Reciprocity and open circuit voltage in solar cells

Tom Markvart
Engineering Sciences, University of Southampton, Southampton SO17 1BJ, UK, and
Centre for Advanced Photovoltaics, Czech Technical University, 166 36 Prague 6, Czech Republic

Abstract The equation for open-circuit voltage of a solar cell based on optoelectronic reciprocity is combined with the standard textbook formula to obtain a general result which includes photon recycling as well as losses by carrier transport. It is shown that, in indirect-gap semiconductors, the general expression reduces to the “conventional” and “optoelectronic” expressions in the limits of low and high radiative efficiency.

Statistical and thermodynamic techniques are providing new tools to underpin as well as probe the fundamentals of photovoltaic conversion. These include, for example, the reciprocity of carrier transport in solar cells[1,2] (which augments an earlier version by Shockley[3]), the principle of optoelectronic reciprocity[4] (discussed also in ref. [5]for a monochromatic converter) and the generation of optical entropy in the conversion of non-concentrated sunlight.[6] These techniques generally focus on the voltage generated by the solar cell rather than on kinetic properties such as current.

By using optoelectronic reciprocity, Rau[4] obtained an expression for the open circuit voltage V_{OC} of a solar cell based on the quantum efficiency of the cell Q_{LED} when operated as a light-emitting diode (see also ref. 7):

$$qV_{OC} = qV_{OC}^{rad} + k_B T_o ln Q_{LED} \qquad (1)$$

where V_{OC}^{rad} is the open-circuit voltage in the radiative limit (in the absence of nonradiative recombination), k_B is the Boltzmann constant, q is the electron charge and T_o is the cell temperature. Since the quantum efficiency Q_{LED} is given by the balance between the quantum yield of luminescence and the probability of photon reabsorption (recycling), Eq. (1) has been used in application to materials with high radiative efficiency, usually direct-bandgap semiconductors. Equation (1), however, does not capture characteristics determined by charge carrier transport in the solar cell.

Equation (1) can be contrasted with the expression

$$qV_{OC} = k_B T_o ln\left(\frac{I_{ph}}{I_o} + 1\right) \qquad (2)$$

obtained in standard texts on solar cell theory,[8,9,10] where I_{ph} and I_o are the photogenerated and dark saturation currents, respectively, determined by solving the carrier transport equations. Unlike the parameters which enter Eq. (1), the currents I_{ph} and I_o depend on the minority carrier diffusion lengths and possibly also on other minority carrier transport parameters, as discussed in detail in most textbooks (see, for example, refs. 8,9,10 and Eqs. (20) and (21) below). The natural question then arises about the relationship between Eqs. (1) and (2).

By taking into account both carrier transport and features associated with photon emission / reabsorption and nonradiative recombination, in this note we obtain an expression for the open-circuit voltage which combines Eqs. (1) and (2) and extends the applicability of the optoelectronic expression (1) to materials with low radiative efficiency such as silicon.

To begin with we define the relevant quantities. The photon flux of black-body radiation at temperature T passing through a unit perpendicular area per unit solid angle per unit frequency (ν) per unit time is given by (see e.g. ref. 11)

$$\phi_{bb}(\nu,T) = \frac{2(\nu/c)^2}{e^{h\nu/k_BT}-1} \qquad (3)$$

where h is the Planck constant, k_B is the Boltzmann constant and c is the speed of light. Perceiving solar radiation as due to a black body at temperature $T_S \approx 5800$K, the total photon flux Φ_S incident on the cell and the total black-body photon flux Φ_o^{bb} at temperature T_o are given by

$$\Phi_S = \omega_S A \int_{Eg/h}^{\infty} \phi_{bb}(\nu,T_S)\, d\nu \qquad (4)$$

$$\Phi_o^{bb} = \pi A \int_{Eg/h}^{\infty} \phi_{bb}(\nu,T_o)\, d\nu \qquad (5)$$

where A is the area of the cell and ω_S is the solid angle subtended by the Sun ($6.85\text{x}10^{-5}$ sterad). We also define the average integrated quantum efficiencies EQE_S and EQE_o for the incident and emitted radiation:

$$EQE_{o,S} = \frac{\int_{Eg/h}^{\infty} EQE(\nu)\phi_{bb}(\nu,T_{o,S})d\nu}{\int_{Eg/h}^{\infty} \phi_{bb}(\nu,T_{o,S})d\nu} \qquad (6)$$

where $EQE(\nu)$ is the external quantum efficiency of the cell at frequency ν.

