material-dependent, but we here build a model that fulfills sensible minimal conditions. The heat transfer rate from the carrier population to the lattice \( Q_l \) should increase when the total number of carriers increases because the heat capacity also increases with the total number of carriers. Therefore, it should scale with the intrinsic carrier concentration at the given temperature as well as with the QFLS \( \Delta \mu_H \) in the absorber. Assuming an undoped, charge neutral absorber, the ratio between intrinsic population of electrons/holes and the actual populations of electrons/holes is given by \( \exp(-\Delta \mu_H/(2kT_H)) \), dividing the impact of the QFLS equally between electron and hole populations.

The heat transfer rate to the lattice should also increase for higher temperatures in the absorber. The simplest model that fulfills these criteria is given by

\[
Q_l = k \Phi E_{g} / (2kT_H) \Phi \Delta \mu_H / (2kT_H) (T_H - T_C),
\]

with a proportionality constant \( k \). This is a carrier-density-dependent heat equation. \( k \) incorporates the density of states at the band gap but not the carrier concentration due to temperature, band gap and QFLS, whose influence is captured separately in the two exponential factors in Equation (17). In the limit of vanishing band gap, we obtain \( Q_l(T_H) = k(T_H - T_C)^2 \) that is, Fourier’s heat conduction equation.

Note that, if heating is slowed because of hot phonon effects, the heat transfer rate will saturate for high carrier densities, which is not included in our simplified cooling model.

To illustrate the impact of carrier cooling on the HCSC, we show in Figure 3 A few example light I–V curves and voltage-dependent efficiencies, calculated for a black body absorber \( E_g = 0 \).

We assume a concentration factor of 1,000, corresponding to a realistically achievable solar concentration. A carrier cooling rate of 0 W/(K m²) already precludes efficient operation and a rate of 5 x 10⁻⁴ W/(K m²) leads to nearly vanishing efficiencies, even in this idealised model.

### 3 IMPACT IONISATION MODEL

In the impact ionisation model of hot carrier solar cells, illustrated in Figure 2A, a total thermal equilibrium within the hot carrier population in the absorber is assumed. This requires that energy redistribution by electron–hole scattering (i.e., Auger recombination and impact ionisation processes) occurs faster than energy is deposited in the system by photo-generation process of electrons and holes and extracted through the energetically narrow contact.

The main determinant of the timescale of Auger recombination and impact ionisation compared with the timescale of electron–electron and hole–hole scattering is the size of the band gap compared with the temperature of carriers. Auger recombination requires the presence of two electrons and one hole or two holes and one electron. Thus, the likelihood of the process depends exponentially on
the ratio between band gap and temperature. Impact ionisation on the other hand requires a carrier with excess energy at least as large as the band gap, which again depends exponentially on the ratio between band gap and temperature.

Therefore, in the absence of a band gap, that is, in metallic absorbers, no two distinct populations of carriers exist and the Impact Ionisation model applies. This model should also approximate a semiconductor where the band gap of the material is on the same order of magnitude or less as the thermal energy of the hot carriers.

In the absence of a quasi-Fermi level separation in the hot carrier system, Equation (11) fixes the temperature as a function of applied voltage at ideal energy selective contacts

$$T_H(V) = \frac{T_c}{1 - \frac{E_c}{E_g}}.$$  \hspace{1cm} (18)

Because the emission from the thermally equilibrated hot carrier system is determined by temperature and absorptivity of the hot carriers, this also means that the electroluminescence properties ($\phi_{em}$ and $E_{em}$) as function of voltage are independent of carrier cooling. The impact ionisation model describes a thermal emitter, and only the energy balance, not the carrier balance, is important.

The temperature of the carriers is fixed by the applied voltage according to Equation (18). Thus, carrier cooling does not reduce the temperature of the carriers in the presence of ideal energy selective contacts. What then is its impact on the characteristics of the hot carrier solar cell in the dark?

