Charge Carrier Collection and Contact Selectivity in Solar Cells

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The electronic properties of the contacts to a photovoltaic absorber material are important for the final efficiency of any type of solar cell. For highly efficient solar cells based on high quality absorber materials like single-crystalline silicon, polycrystalline Cu(In,Ga)Se₂, CdTe, or metal-halide perovskites, contact formation is even the decisive processing step determining the final efficiency. The present paper combines recently developed quantitative concepts for the description of contacts to solar cells in terms of their selectivity toward a more general description that is valid for all types of solar cells and all types of contacts. It is shown that the built-in voltage is an important parameter to influence the selectivity of contacts to photovoltaic absorber materials. It is also shown that the contact selectivity is mathematically related to the collection efficiency which can be measured by luminescence based techniques.

1. Introduction

It is fair to say that most relevant, high-efficiency solar cell technologies are limited by their contacts. This is true for metal halide perovskites where the bulk material can be rather close to its radiative limit[1–4] whereas introduction of contact layers to these materials increases recombination and therewith limits the achievable open-circuit voltage.[5–7] Thus, contact passivation becomes increasingly important for further improving power conversion efficiencies in halide perovskite solar cells.[3,8–12] Furthermore, the technologically dominant silicon wafer based solar cells are limited by the formation of the doped emitter and the Ohmic contacts as far as the classical homojunction technology is concerned.[13,14] The silicon heterojunction (SHJ) approach provides better contact passivation and therefore higher open-circuit voltages $V_{OC}$ than the classical technology.[15] Here, the critical interplay between contact recombination and contact resistance defines the process window for optimizing $V_{OC}$ versus the fill factor of the solar cell.[16] Recent progress in SHJ technology is due to minimizing the contact resistance while keeping the high level of $V_{OC}$.[17] For Cu(In,Ga)Se₂ and CdTe thin-film solar cells, the interface between the Cu(In,Ga)Se₂ absorber and the CdS buffer layer[18,19] and the interface between the CdTe absorber and the Ohmic back contact in the latter case are considered the most critical issues.[20–22] Only epitaxially grown GaAs solar cells realize efficiencies close to the radiative limits on the device level due to the epitaxial contact formation between the GaAs absorber and the AlInP and GaInP contact materials.[23–25]

Thus, charge-carrier separation and recombination at the contact interfaces are one of the most prominent challenges in most of today’s relevant solar cell technologies. In addition, perfect charge-carrier separation is one of the critical issues that are necessary to bring the efficiency of solar cells close to their theoretical limit. In this context, the role of the built-in field was intensely discussed in the 1990s/early 2000s, especially for the case of organic and dye sensitized solar cells.[26] On the one hand, “perfect” selectivity of the contacts was considered as necessary and sufficient condition for the collection of all photo-generated charge carriers.[27] On the other hand it was stated that whenever in a device a voltage appears at its electrical terminals there must be a capacitive element that accommodates the electrical charge to build up the change of electrical potential.[26,28–30]

The present paper discusses the functionality of contacts to solar cells in terms of the quantitative concept for the selectivity introduced by Brendel and Peibst[31] (BP). We generalize this concept for all solar cells by removing the restrictions to crystalline silicon used in the original paper and compare the approach of BP with an alternative definition of contact selectivity by Roe, Egelhofer, and Lonergan[32] (REL) that corresponds to a physical situation described earlier by Würfel et al.[33] We show that the two different approaches cover complementary situations and combine them into a more general model for contact selectivity. We discuss the influence of the built-in potential on the selectivity of contacts and show that the asymmetry provided by the built-in potential is an important lever to design the contact selectivity defined in either way (BP or REL). Different optimization strategies for contacts are demonstrated for different contact types and, finally, it is shown that the selectivity is related to the photocurrent collection efficiency[34–36] a quantity that is measurable by electro-modulated luminescence measurements.
2. Contact Selectivity

A critical issue for the technological development of contacts to solar cell as well as for the conceptual understanding thereof was the lack of a quantitative measure for the selectivity of a contact to a photovoltaic material, i.e., selective contacts were either “perfect”\(^{[27]}\) or “nonperfect.” In other cases, only one aspect of selectivity—such as the surface recombination velocity of minority carriers—was treated quantitatively while other aspects (effect on majority carriers) was only discussed qualitatively.\(^{[137]}\) This deficiency has been removed while other aspects (effect on majority carriers) was only treated quantitatively by the papers of Brendel and Peibst\(^{[31]}\) and Roe, Egelhofer, and Lonergan\(^{[32]}\) who have introduced a quantitative but not identical measure for the selectivity. Let us therefore first discuss the two different approaches to understand the similarities and differences.