Thus equipped, we can use the optoelectronic reciprocity[4] to write the photon flux emitted by an LED or solar cell on application of voltage V in the form

$$\Phi_o^{cell} = \pi A$$

$$\left(e^{qV/k_BT_o}-1\right)\int_{Eg/h}^{\infty} EQE(\nu)\phi_{bb}(\nu,T_o)\, d\nu =$$
$$= EQE_o\Phi_o^{bb}\left(e^{qV/k_BT_o}-1\right) \qquad (7)$$

At the same time, the solar cell/ LED produces current given by the usual ideal diode equation[8]

$$I = I_o\left(e^{qV/k_BT_o}-1\right) \qquad (8)$$

Since the quantum efficiency of the LED is defined by

$$Q_{LED} = \frac{q\Phi_o^{cell}}{I} \qquad (9)$$

the dark saturation current I_o can be determined in terms of a ratio of the two quantum efficiencies, of the solar cell and LED:

$$I_o = q\frac{EQE_o}{Q_{LED}}\Phi_o^{bb} \qquad (10)$$

In a similar fashion we can write, for the photogenerated current I_{ph}

$$I_{ph} = qEQE_S\Phi_S \qquad (11)$$

Inserting (10) and (11) into (2) and neglecting the unity in the argument of the logarithm we obtain

$$qV_{OC} = k_BT_o ln\left(\frac{\Phi_S}{\Phi_o^{bb}}\right) + k_BT_o ln\left(\frac{EQE_S}{EQE_o}\right) +$$
$$+ k_BT_o lnQ_{LED} \qquad (12)$$

The first term in (12) is just the open-circuit voltage of an ideal solar cell, as given by the Shockley-Queisser detailed balance[12] and the last term corresponds to a similar term in Eq. (1). The second term extends expression (1) to include carrier transport features contained in the photovoltaic EQE's. When there are no carrier transport losses, EQE_S reduces to the absorptivity of the cell for incident radiation, and EQE_o to the emissivity (and by Kirchhoff's law, to the absorptivity) of the emitted radiation at the temperature of the solar cell. The sum of the first two terms then becomes the open-circuit voltage in the radiative limit and Eq. (12) reduces to Eq. (1).

An equation equivalent to (12) also follows from Eq. (10) in ref. 13 by introducing the quantum efficiencies but is given here with a different emphasis and interpretation. As will be shown further below, the meaning of the second and third terms in (12) can be understood best in the limits of low and near-unit internal quantum efficiency Q. The second term then represents the "round-trip" losses in the carrier transport in the "traditional" picture of solar cell operation under open circuit voltage, from carrier generation → transport to junction → transport to the recombination site. The third term, on the other hand, describes photon emission and "outcoupling" of light from the solar cell. The key concept in this term is photon recycling (elucidated with particular clarity by Martí et al.[14] and discussed in the context of the present paper by Rau et al.[15]). It is worth noting that, in the presence of nonradiative recombination, photon recycling hinders the escape of photons from the structure and enhances nonradiative losses (see also ref. 15).

