

# Ideal solar cell equation in the presence of photon recycling

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Previous derivations of the ideal solar cell equation based on Shockley's  $p$ - $n$  junction diode theory implicitly assume negligible effects of photon recycling. This paper derives the equation in the presence of photon recycling that modifies the values of dark saturation and light-generated currents, using an approach applicable to arbitrary three-dimensional geometries with arbitrary doping profile and variable band gap. The work also corrects an error in previous work and proves the validity of the reciprocity theorem for charge collection in such a more general case with the previously neglected junction depletion region included. © 2014 AIP Publishing LLC.

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## I. INTRODUCTION

As a classical theory in the field of semiconductor physics, the well-known Shockley ideal diode equation<sup>1</sup> gives the dark current-voltage characteristics of ideal  $p$ - $n$  junction diodes. It was established by Shockley from a particular model with the following assumptions:<sup>1</sup> (A1) Ohmic voltage drops are negligible; (A2) the junction depletion region is narrow compared to the carrier diffusion lengths, and the changes in electron and hole currents traversing in this region are negligible; (A3) the abrupt depletion-layer approximation applies (i.e., the built-in potential and the applied voltage are sustained by a dipole layer with abrupt boundaries, and outside the dipole layer the semiconductor is quasi-neutral with negligible electric field); (A4) the low-injection condition holds in quasi-neutral regions (QNRs), where constancy of material parameters with injection level is also assumed; (A5) the Boltzmann approximation for carrier distributions is valid; (A6) the properties, in particular the doping density, are uniform in each QNR. In addition, light plays no role in Shockley's original<sup>1</sup> treatment, implying (A7) the neglect of photon recycling effects. Photon recycling is the phenomenon by which a photon generated by radiative recombination is subsequently reabsorbed. Its importance has been recognized and studied in several works<sup>2–8</sup> especially for III–V compound semiconductors. In particular, Marti *et al.*<sup>6</sup> showed that the neglect of photon recycling effects in Shockley's  $p$ - $n$  junction diode theory<sup>1</sup> is the main cause for the discrepancy between its predicted light current-voltage characteristic and that used in the detailed balance theory<sup>9</sup> to calculate the limiting efficiency of  $p$ - $n$  junction solar cells.

The original theory<sup>1</sup> has been extended by several<sup>10–12</sup> authors. However, light generally continues to play no role in such work except as a source of generation of photocurrent. It is unclear whether the ideal solar cell equation still holds in the presence of photon recycling. The present work

investigates the derivation of the ideal solar cell equation in this case using an approach applicable to arbitrary three-dimensional geometries with arbitrary doping profile and variable band gap, removing assumptions (A6) and (A7) from the previously listed assumptions. In the meanwhile, the present work identifies an error in the previous<sup>7</sup> work and shows that the reciprocity theorem for charge collection<sup>13</sup> also applies in the presence of photon recycling even with the previously<sup>7,13–17</sup> neglected junction depletion region included.

## II. GOVERNING EQUATIONS

Under Boltzmann statistics, the electron and hole current densities,  $\mathbf{J}_n$  and  $\mathbf{J}_p$ , can be most fundamentally expressed in terms of the gradients of the corresponding quasi-Fermi levels,  $E_{fn}$  and  $E_{fp}$ , for both non-degenerate materials and degenerate materials with non-uniform band structure:<sup>18,19</sup>

$$\mathbf{J}_n = n\mu_n \nabla E_{fn}, \quad (1a)$$

$$\mathbf{J}_p = p\mu_p \nabla E_{fp}, \quad (1b)$$

where  $n$  and  $p$  are the carrier concentrations and  $\mu_n$  and  $\mu_p$  are the carrier mobilities.

When both carrier concentrations are non-degenerate,

$$pn = p_0 n_0 \exp[(E_{fn} - E_{fp})/(kT)], \quad (2)$$

where  $p_0$  and  $n_0$  are the equilibrium carrier concentrations,  $k$  and  $T$  are the Boltzmann constant and temperature in Kelvin, respectively. This equation is also applicable to degenerate materials provided that the majority carrier concentration does not differ significantly from its thermal equilibrium value as can be deduced from assumptions (A1) and (A4).