In their paper, BP assume that a contact to a solar cell introduces an interface recombination current

\[
J_S = J_{S,0} \left[ \exp \left( \frac{V}{V_{th}} \right) - 1 \right]
\]

(1)

following a diode law where \(J_{S,0}\) denotes the saturation value of the interface recombination current, \(V_{th}\) the thermal voltage, and \(V_i\) the internal voltage, i.e., the split between the electron and the hole quasi-Fermi-level within the photovoltaic absorber. At the same time the contact represents an Ohmic resistance \(R_C\) (in units \(\Omega\) cm\(^2\)) to the majority carrier current. With this BP\(^{[31]}\) define a value for the selectivity

\[
\Sigma := \frac{V_{th}}{R_C J_{S,0}}
\]

(2)

Thus, Equation (2) puts the Ohmic resistance \(R_C\) for majority carriers into relation with the (zero bias) recombination resistance \(V_{th}/J_{S,0}\) of the minority carriers. Note that the actual ratio between Ohmic and recombination resistance at a certain internal voltage bias \(V_i\) is given by the differential selectivity

\[
\Sigma_i := \frac{1}{R_C} \left( \frac{dJ_i}{dV_i} \right)^{-1} = \frac{V_{th}}{R_C J_{S,0}} \exp \left( -\frac{V_i}{V_{th}} \right) = \Sigma \exp \left( -\frac{V_i}{V_{th}} \right)
\]

(3)

which decreases exponentially with increasing \(V_i\). Equation (3) gives prominence to the fact that the ratio between resistive and recombination losses depends on the actual minority carrier concentration under bias. The use of saturation values in Equation (2) is therefore justified for a given diode ideality factor \(n_d\) for the recombination process (\(n_d = 1\), in the following).

The key idea of Equation (2) is that the selectivity is high if the recombination of minority carriers is low (low \(J_{S,0}\)) and if the series resistance is low. Then all majority carriers will be easily extracted, no voltage drops over the series resistance and no photovoltaic is lost due to recombination of minority carriers. In contrast if the series resistance and the recombination current are high, both voltage losses will be high and the contact contributes to a reduced efficiency. Because of the a priori distinction between majority and minority carriers underlying Equation (2), we denote the BP model as a resistive model.

The current density \(J\) versus (external) voltage \(V\) relationship underlying this model is given by the implicit equation

\[
J = J_1 - J_{S,0} \left[ \exp \left( \frac{V - J_{R_C}}{V_{th}} \right) - 1 \right]
\]

(4)

where \(J_1\) denotes the photogenerated circuit current density

The assumptions underlying the selectivity definition of REL\(^{[32]}\) are substantially different to the BP model. Here it is assumed that at the surfaces of a photovoltaic absorber the concentrations \(c_m\) and \(c_m\) of majority carrier and minority carriers drive the respective majority and minority carrier currents according to

\[
f_{m,m} = J_{m,m,0} \left( \frac{c_{m,m,0}}{c_{m,0}} - 1 \right)
\]

(5)

where \(J_{m,m,0}\) denotes the a saturation current density for majority/minority carriers at the respective contact \(i = 1, 2\), and \(c_{m,m,0}\) denote the corresponding equilibrium carrier concentrations. Note that electrons and holes interchange their role as minority and majority carriers at the two different contacts. The selectivity in the REL-model is then defined by the ratios of the saturation current densities of majority and minority carriers according to

\[
\Sigma_k := \frac{f_{m,m}}{f_{m,m,0}}
\]

(6)

where the subscript \(k\) represents the kinetic character of the underlying Equations (5). We note that the REL model does not explicitly discuss any resistive losses (unlike the BP model) while it shares the inverse dependence on the saturation current density of minority carriers with the BP model (\(f_{m,0}\) in the REL model and \(J_{S,0}\) in the BP model).

In order to understand the differences of the resistive (BP) and the kinetic (REL) approach we first look at the generic band diagram of a solar cell as shown in Figure 1a. Here we consider an absorber layer sandwiched between two metallic contacts on each side of the solar cell. We consider the photogenerated current density \(J_1\), recombination current densities \(J_{S(1,2)}\) at the contact/absorber interfaces and the majority carrier current densities \(f_{m(1,2)}\). This setting corresponds to the (BP) model where recombination takes place at the contact/absorber interfaces. The appropriate equivalent circuit is shown in Figure 1b where the (interface) recombination takes place via two diodes \(J_{S(1,2)}\) and majority current densities give rise to voltage drops across two contact resistors \(R_{C(1,2)}\) which are the resistances related to the majority carrier currents \(f_{m(1,2)}\). This resistive equivalent circuit is easily simplified to a simpler one by adding up the two recombination currents to \(J_S = J_{S(1)} + J_{S(2)}\) and the set of equations to \(R_C = R_{C(1)} + R_{C(2)}\) as shown in Figure 1c. This equivalent circuit might also be looked at as a single-sided version of the model (e.g., in the limit \(J_{S(1)} \gg J_{S(2)}\) and \(R_{C(1)} \gg R_{C(2)}\)).