It is of interest to see how Eq. (12) and, in particular, the expression (10) for the dark saturation current I_o , compare with the result given in standard texts on solid-state diodes and solar cells (see, for example, ref. 8):

$$I_o = qR_o \tag{13}$$

where R_o, if multiplied by the voltage factor in (8), is the total recombination rate integrated over the volume. To bring Eqs. (10) and (13) into closer correspondence we write the reciprocity theorem for charge carrier transport to the radiative component of R as

$$R_{o,rad} = \int \frac{p_o}{\tau_{rad}} \eta_{col} d\mathcal{V} \tag{14}$$

where p_o is the equilibrium minority-carrier density. With the use of (14), the dark saturation current (13) becomes

$$I_o = q\frac{R_{o,rad}}{Q} \tag{15}$$

where Q is the quantum yield for photon emission

$$Q = \frac{R_{o,rad}}{R_o} \tag{16}$$

To progress we need to examine more closely Eq. (14) for the radiative recombination rate. To this end we note that $\mathcal{V}\, p_o/\tau_{rad}$ is the total rate of radiative recombination events in thermal equilibrium. The resulting thermal photon flux emitted by the cell can be equated to $\varepsilon\Phi_o^{bb}$, where ε is the emissivity which, by Kirchhoff's law, is equal to the absorptivity a. Since internally emitted photons will be emitted to the exterior of the structure unless reabsorbed (with average probability r, say), we can write

$$(1-r)\mathcal{V}\, p_o/\tau_{rad} = a\, \Phi_o^{bb} \tag{17}$$

which transforms, with the use of (14), equation (15) into

$$I_o = \frac{q}{Q(1-r)} a\langle\eta_{col}\rangle\Phi_o^{bb} \tag{18}$$

where

$$\langle\eta_{col}\rangle = \frac{1}{\mathcal{V}}\int \eta_{col}\, d\mathcal{V} \tag{19}$$

is the average collection probability.

Equation (18) provides a clear link between the more general Eq. (10) for I_o and the standard textbook expression (13): Eq. (18) represents an approximation valid in the limit of low radiative efficiency when reabsorption of radiation outside the "escape cone" (and not trapped by total internal reflection) can be neglected. Indeed, the factor $Q(1 - r)$ is an approximation for Q_{LED} in the limit of small Q,[16] and it can readily be shown from the definition that $EQE(\alpha)$ becomes $a\langle\eta_{col}\rangle$ in the limit of small absorption coefficient α. The reabsorption probability r then includes only contributions from radiation trapped by total internal reflection.

Figure 1 illustrates the results considered in this paper for the open circuit voltage in silicon as a function of the quantum yield Q (Eqs. (1) and (13), and V_{oc} obtained by substituting Eq. (18) into (2); we assumed, for simplicity, that EQE_S for the incident light is equal to unity). Neglecting surface recombination, the standard results for I_o and $EQE(\alpha)$ are[10]

$$I_o = Aqp_o\frac{D}{L}tanh\left(\frac{W}{L}\right) \tag{20}$$

$$EQE(\alpha) =$$

$$= \frac{\alpha L}{1-\alpha^2 L^2}\left\{tanh\left(\frac{W}{L}\right) - \alpha L\left(1 - \frac{e^{-\alpha W}}{cosh\left(\frac{W}{L}\right)}\right)\right\} \underset{\alpha\to 0}{\longrightarrow} \alpha L\, tanh\left(\frac{W}{L}\right) \qquad (21)$$

where L and D are the minority-carrier diffusion length and diffusion constant, and W is the thickness of the quasi-neutral region. In this case, typical for indirect-gap semiconductors, the two formulas (1) and (2) combined with (14) provide an accurate description of the open-circuit voltage in the two overlapping regions of small and near-unit values of Q, with the more general formula (12) providing a more complete overarching picture. The situation becomes more complicated for direct-gap semiconductors where photons may contribute towards carrier / energy transport to the junction, and there is no clear separation between the two approximate limiting formulae.

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Figure caption

Fig. 1. The open circuit voltage as given by the three different theories considered in this paper. $V_{oc}(SQ)$ denotes the ideal open circuit voltage under one-sun illumination, as given by the Shockley-Queisser theory.