Dark I–V curves, assuming a perfect black body absorber, are shown in Figure 4A for different values of the cooling rate $\kappa$.

Because carrier cooling reduces the energy that is available to the hot carriers, the current that is required to maintain the temperature in the carrier system and the electroluminescence, dictated by the voltage applied at the contacts, increases with increasing cooling rate. This is analogous to the reciprocity relation in single junction solar cells where the voltage determines the electroluminescence intensity, but the current at a given voltage is also inversely proportional to the external luminescence extraction efficiency of the device. A substantial, intermediate, exponential regime is found for large cooling rates but eventually the rise in current with voltage is super-exponential, corresponding to a rapid rise in temperature with the applied voltage.

The presence of a band gap reduces the overall emission rate and it also reduces the impact of thermal radiation from the environment on the I–V curve, leading to an exponential regime for low voltages (see Figure 4B) that also turns into a super-exponential regime for large voltages. The impact of carrier cooling on the I–V curve is similar to the case without band gap, yet the value of $\kappa$ at which an appreciable impact of cooling on the I–V curve is observed, is much higher when a band gap is present. This is due to the exponential dependence of the carrier density on the ratio between band gap and temperature. At small applied voltages, which translate into small absorber temperatures, carrier densities and therefore heat transfer rates, are reduced by orders of magnitude compared with the case without band gap.

![FIGURE 4](https://example.com/fig4) Logarithmic dark I–V characteristics of (A) a black body ($E_g = 0$) hot carrier solar cell calculated with the impact ionisation model, assuming ideal energy selective contacts and with different cooling rates $\kappa$, and (B) a hot carrier solar cell with band gap of $E_g = 0.5$ eV with different cooling rates. The voltage is normalised by the energy difference $E_c = 1$ eV between the two contacts. In the dark, the electronic power flow is always directed into the absorber for positive and negative bias [Colour figure can be viewed at wileyonlinelibrary.com]

Note that in both, single junction and hot carrier, cases (depicted in Figure 4), the interpretation of the I–V curve is complicated by the presence of a finite series resistance $R_s$, which we have not included in our calculation because we assume an ideal contact. In the presence of series resistance, the same current requires a larger voltage drop across the device, and therefore, series resistance reduces the emission from the active region (in single junction solar cells) or the temperature of the hot carriers (in hot carrier solar cells) for a given applied bias.

Unlike the dark I–V curve of a conventional solar cell, the I–V curve of a hot carrier solar cell without a band gap (Figure 4A) shows only a small exponential regime.

4 | CARRIER NUMBER
CONSERVATION MODEL

In the carrier conservation model for a hot carrier solar cell that was developed by Ross and Nozik, it was assumed that each absorbed photon would lead to exactly one conduction electron. Conservation of the number of excited carriers in a semiconductor is an overconstraint and can be broken by, in principle avoidable,
nonradiative recombination through defect states as well as unavoidable Auger recombination and impact ionisation. Unlike defects, Auger recombination and impact ionisation are inevitable, but their importance decreases exponentially with the ratio between the energy separation between quasi-Fermi levels and band edges and the temperature of the carriers, that is, exponentially with \((E - \Delta\mu_H)/(kT_H)\).

To fulfil excited carrier number conservation and energy conservation simultaneously, a second degree of freedom in the Fermi–Dirac distribution of the carrier population is required. Quasi-thermal equilibrium established within a population of electrons and a population of holes can be described by a quasi-Fermi level separation.\(^{45}\) Thus, it is a natural choice to allow for a quasi-Fermi level separation between electrons and holes in the absorber for hot carrier solar cells as well.