The kinetic (REL) model considers majority current densities \(f_{m}\) and minority current densities \(f_{m,0}\) across the contact layers into the metallic contact as shown in Figure 1d. Since
minority carriers that leave the absorber finally recombine with majority carriers, the current densities \( J_{\text{m}(1,2)} \) are recombination losses. The current densities are driven by the difference between the quasi-Fermi-levels \( E_{\text{Fn}} \) and \( E_{\text{Fp}} \) of electrons and holes in the absorber and the Fermi-level in the contacts as illustrated by the nonequilibrium band diagram (Figure 1d). The corresponding equivalent circuit is depicted in Figure 1e (see the Supporting Information). As can be easily seen, the kinetic model describes a fundamentally different situation as compared to the resistive model (Figure 1c). First, it is important to stress that the REL connects the electrochemical potentials of electrons and holes \( E_{\text{Fn}} \) and \( E_{\text{Fp}} \) to the external voltage \( V \) which describes the change in electrostatic potential at the two terminals of the solar cell relative to the situation at \( V = 0 \) V. Note that the electrostatic potential difference between the contacts is \( V_{\text{bi}} - V \), i.e., it depends on the built-in voltage and the external voltage. Second, the kinetic model takes into account that the open-circuit voltage measured externally can be lower than the split of the quasi-Fermi-levels inside the absorber, a frequently observed feature\(^{[37–41]} \) that is not covered by the resistive model. This is possible in the kinetic model because both types of carriers can move from the absorber into the contact implying a drop of both quasi-Fermi-levels and hence a loss of free energy. At open circuit, majority and minority currents cancel out but the loss of free energy remains. Finally, the REL model contains no internal limitation (e.g., by bulk recombination) to the internal split of the quasi-Fermi-levels which me may denote as the internal voltage \( qV_{\text{I}} = E_{\text{Fn}} - E_{\text{Fp}} \). Adding such a limitation is important for the completeness of any model for selective contacts as will be shown below.

Figure 2 illustrates the different consequences of variations of the selectivity. Both models reproduce the ideal solar cell curve given by Equation (4) and \( R_C = 0 \) if the respective selectivities \( \Sigma_r \) and \( \Sigma_k \) are infinitely large (black curve). However introducing finite selectivity values \( \Sigma_r = \Sigma_k = 5 \times 10^{12} \) (by increasing \( R_C \) or decreasing \( J_M,0 \), respectively) leads to clearly different consequences for both models. Whereas in the resistive case (green line) the typical resistive loss across the resistor \( R_C \) leads to a deterioration of the fill factor, we find for the REL model (solid red line) primarily a substantial decrease of the open-circuit voltage. In the REL model the internal voltage \( V_I \) (dashed red line) increases at each given current density above the values of the perfect reference curve whereas for the BP model the internal \( JV \) curve remains always ideal (black curve). Also the different dependence of the efficiency on the two types of selectivities (inset of Figure 2) demonstrates that both approaches describe rather different situations with different consequences.

### 3. Role of Built-In Potential

In the context of understanding the working principle of solar cells, the built-in potential has played a remarkably controversial role.\(^{[26]} \) This is partly due to the fact that it is convenient, but finally incorrect,\(^{[33]} \) to explain the working principle of, e.g.,

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**Figure 1.** a) Band diagram illustrating the resistive model following Brendel and Peibst.\(^{[31]} \) b) The equivalent circuit associated with the resistive model that can be simplified to the circuit shown in (c). d) Band diagram illustrating the kinetic model of Roe, Egelhofer, and Lonergan\(^{[32]} \) with the e) equivalent circuit associated with this model. Note that under operating conditions (\( V < V_{\text{OC}} \)), we have \( V_n < 0 < V < V_p \) for the internal voltages \( V_n, V_p \) such that all diodes in (e) are under forward bias conditions. f) An extended equivalent circuit which incorporates all aspects of the two models in the limit of small voltage drops over the majority carrier diodes \( J_{\text{m}(1,2)} \).
a pn-junction solar cell using the electric field as the driving force to separate charge carriers. This picture not only cannot explain how charge separation works if 99% of the volume of a solar cell is completely field-free and any built-in fields exist only at the very edges of the device (as is the case for crystalline Si but also for dye-sensitized solar cells) but also ignores the fact that charge carriers in fact will move against the direction of the electrical field, where we have to bear in mind that at the beginning of the cause-effect chain is the change of the chemical potentials of electrons and holes by generation of nonequilibrium carriers.