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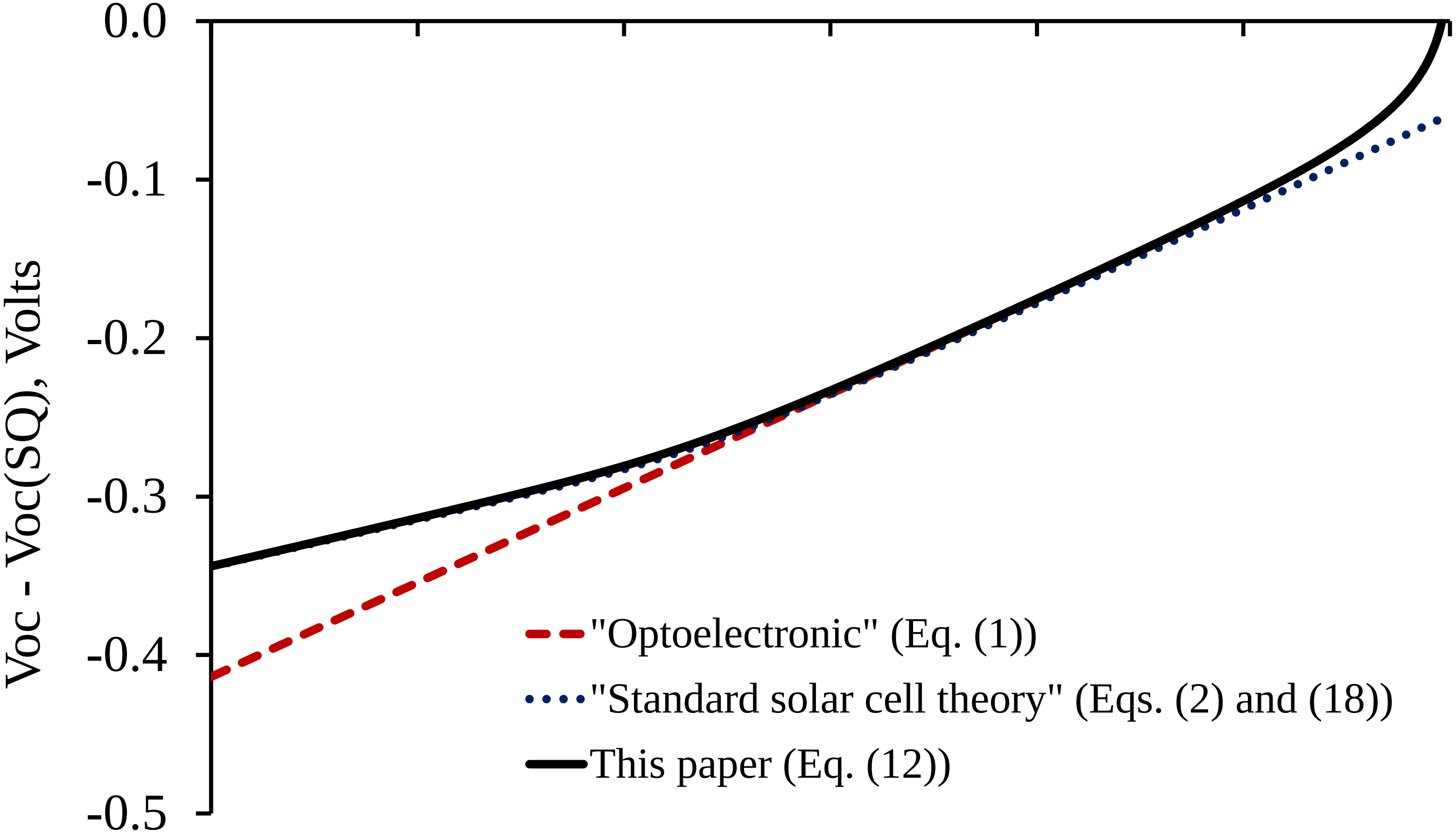
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
Voc - Voc(SQ), Volts
"Optoelectronic" (Eq. (1))
"Standard solar cell theory" (Eqs. (2) and (18))
This paper (Eq. (12))