Allowing for a quasi-Fermi level separation, \(\Delta\mu_H\) complicates the relationship between applied voltage and temperature in the absorber as \(\Delta\mu_H\) constitutes another independent variable \((4)\). It has been shown that this carrier number conservation model, in combination with ideal energy selective contacts, leads to unphysical predictions.\(^{27}\) In fact, finite macroscopic differences in temperature and quasi-Fermi level separation result from infinitesimal changes in contact energy, when the contact energy crosses the mean energy of the absorbed photons. This can be seen by inserting the equation for carrier number conservation

\[
I = q(\phi_{abs} - \phi_{em}),
\]

into the equation for energy conservation

\[
\frac{I}{q}E_c = \dot{E}_{abs} - \dot{E}_{em},
\]

leading to

\[
\frac{\phi_{em}}{\phi_{abs}} = \frac{(E_{abs})}{(E_{em})} = \frac{E_c}{\mu_H - \mu_c - \frac{kT_c}{q}V}.
\]

Equation (21) forces the temperature of the absorber to be higher than the mean temperature of the absorbed radiation when the mean energy of the absorbed photons \((E_{abs}) = E_{abs}/\phi_{abs} > E_c\) and smaller when \((E_{abs}) < E_c\), creating a sharp cross-over point in absorber properties. However, allowing for the inevitable presence of a small Auger interaction rate and a finite band width of the contact in real devices without compromising the essence of the model\(^{26}\) mitigates this conceptual problem.

It also implies that \(\phi_{em}\) cannot be chosen to be arbitrarily small for any given combination of illumination conditions and contact energy. As a consequence, the short circuit current obtained with this model may be substantially smaller than the absorbed photon flux.

Assuming ideal energy selective contacts, the quasi-Fermi level separation \(\Delta\mu_H\) in the absorber is a function of absorber temperature \(T_H\), contact energy \(E_c\), and applied voltage

\[
\Delta\mu_H = E_c - \frac{T_H}{T_c}(E_c - qV).
\]

The product \(np\) of the densities of electrons in the conduction band and holes in the valence band is proportional to \(e^{\Delta\mu_H/(kT_H)}\). An unusual, yet not unphysical prediction, of the carrier number conservation model is the presence of temperatures in the absorber that are higher than the illumination temperature if the contact energy is smaller than the average energy of the absorbed photons. This higher temperature is compensated for by a negative QFLS \(\Delta\mu_H\) (see Figure 2C). A negative QFLS leads to an exponential decrease in the \(np\) product and accordingly an exponential decrease in the emitted luminescence. This phenomenon is called negative luminescence, that is, less intense luminescence than expected for a thermal source with the same temperature and emissivity, and has been reported in various semiconducting materials under reverse bias.\(^{46,47}\) This way, the emitted photon flux will be lower than the incoming photon flux, despite the higher temperature in the absorber.

The possibility of negative luminescence in hot carrier solar cells is related to the possibility of spontaneous negative luminescence and energy harvesting in reverse bias using a diode exposed to a cold environment, which also requires carrier number conservation. This so-called thermoradiative diode\(^{48,49}\) is possible because it rejects proportionally more entropy than energy from the converter and the ultimate efficiency of the process is limited only by the Carnot efficiency.\(^{50}\) In contrast to the thermoradiative diode, however, the negative QFLS in the absorber region of a hot carrier solar cell with carrier number conservation is present despite a forward bias applied at the contacts. The temperature differential between contacts and absorber allows for a turn-over of negative QFLS to positive bias.

\[\text{Δμ}_H = E_c - \frac{T_H}{T_c}(E_c - qV).\] (22)

### 4.1 Results without carrier cooling

We first examine the carrier conservation model in the absence of carrier cooling \((κ = 0)\). The ideal dark I–V curves, shown in Figure 5 for
the example of a band gap of 1 eV and contact energies $E_c = 1.2, 1.4$ and $1.6$ eV, exhibit an exponential increase over a wide range of biases, but diverge strongly from it at low bias.

To understand this behaviour, we need to look at the temperature and QFLS in the absorber as a function of bias, shown in Figure 6.