Next, the electrons and holes move in different directions as determined by the electrochemical potential. This in turn leads to a rearrangement of the electrostatic potential and to the steady-state band diagram of a pin-type (Figure 3b) or pn-type (Figure 3d) solar cell under light and voltage bias. The capacitive element accommodating this change of electrostatic potential extends over the entire absorber in the pin- and across the space charge region in case of a pn-type junction as sketched in Figure 3b.d. Let us now assume that carrier mobilities are high enough such that the steady-state quasi-Fermi-levels $E_{F,n}$ and $E_{F,p}$ are flat and both types of devices will be controlled by the absorber/contact interfaces. If we assume further the same material parameters and thickness for the absorber, and, especially, the same built-in potential $V_{bi}$, the carrier concentrations at the absorber/contact interfaces of both, the pin- and the np-device, will be the same. Since all resistive and recombination losses depend exclusively on the carrier concentrations at these interfaces, we expect a major influence of $V_{bi}$ on the selectivity, regardless whether this potential is built up within a pin-, a pn-, or any other device structure. Finally, Figure 3e,f illustrate the difference between the assumptions of the BP-model, where we have an electrostatic potential difference $\Delta V_{c} = J_{R}c$ across the contact, and the REL-model, where both, majority currents and minority currents, result from the nonequilibrium concentrations of both types of carriers. Figure 3f also illustrates the definitions of the voltages $V_{c}$ and $V_{0}$ that are used in the equivalent circuit model (Figure 1e, Equations S1–S4 in the Supporting Information).

To derive a quantitative relation between selectivity and the built-in potential $V_{bi}$, we will denote the species with the lower equilibrium concentration as the minority carriers specific to the respective contact. Recombination will be proportional to...
The concentration of the minority carriers. Let us assume the band diagram shown in Figure 1a where the electron contact is at the edges of the space charge region for the pn-device. The band diagrams also show that the respective minority carrier concentrations at the contacts change from the equilibrium a,c) to the nonequilibrium situations b,d) at the edges of the space charge region for the pn-device. The band diagrams also show that the respective minority carrier concentrations at the contacts change from the equilibrium a,c) to the nonequilibrium situation b,d) in the same way for both types of junctions. The difference between the BP model and the REL model is outlined in (e) and (f). The resistive BP model requires an additional capacitor such that a loss voltage \( \Delta V_{bi} = jR_{th} \), drops over the contact (only electron contact shown). The electron quasi-Fermi-level is parallel to the conduction band edge through the contact. In contrast, for the REL-model (f) the band edges through both contacts remain flat, like assumed for thermodynamic equilibrium in (a,c). Electron and hole currents are driven by the quasi-Fermi concentrations of the respective charge carriers inside the absorber material. Also indicated are the voltages \( V_{th} \) and \( V_{ph} \) used in the equivalent circuit model (Figure 1e, Equations S1–S4 in the Supporting Information) as well as the scales of electron energy \( E \) (positive direction up) and of the electrostatic potential (positive direction down). The zero for both scales is set to the energy/potential of the electron contact (left contact) in accordance with the equivalent circuit shown in Figure 1e.

As shown in the Supporting Information we then find for the resistive (BP) definition of the selectivity of the electron-contact

\[
\Sigma = \frac{V_{th}}{w_C} \frac{\mu_e N_C}{\mu_v N_v} \exp \left( \frac{V_{bi}}{V_{th}} \right)
\]

(7)

where \( w_C \) is the width of the contact layer and \( \mu_e \) the electron mobility. The symbols \( N_C/N_v \) denote the effective density of states in the conduction and valence band, and \( \mu_v \) the interface recombination velocity for holes. For the contact with holes as majority carriers the symbols for holes and electrons must be interchanged.

With similar arguments shown in the Supporting Information one finds for the REL model the proportionality

\[
\Sigma_i = \frac{\mu_e N_C}{\mu_v N_v} \exp \left( \frac{V_{th}}{V_{th}} \right)
\]

(8)

Note that Equation (8) assumes perfect antisymmetry of the band diagram and assumes equal densities of states in contact and absorber material as well as no band discontinuities between the two materials. Equation (8) also assumes that the transport in the contact is rate limiting and not the charge transfer from the absorber into the contact material. As discussed above, Equations (7) and (8) rely only on arguments based on carrier concentrations at the absorber/contact interfaces and therefore are valid regardless how the potential \( V_{bi} \) is built up through the device. If the quasi-Fermi-levels \( E_{Fn} \) and \( E_{Fp} \) are flat and we further assume that the respective majority carrier concentrations are fixed at the contacts, only the minority carrier concentrations will reflect the change of the internal voltage \( qV_i = E_{Fn} - E_{Fp} \). Thus, the actual concentration \( m \) of minority carriers, and herewith the recombination losses, at the interface will depend on the equilibrium concentration \( m_0 \) via

\[
m = m_0 \exp \left( \frac{V_{th}}{V_{th}} \right)
\]

(9)

This is how the built-in potential \( V_{bi} \) controls recombination via \( m_0 \). A view to Figure 3b,d demonstrates further that this control is independent of whether the electrostatic field is built-up via a pin- or a pn-junction.