The carrier temperature of the absorber initially rises with bias and is then constant across a large bias regime in which absorption from the environment can be neglected compared with emission from the cell. This is also the regime of the exponential behaviour in the I–V curve. In this regime, the QFLS in the absorber changes at a rate proportional to the change in applied bias, that is,

$$\Delta \mu_H(V_1) - \Delta \mu_H(V_2) = \frac{T_H}{T_c}(qV_1 - qV_2).$$

Increasing contact energy increases the carrier temperature in the exponential regime but leads to a delayed rise of carrier temperature with bias.

In the regime in which carrier temperature rises with bias, we observe a decrease in the QFLS between electrons and holes to negative values. Thus, negative luminescence is predicted in this regime; the temperature difference between absorber and contacts is compensated by a negative QFLS. The onset of this regime and also the absolute value of the QFLS reached depend on the contact energy. The QFLS decreases more slowly from zero for higher contact energies but decreases to a deeper minimum.

The Boltzmann approximation begins to break down at voltages near the contact energy $E_c$ and a breakdown of the Boltzmann approximation results in a deviation from the exponential behaviour. Note, however, that the breakdown of the Boltzmann approximation is accompanied by substantial carrier populations in both the valence and conduction bands of the absorber. The assumption of negligible Auger recombination is only valid for small carrier populations, so when the Boltzmann approximation breaks down, the carrier conservation model also breaks down.

### 4.2 Impact of carrier cooling

Now, we consider the impact of carrier cooling on the dark I–V and electroluminescence properties. Figure 7 shows I–V characteristics for a hot carrier solar cell with a band gap of $E_g = 1$ eV, ideal selective contacts with $E_c = 1.4$ eV and several different cooling rates.

The presence of carrier cooling leads to an exponential regime for small biases, a cross-over regime where the dark I–V deviates from exponential behaviour, and then again a region of exponential behaviour. For larger cooling rates, the cross-over regime is shifted towards ever larger bias, so that the dark I–V approximates the behaviour seen from an ideal light emitting diode/solar cell over an ever increasing regime. The hot carrier solar cell of the carrier conservation model in the limit of large cooling rates thus behaves exactly as a single junction diode in the Shockley Queisser model, that is, with infinite conductivity and no nonradiative recombination. That carriers are injected at an energy $E_c$ instead of the band gap energy $E_g$ does not change the radiative saturation current, if the carriers efficiently cool to the lattice temperature.

To understand the origin of the cross-over better, we need to again examine the behaviour of temperature and QFLS in the absorber (see Figure 8).
In the cross-over regime, the temperature of the carriers in the absorber increases until it, surprisingly, reaches the same maximal value as in the absence of cooling. This cross-over regime manifests in a change of spectral shape of the electroluminescence due to the increased carrier temperature. The voltage at which this cross-over occurs is related to the cooling rate of the carriers. The QFLS simultaneously decreases, and once the temperature saturates, it increases linearly with applied bias, leading to the second regime of exponential behaviour.

The total energy flux radiatively emitted by the device can be calculated from the temperature and electrochemical potential distribution and is shown in Figure 9.

In the cross-over regime, the temperature of the carriers in the absorber increases until it, surprisingly, reaches the same maximal value as in the absence of cooling. This cross-over regime manifests in a change of spectral shape of the electroluminescence due to the increased carrier temperature. The voltage at which this cross-over occurs is related to the cooling rate of the carriers. The QFLS simultaneously decreases, and once the temperature saturates, it increases linearly with applied bias, leading to the second regime of exponential behaviour.

The total energy flux radiatively emitted by the device can be calculated from the temperature and electrochemical potential distribution and is shown in Figure 9.

Interestingly, the device without cooling shows the lowest radiative energy flux at low bias, which is due to the large negative bias in the absorber region. The emission rate only starts to increase when the temperature has saturated. This is because of the strict constraints in the carrier conservation model in which the total net emitted energy has to equal the net energy supplied by the current and the net photon flux also has to be the same as the current density. These strict requirements are lifted by the presence of cooling, which provides another mechanism to balance energy and particle flows. Consequently, strong net emission is possible at any temperature, not only the temperature that equalises the mean emitted photon energy with the contact energy.