The extension of the present approach toward more general situations is straightforward but exhaustive. Especially relaxing the antisymmetry assumption will lead to a cumbersome calculation of the two different selectivities of the two contacts individually. However, as shown in the Supporting Information, we find a useful equation for the product of the selectivities \( \Sigma(1) \) and \( \Sigma(2) \) of the contacts 1 and 2. This “product rule” is independent of the assumptions on the band diagram and the junction and describes the influence of the selectivity-product on \( V_{bi} \) via

\[
\Sigma(1) \Sigma(2) = \Sigma(1) \Sigma(2) \exp \left( \frac{2V_{th}}{V_{th}} \right)
\]

(10)

Equation (10) holds for both definitions of the selectivity (\( \Sigma_i \) and \( \Sigma_0 \)). We may denote the prefactors \( \Sigma(1) \) and \( \Sigma(2) \) in Equation (10) as the intrinsic selectivities of the contacts whereas the exponential term contains the built-in voltage.
Equation (10) nicely demonstrate how the dispute “selective contacts versus built-in potential” is to be solved: In principle, a “perfectly selective” [33, 43] contact, i.e., \( \Sigma \rightarrow \infty \), can be achieved by a proper choice of the parameters in the prefactors \( \Sigma_0^n \) and \( \Sigma_0^m \) in Equations (7) and (8), e.g. by putting the respective majority carrier mobilities to infinity. However, the possibility to control the contact selectivity via the built-in voltage is practically much more attractive, because this quantity enters exponentially in Equations (7) and (8). Furthermore, the built-in voltage in many cases is reasonably well controlled by doping of the contact layers or by a proper choice of work functions of the contact materials explaining why any solar cell of significant efficiency possesses a built-in potential.

It is important to stress that our arguments do not rely on carrier separation in the bulk of the absorber material via the built-in field (the spatial derivative of the built-in potential). This argument is only valid if the carrier mobilities in the absorber are below a critical threshold. It is rather that the built-in potential is an important quantity that minimizes majority and minority carrier related losses at the contacts. Finally, we emphasize that our argument does not rely on a specific assumption on how the built-in potential is arranged, i.e., by a pin-junction (which is used as an illustration), or by a p-n-junction, or by suitable work functions of the contact materials. The argument is rather based on the concentration differences of the respective minority and majority carriers at both contact absorber interfaces. These differences are determined by the built-in potential.

4. Contact Area Optimization

The strength of the concept of selectivity is given by the fact that it provides a very illustrative picture for the optimization of contacts. Here, we give some analytical approximations that enable to use this tool outside the range of the phenomenological relations of ref. [31] which are designed for the application to crystalline silicon solar cells.

The maximum output power \( P \) arising from Equation (4) is to a very good approximation given by the expression

\[
P = J_{SC} V_{OC} F_F \left( 1 - \frac{J_{SC} R_C}{V_{OC}} \right) = J_{SC} V_{th} \ln \left( \frac{J_{SC}}{J_{S,0}} \right) F_F \frac{J_{SC}}{J_{S,0}} F_{R} R_C
\]

(11)

where the dependence of the fill factor \( F_F \) (without series resistance) as well as the effect of the (contact) series resistance is described by the phenomenological equations of ref. [45]. Within these equations \( F_F \) is expressed as a function of the open-circuit voltage normalized to the thermal voltage, i.e., \( F_F = \frac{F_F(\frac{V_{OC}}{V_{th}})}{V_{OC}} \).

The optimization problem addressed by BP [31] is that of the optimum area fraction in a situation where the contacts are restricted to only a small fraction \( f \) of the respective cell surface. If one assumes that the characteristic length scale of these point contacts is small with respect to the diffusion length of minority carriers in the absorber and that the noncontact area is perfectly passivated but also nonconductive, we can replace \( J_{S,0} \) by \( f J_{S,0} \) and \( R_C \) by \( R_C^{opt} \) in Equation (11), thus variations of \( f \) leave the selectivity unchanged. However, a variation of the contact area fraction allows us now to trade higher recombination losses for reduced recombination losses and see whether this trade can improve efficiency.