In this work, we presented the dark I–V and electroluminescence of hot carrier solar cells with ideal energy selective contacts as tools for understanding and characterising hot carrier device properties. Hot carrier solar cells are electronic heat engines in conjunction with a hot carrier absorber and when operated in reverse, the electronic heat engine acts as an electronic heat pump instead, heating the carriers in the absorber that subsequently emit radiation and heat the lattice.

Low band gap absorbers with dominant Auger processes and ideally energy selective contacts show only a small exponential regime, and the carrier temperature is determined by the ratio between applied voltage and contact energy. Heat transfer to the lattice manifests as increase in current density, whereas the voltage dependence of the electroluminescence properties is unaffected by the cooling rate.

Large band gap absorbers, for which Auger processes are slow, do show an exponential regime. We underline that the prediction of a negative QFLS in the absorber, which arises from the carrier conservation model with energy selective contacts, is not unphysical and results in negative luminescence. In hot carrier absorbers with large band gap, the exact features of the deviations from the exponential regime depend on the heat transfer rate, allowing for the measurement of these rates from the dark I–V. The carrier temperature is bias, contact energy, and heat transfer dependent but saturates at high bias and eventually becomes independent of heat transfer.

A finite Auger recombination and impact ionisation rate, which interpolates between the two extreme models discussed in the paper, leads to a decrease in the absolute value of the QFLS compared with the prediction without Auger processes. This pushes the electronic system closer to an equilibrium between electrons and holes. Auger processes also lead to a decrease in carrier temperature for the negative luminescence regime, because impact ionisation, which reduces the kinetic energy of the carriers, dominates in that regime. Conversely, an increase in carrier temperature is expected in the positive regime.

### Figure 8
(A) Temperature and (B) quasi-Fermi level separation (QFLS) in the absorber in the dark as a function of applied bias at the contacts, calculated with the carrier conservation model for different cooling rates $\kappa$, an absorber band gap of $E_g = 1$ eV and a contact energy of $E_c = 1.4$. [Colour figure can be viewed at wileyonlinelibrary.com]

### Figure 9
Total energy flux radiatively emitted from the hot carrier device (on logarithmic scale) as a function of applied bias in the dark for different cooling rates $\kappa$. The dashed line indicates the energy absorbed from the ambient. [Colour figure can be viewed at wileyonlinelibrary.com]

5 | CONCLUSIONS

In this work, we presented the dark I–V and electroluminescence of hot carrier solar cells with ideal energy selective contacts as tools for understanding and characterising hot carrier device properties. Hot carrier solar cells are electronic heat engines in conjunction with a hot carrier absorber and when operated in reverse, the electronic heat engine acts as an electronic heat pump instead, heating the carriers in the absorber that subsequently emit radiation and heat the lattice.

Low band gap absorbers with dominant Auger processes and ideally energy selective contacts show only a small exponential regime, and the carrier temperature is determined by the ratio between applied voltage and contact energy. Heat transfer to the lattice manifests as increase in current density, whereas the voltage dependence of the electroluminescence properties is unaffected by the cooling rate.

Large band gap absorbers, for which Auger processes are slow, do show an exponential regime. We underline that the prediction of a negative QFLS in the absorber, which arises from the carrier conservation model with energy selective contacts, is not unphysical and results in negative luminescence. In hot carrier absorbers with large band gap, the exact features of the deviations from the exponential regime depend on the heat transfer rate, allowing for the measurement of these rates from the dark I–V. The carrier temperature is bias, contact energy, and heat transfer dependent but saturates at high bias and eventually becomes independent of heat transfer.

A finite Auger recombination and impact ionisation rate, which interpolates between the two extreme models discussed in the paper, leads to a decrease in the absolute value of the QFLS compared with the prediction without Auger processes. This pushes the electronic system closer to an equilibrium between electrons and holes. Auger processes also lead to a decrease in carrier temperature for the negative luminescence regime, because impact ionisation, which reduces the kinetic energy of the carriers, dominates in that regime. Conversely, an increase in carrier temperature is expected in the positive regime.
QFLS regime, because Auger recombination, which decreases the kinetic energy of the carriers, dominates. If realistic contacts with a finite width are considered, the results are expected to change qualitatively, but the rise in carrier temperature, detectable as a change in spectral shape of the electroluminescence, is always associated with nonexponential (and non-ohmic) behaviour in the dark I–V.

ACKNOWLEDGEMENTS
This work was partially funded through the Australian Research Council Discovery Programme through project DP170102677. M.P.N. thanks the UNSW Scientia Program for on-going support. M. D. acknowledges support by AINSE Limited through a PGRA award.

ORCID
Andreas Pusch https://orcid.org/0000-0002-6115-9117

REFERENCES
1. Hirst LC, Ekins-Daukes NJ. Fundamental losses in solar cells. Prog Photovolt Res Appl. 2011;19(3):286-293. https://doi.org/10.1002/pip.1024
2. Green MA, Brenner SP. Energy conversion approaches and materials for high-efficiency photovoltaics. Nat Mater. 2016;16:23. https://doi.org/10.1038/nmat4676
3. Ross RT, Nozik AJ. Efficiency of hot-carrier solar energy converters. J Appl Phys. 1982;53(5):3813-3818. https://doi.org/10.1063/1.331124
4. Würfel P. Solar energy conversion with hot electrons from impact ionisation. Sol Energy Mater Sol Cells. 1997;46(1):43-52.
5. Shah J. Hot Carriers in Semiconductor Nanostructures: Physics and Applications. First: Academic Press; 1992.
6. Clady R, Tayebjee MJ, Aliberti P, et al. Interplay between the hot phonon effect and intervalley scattering on the cooling rate of hot carriers in GaAs and InP. Prog Photovolt Res Appl. 2012;20(1):82-92. https://doi.org/10.1002/pip.1121
7. Hirst LC, Fuji H, Wang Y, et al. Hot carriers in quantum wells for photovoltaic efficiency enhancement. IEEE J Photovoltaics. 2014;4(1):244-252.
8. Esmaeilpour H, Whiteside VR, Piyathilaka HP, et al. Enhanced hot electron lifetimes in quantum wells with inhibited phonon coupling. Scientific Reports. 2018;8:12473.
9. Chen F, Cartwright AN, Lu H, Schaff WJ. Time-resolved spectroscopy of recombination and relaxation dynamics in InN. Appl Phys Lett. 2003;83(24):4984-4986. https://doi.org/10.1063/1.1633973
10. Gabor NM, Song JCW, Ma Q, et al. Hot carrier–assisted intrinsic photoresponse in graphene. Science. 2011;334(6056):648-652.
11. Tirolciu KJ, Song JCW, Jensen SA, et al. Photoexcitation cascade and multiple hot-carrier generation in graphene. Nat Phys. 2013;9(4):248-252. https://doi.org/10.1038/nphys2564
12. Song JCW, Levitov LS. Energy flows in graphene: hot carrier dynamics and cooling. J Phys Condens Matter. 2015;27(1):164201.
13. Hopper TR, Gorodetsky A, Frost JM, et al. Ultrafast intraband spectroscopy of hot-carrier cooling in lead-halide perovskites. ACS Energy Lett. 2018;3(9):2199-2205. https://doi.org/10.1021/acsenergylett.8b01227
14. Tamming RR, Butkus J, Price MB, et al. Ultrafast spectrally resolved photoinduced complex refractive index changes in CsPbBr3 perovskites. ACS Photon. 2019;6(2):345-350. https://doi.org/10.1021/acsphotonics.9b00091
15. Joshi PP, Maehlken SF, Zhu X. Dynamic screening and slow cooling of hot carriers in lead halide perovskites. Adv Mater. 2019;31(47):1803054. https://doi.org/10.1002/adma.201803054