Figure 4 illustrates the contact optimization problem resistive versus recombination losses as a function of the contact resistance \( R_C \) and the contact interface recombination saturation current density \( J_{S,0} \). The isolines for the output power (or the efficiency) as represented by the solid lines demonstrate that high efficiencies require both low values of \( J_{S,0} \) as well as of \( R_C \). The steep decline of the isoefficiency lines toward higher contact resistances \( R_C \) highlights the critical role of resistive losses. The dashed lines correspond to a constant selectivity \( \Sigma_0 \). For the optimization problem we have from Equation (4)

\[
\Sigma_0 (f) = \frac{V_{th}}{R_C (f) J_{S,0} (f)} = \frac{V_{th}}{R_C^{opt} J_{S,0}^{opt}} = \frac{V_{th}}{R_C^{opt} J_{S,0}^{opt}}
\]

(12)

i.e., variations of the area fraction \( f \) leave the selectivity unchanged. Thus, decreasing the area fraction \( f \) shifts the \( (R_C J_{S,0}) \) values along an isoselectivity line toward larger values of \( R_C \) (more resistive losses) and smaller values of \( J_{S,0} \) (less contact recombination losses). The dotted vertical line corresponds to the optimum contact resistance \( R_C^{opt} \) from Equation (11).
Therefore, a contact with a full area resistance $R_{C,full}$ can be optimized by restricting it to a reduced area fraction $f = R_{C,full}^2 / R_{C,full}^2 < 1$, whereas for $R_{C,full}^2 \geq R_{C,full}^2$ such an optimization is not possible. Up to this point the present Figure 4 corresponds exactly to Figure 2 of ref. [1]. We only added normalized axes (top and right) for both quantities $R_C$ and $J_{th}$ in order to illustrate the general applicability of the approach.

To illustrate the optimization procedure, Figure 5 depicts the solar cell’s output power as a function of the contact resistance $R_C$ for constant selectivities $\Sigma_x$ i.e., along the isoselectivity lines in Figure 4. Because of $R_C = R_{C,full}^2/f$ this representation is implicit for the optimization of the contact area (as well as for the contact thickness $w_C$ as shown below). Again, we use axes according to the parameters of ref. [1] as well as normalized axes. Note that the normalization of the output power axis (top right) to $J_{th}V_{th}$ allows to read the figure representing the normalized product $V_{OC,FF}/V_{th}$. This illustrates the fact that the area optimization problem is about optimizing recombination losses (decreasing $V_{OC}$) versus resistive losses (decreasing the fill factor $FF$).

Figure 5 also demonstrates that the analytical approximation for the optimum contact resistance $R_{C,OPT}$ (short-dashed line at $R_{C,OPT}^2 = V_{th}/J_{opt}$) and the resulting optimum output power $P_{opt}$ (full symbols) are very good approximations to the values obtained by numerically evaluating the diode equation, Equation (3), (open symbols).

The definition of selectivity given by Equation (5) for the REL model allows for a similar view to area optimization because $\Sigma_x = (J_{M,0}f)/(J_{M,0}f)$ is constant. Figure 6 shows the isoefficiency and the isoselectivity ($\Sigma_x$) lines for the REL model in analogy to Figure 4 (for the BP model). Note that we have chosen the inverse majority carrier saturation current density $1/J_{M,0}$ for the x-axis in order to be visually comparable to the $R_C$-axis in Figure 4. By comparing Figure 4 and Figure 6, we see that on the one hand similar selectivities $\Sigma_x$ and $\Sigma_C$ cover a similar efficiency range. On the other hand, the asymptotic behavior of the isoselectivity ($\Sigma_x$) lines toward high values for $1/J_{M,0}$ (i.e., high majority carrier resistance) is different to what is seen in Figure 4 for high $R_C$. In the REL model the isoselectivity lines approach an optimum efficiency line in the direction of high values for $1/J_{M,0}$ and therefore there is no finite optimum majority carrier resistance.