16. White TP, Catchpole KR. Plasmon-enhanced internal photoemission for photovoltaics: theoretical efficiency limits. Appl Phys Lett. 2012;101(7):73905. https://doi.org/10.1063/1.4746425
17. Hathwar R, Zou Y, Jirauschek C, Goodnick SM. Nonequilibrium electron and phonon dynamics in advanced concept solar cells. J Phys D Appl Phys. 2019;52(9):93001. https://doi.org/10.1088/2053-2573/a64632
18. Aebisher U. Quantum transport simulation of hot carrier photocurrent generation in quantum well solar cells. Semicond Sci Technol. 2019;34(9):94002. https://doi.org/10.1088/1361-6641/ab312d
19. Dimmock JAR, Day S, Kauer M, Smith K, Heffernan J. Demonstration of a hot-carrier photovoltaic cell. Prog Photovolt Res Appl. 2014;22(2):151-160. https://doi.org/10.1002/pip.2444
20. Hirst LC, Walters RJ, Führer MF, Ekins-Daukes NJ. Experimental demonstration of hot-carrier photo-current in an InGaAs quantum well solar cell. Appl Phys Lett. 2014;104(23):231115. https://doi.org/10.1063/1.4883648
21. Nguyen D-T, Lombez L, Gibelli F, et al. Quantitative experimental assessment of hot carrier-enhanced solar cells at room temperature. Nat Energy. 2018;3(3):236-242. https://doi.org/10.1038/s41560-018-0106-3
22. Rau U. Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells. Phys Rev B. 2007;76:85303. https://doi.org/10.1103/PhysRevB.76.085303
23. Aebisher U, Rau U. Microscopic perspective on photovoltaic reciprocity in ultrathin solar cells. Phys Rev Lett. 2017;118:247702. https://doi.org/10.1103/PhysRevLett.118.247702
24. Nolas GS, Sharp J, Goldsmid HJ. Thermoelectrics, Basic Principles and New Materials Developments. 2nd ed. Berlin Heidelberg: Springer; 2017.
25. Callen HB. The application of Onsager’s reciprocal relations to thermoelectric, thermonuclear, and galvanomagnetic effects. Phys Rev. 1948;73:1349-1358. https://doi.org/10.1103/PhysRev.73.1349
26. Takeda Y, Ito T, Suzuki R, Motohiro T, Shrestha S, Conibeer G. Impact ionization and auger recombination at high carrier temperature. Sol Energy Mater Sol Cells. 2009;93(6):797-802. 17th International Photovoltaics Science and Engineering Conference.
27. Würf P, Brown AS, Humphrey TE, Green MA. Particle conservation in the hot-carrier solar cell. Prog Photovolt Res Appl. 2005;13(4):277-285. https://doi.org/10.1002/pip.584
28. Takeda Y, Motohiro T, König D, et al. Practical factors lowering conversion efficiency of hot carrier solar cells. Applied Physics Express. 2010;3(10):104301.
29. Marti A, Luzque A. Electrochemical potentials (quasi-Fermi levels) and the operation of hot-carrier, impact-ionization, and intermediate-band solar cells. IEEE J Photovoltaics. 2013;3(4):1298-1304.
30. Limpert S, Bremner S, Linke H. Reversible electron–hole separation in a hot carrier solar cell. New J Phys. 2015;17(9):95004.
31. Limpert SC, Brenner S, Linke H. Reversible electron–hole separation in a hot carrier solar cell. New J Phys. 2015;17(9):95004.
32. Le Bris A, Guilleminodes J-F. Hot carrier solar cells: achievable efficiency accounting for heat losses in the absorber and through contacts. Appl Phys Lett. 2010;97(11):113506. https://doi.org/10.1063/1.3489405
33. Konovolov I, Ploss B. Modeling of hot carrier solar cell with semi-infinite energy filtering. Sol Energy. 2019;185:59-63.
34. Ferry DK. In search of a true hot carrier solar cell. Semicond Sci Technol. 2019;34(4):44001.
35. Mahan GD, Sofo JO. The best thermoelectric. Proc Natl Acad Sci. 1996;93(15):7436-7439.
36. Humphrey TE, Linke H. Reversible thermoelectric nanomaterials. Phys Rev Lett. 2005a;94:96601. https://doi.org/10.1103/PhysRevLett.94.096601
37. Datta S. Lessons From Nanoelectronics, a New Perspective on Transport—Part a: Basic Concepts. Second: World Scientific; 2017.