This fact is more clearly illustrated in Figure 7a where we show the development of the output power along various isoselectivity lines ($\Sigma_x = \text{const}$) as a function of $1/J_{M,0}$. Note that the analogous Figure 5 for the BP model displayed maxima for the output power at finite values for $R_C$. In contrast in Figure 7, the output power increases monotonously toward asymptotic values at $1/J_{M,0} \to \infty$, i.e., at infinite majority carrier resistance. The fact that infinite series resistance leads to the optimum efficiency is obviously unphysical. The reason for this behavior is illustrated by the external and internal open-circuit voltages $V_{OC,EXT}$, $V_{OC,INT}$ also shown in Figure 8. At low values of $1/J_{M,0}$ both values increase because of the implicit decrease of recombination (decrease of $J_{M,0}$ with decreasing $f$). At the point where the output power $P$ starts to saturate the
externally measured \( V_{OC} \) saturates as well. In contrast, the internal value \( V_{OC}^{int} = (E_F - E_P) / q \) increases with an even steeper slope. This is because this internal voltage is needed to drive the majorities and minority carriers out of the absorber material and because the REL model provides no limitation for the split of the quasi-Fermi-levels \( E_F \), \( E_P \) inside the absorber or at the immediate absorber/contact interface. Thus, the detrimental effect of decreasing \( J_{M,0} \) values is compensated by extremely high internal voltages in the REL model. Without any additional internal limitation the REL model risks to describe unphysical situations. This shortcoming of the REL model is removed by the extended model described in the following.

5. Extended Model

The physically implausible high internal voltages of the REL model depicted in Figure 7a are avoided by a combination of the model with the BP model as shown by the general equivalent circuit in Figure 1f. Here we have added an internal loss diode \( j_B \) to the equivalent circuit of the REL model (Figure 1e).

This diode may represent bulk recombination or recombination at the immediate absorber contact interfaces which is subject to the quasi-Fermi-levels inside the absorber. In both cases the split of the quasi-Fermi-levels and hence the internal voltage \( V_{OC}^{int} \) will be limited. For instance, setting \( j_{B,0} \) equal to the saturation current given by radiative recombination allows for a connection to a general upper conversion limit, as described by the Shockley-Queisser model. Note further that by identifying \( j_B \) with \( j_s \), neglecting \( j_m \), and linearizing \( J_M \), Figure 1f turns into Figure 1c (i.e., the BP case). This is however only possible for small variations of the majority carrier densities from the equilibrium value.

Figure 7b shows the output power and the external and internal open circuit voltages for the combined model (analogous to Figure 6a for the REM model). Here, we see that adding an additional loss channel via the internal recombination diode \( j_B \) (Figure 1f) limits the internal open circuit voltage \( V_{OC}^{int} \) according to its saturation current density \( j_{B,0} = 5.5 \times 10^{-14} \text{ mA cm}^{-2} \), a value that corresponds to the radiative recombination limit for a band gap energy of 1.12 eV (compatible with \( J_{SC} = 43.6 \text{ mA cm}^{-2} \) and \( V_{th} = 25.7 \text{ mV} \)). As can be seen from Figure 7b, this added recombination channel defines an optimum for the output power at finite values of the inverse majority carrier saturation density \( 1/J_{M,0} \). With decreasing \( \Sigma_k \), this optimum shifts toward higher values of \( 1/J_{M,0} \) because of the higher recombination losses caused by the correspondingly higher values of \( J_{M,0} / \Sigma_k \). It is also seen that considerable differences between the internal \( V_{OC}^{int} \) and the externally measured \( V_{OC} \) are possible as an important feature of the REL model. However, unlike in Figure 7a, the values of \( V_{OC}^{int} \) are now limited to values below 881 mV, corresponding to the radiative limit. Note that other limitations by bulk recombination can be introduced by a choice of \( J_{B,0} \) larger than the radiative value.
6. Selectivity and Photocurrent Collection Efficiency

Up to now, experimental data on the selectivity of contacts to solar cells, with a focus on silicon wafer based solar cells, have been gained from separate measurements of contact resistivity and interface recombination.[31,49–51] Here, we stress that the selectivity in both versions[31,32] is closely correlated to the current transport efficiency defined by Wong and Green[34] (also called photocurrent collection efficiency). This quantity is defined as the derivative of the current \( j \) (collected at the solar cell terminals at constant external voltage) with respect to the internally generated short circuit current \( j_L \) according to

\[
\eta_{PC} := \frac{dj}{dj_L} \quad (13)
\]

The photocurrent collection efficiency must clearly be related to the contact selectivities defined above: If a contact is highly selective and \( V \) is small enough that bulk recombination is negligible, \( dj = dj_L \) and \( \eta_{PC} = 1 \). If a contact is however less selective an increase in the internally generated \( j_{SC} \) might not lead to the same increase in \( j_{cont} \) because some of the internally generated charge carriers recombine at the wrong contact.