38. O’Dwyer MF, Humphrey TE, Lewis RA, Zhang C. Electronic and thermal transport in hot carrier solar cells with low-dimensional contacts. Microelectron J. 2008;39(3):656-659. The Sixth International Conference on Low Dimensional Structures and Devices.

39. Limpert S, Burke A, Chen I-J, et al. Bipolar photothermoelectric effect across energy filters in single nanowires. Nano Lett. 2017;17(7):4055-4060. https://doi.org/10.1021/acs.nanolett.7b00536

40. Dimmock JAR, Kauer M, Wu J, Liu H, Stavrinou PN, Ekins-Daukes NJ. A metallic hot-carrier photovoltaic device. Semicond Sci Technol. 2019;34(6):64001.

41. Würfel P. The chemical potential of radiation. J Phys C Solid State Phys. 1982;15(18):3967-3985.

42. Humphrey TE, Linke H. Quantum, cyclic, and particle-exchange heat engines. Physica E: Low-dimensional Syst Nanostruct. 2005b;29(1):390-398. Frontiers of Quantum.

43. Xiao TP, Chen K, Santhanam P, Fan S, Yablonovitch E. Electroluminescent refrigeration by ultra-efficient GaAs light-emitting diodes. J Appl Phys. 2018;123(17):173104.

44. Santhanam P, Gray DJ, Ram RJ. Thermoelectrically pumped light-emitting diodes operating above unity efficiency. Phys Rev Lett. 2012;108:97403. https://doi.org/10.1103/PhysRevLett.108.097403

45. Würfel P. Is an illuminated semiconductor far from thermodynamic equilibrium?. Sol Energy Mater Sol Cells. 1995;38(1):23-28.

46. Berdahl P, Malyutenko V, Morimoto T. Negative luminescence of semiconductors. Infrared Phys. 1989;29(2):667-672.

47. Malyutenko V. Negative luminescence in semiconductors: a retrospective view. Physica E: Low-dimensional Syst Nanostruct. 2004;20:553-557.

48. Strandberg R. Theoretical efficiency limits for thermoradiative energy conversion. J Appl Phys. 2015;117(5):55105. https://doi.org/10.1063/1.4907392

49. Ono M, Santhanam P, Li W, Zhao B, Fan S. Experimental demonstration of energy harvesting from the sky using the negative illumination effect of a semiconductor photodiode. Appl Phys Lett. 2019;114(16):161102. https://doi.org/10.1063/1.5089783

50. Pusch A, Gordon JM, Mellor A, Krich JJ, Ekins-Daukes NJ. Fundamental efficiency bounds for the conversion of a radiative heat engine’s own emission into work. Phys Rev Appl. 2019;12:64018. https://doi.org/10.1103/PhysRevApplied.12.064018

How to cite this article: Pusch A, Dubajic M, Nielsen MP, Conibeer GJ, Bremner SP, Ekins-Daukes NJ. Optoelectronic reciprocity in hot carrier solar cells with ideal energy selective contacts. Prog Photovolt Res Appl. 2021;29:433–444. https://doi.org/10.1002/pip.3386