Measurements of \( \eta_{PC} \) rely on the network theorem of Wong and Green[44] that states that the local photocurrent collection efficiency \( \eta_{PC} \) equals the differential change \( \Delta V_{loc} \) of the local voltage across the junction with respect to a change \( dV \) of the external voltage. Hence, we have

\[
\eta_{PC} = \frac{\Delta V_{loc}}{dV} \quad (14)
\]

With this, \( \eta_{PC} \) becomes measurable by electro-modulated luminescence measurements because of the dependence of the luminescence emission on the local junction voltage as described by the optoelectronic reciprocity relation.[52] Thus, using electroluminescence images at different external voltages allows one to obtain \( V_j \) from the absolute electroluminescence intensity and compute the derivative given by Equation (14). Given that electroluminescence can also easily be performed using imaging systems (providing a local \( V_j \)), the collection efficiency is then accessible also as a function of position on the solar cell. Experimentally, this opportunity has been demonstrated in various publications for crystalline silicon solar cells[53,54] for a GaAs solar cell[55] and for a Cu(In,Ga)Se₂ module.[61] Moreover the local measurement values can be averaged over the cell area to yield a global value \( \eta_{PC}^{glob} \).[35]

Thus, a powerful toolbox for the analysis of the different variants of the current collection efficiency measurable directly at a working device is available. In the following we use a linearization of the equivalent circuit of our extended selectivity model as shown in Figure 8 to derive relationships between the selectivities \( \Sigma \) and \( \Sigma \), on the one side and the photocurrent collection efficiency \( \eta_{PC} \) on the other side. It is important to stress that the collection efficiency \( \eta_{PC} \) is a differential quantity, i.e., only defined for small variations around a given bias point. Therefore, we need analogous, differential, definitions for \( \Sigma \) and \( \Sigma \). Therefore, we determine the differential selectivities from the linearized equivalent circuit model in Figure 8: \( \Sigma_k := R_k/(R_{in}^{(1)} + R_k^{(1)}) \), \( \Sigma_k^{(2)} := R_k^{(2)}/R_{in}^{(2)} \), and \( \Sigma_k^{loc} := R_k^{loc}/R_{in}^{loc} \). We note, that these differential values are not identical to the (saturation) values defined by Equations (2) and (6). An extensive analysis of the linearized model is performed in the Supporting Information. We mention here only the results for the BP model and the REL model as the limiting cases of the extended model. For the resistive BP model, the global differential photocurrent collection efficiency is given by

\[
\eta_{PC}^{glob} = \frac{\Sigma_r}{1 + \Sigma_{loc}} \quad (15)
\]

Thus, \( \eta_{PC}^{glob} \) and \( \Sigma_r \) are interrelated by a simple function with \( \eta_{PC}^{glob} \rightarrow 1 \) if \( \Sigma_{loc} \rightarrow \infty \) and \( \eta_{PC}^{glob} \rightarrow 0 \) if \( \Sigma_{loc} \rightarrow 0 \), as one may expect. Analogously, we find for the REL limit of the extended model for the perfect-antisymmetric case \( (R_{in}^{(2)} = R_{in}^{(1)} \) and \( R_k^{(2)} = R_k^{(1)}) \)

\[
\eta_{PC}^{glob} = \left( \frac{\Sigma_r}{1 + \Sigma_{loc}} \right)^{-1} \quad (16)
\]

with \( \Sigma_r = \Sigma_r^{(1)} = \Sigma_r^{(2)} \). The asymptotic behavior for \( \Sigma_{loc} \rightarrow \infty \) of Equation (16) equals that of Equation (15), namely \( \eta_{PC}^{glob} \rightarrow 1 \). Interestingly, we find in the other limit \( \Sigma_{loc} \rightarrow 0 \) a collection efficiency \( \eta_{PC}^{glob} \rightarrow \infty \). This behavior results from a mathematical symmetry within the REL model that allows interchanging the role of minority and majority carriers resulting in an inversion of the direction of the photocurrent as discussed in more detail in the Supporting Information.[56–58]

From the above considerations we would expect that determination of \( \eta_{PC} \) at various voltage and illumination bias conditions should give enough information to draw conclusions whether a given device follows the BP model, the REL model, or the extended model. We would also expect that the corresponding contact selectivities can be determined quantitatively.

7. Conclusion

The present paper has highlighted the importance of a quantitative description of contacts to photovoltaic absorber materials. We have shown that the two distinct definitions for the contact selectivity[31,32] that have been proposed recently are based on two substantially different assumptions and consequently cover rather different situations. To both approaches we have added useful analytical solutions that facilitate their general applicability. We have further proposed to combine the two models into a more general concept. We have shown that the built-in voltage of a solar cell is an important factor directly influencing the selectivity in both models. Thereby we have settled a long-standing debate on the importance of the built-in voltage for photovoltaic functionality. Finally, we have shown that the global photocurrent collection efficiency \( \eta_{PC} \), a quantity that is accessible by experiments, has direct mathematical relations to both definitions for the contact selectivity. Therefore, we have shown how the applicability of the models can be tested by future experiments.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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