Defining  $\omega(\mathbf{r})$  as a normalized excess carrier concentration product,

$$\omega(\mathbf{r}) = [p(\mathbf{r})n(\mathbf{r}) - p_0(\mathbf{r})n_0(\mathbf{r})]/[p_0(\mathbf{r})n_0(\mathbf{r})], \quad (3)$$

it follows from Eq. (2) that

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$$\omega(\mathbf{r}) = \exp[(E_{fn} - E_{fp})/(kT)] - 1. \quad (4)$$

Previous<sup>7,8,16,17,19</sup> work used a normalized excess minority-carrier concentration  $u(\mathbf{r})$ , with  $u(\mathbf{r}) = [p(\mathbf{r}) - p_0(\mathbf{r})]/p_0(\mathbf{r})$  in the n-type QNR, to analyze non-uniformly doped material, as it is an excellent approximation to  $\omega(\mathbf{r})$  in QNRs incorporating the previously mentioned assumption regarding the majority carriers. It will be shown later that one advantage of the present parameterization is its applicability to the entire junction depletion region, denoted by  $\mathcal{J}$  in shorthand form hereafter.

Manipulating Eqs. (1a) and (1b) and combining with Eq. (4) gives

$$\mathbf{J}_p - \mathbf{J}_n \mu_p p / (\mu_n n) = -q D_p (p_0 n_0 / n) \nabla \omega, \quad (5)$$

where  $D_p$  is the hole diffusivity related to  $\mu_p$  by the Einstein relation ( $D_p = kT\mu_p/q$ ) for non-degenerate materials, with  $q$  being the electronic charge. Provided  $|\mathbf{J}_p| \gg \mu_p p |\mathbf{J}_n| / (\mu_n n)$  and  $n \approx n_0$ , as is warranted in the n-type QNR with the present assumptions, the minority-carrier current density is given by

$$\mathbf{J}_p = -q D_p p_0 \nabla \omega. \quad (6)$$

In the presence of photon recycling, the steady-state hole continuity equation is written as

$$\nabla \cdot \mathbf{J}_p / q + U = G_e + G_r, \quad (7)$$

where  $U$  is the net recombination rate, while  $G_e$  and  $G_r$  are the photo-generation rates caused by external illumination and photons from internal radiative recombination, respectively. Note that  $U$ ,  $G_e$ , and  $G_r$  can all be arbitrary functions of position.

$U$  is the sum of the transition rates for band-to-band recombination ( $U_b$ ), which involves radiative ( $U_R$ ) and/or Auger process ( $U_A$ ), and recombination through defects ( $U_t$ ).<sup>20</sup> Invoking assumption (A4) but using present notation, in QNRs, both  $U_b$  and  $U_t$  and hence  $U$  are assumed linear with  $\omega$ , i.e.,  $U_b = \beta_b \omega$ ,  $U_t = \beta_t \omega$ , and  $U = (\beta_b + \beta_t) \omega$ , with  $\beta_b$  and  $\beta_t$  and hence  $\beta_b + \beta_t$  independent of  $\omega$  [but can be position-dependent in this work]. Inside  $\mathcal{J}$ , however,  $\beta_t$  decreases with  $\omega$  and  $U_t$  is no longer linear with  $\omega$ , while  $U_b$  remains linear with  $\omega$  because  $U_R$  remains linear and  $U_A$  is negligible<sup>21</sup> [such 3-body interactions are exceedingly rare inside  $\mathcal{J}$  due to the low carrier concentrations].

In a previous<sup>7</sup> analysis of  $G_r$ , Rau<sup>7</sup> used  $\gamma_{\text{eq}}(\mathbf{r}_b, \mathbf{r}_a)$  to represent the equilibrium generation rate (per unit volume and energy interval) at  $\mathbf{r}_b$  due to photons of energy  $E_\gamma$  emitted from  $\mathbf{r}_a$  and showed that  $\gamma_{\text{eq}}(\mathbf{r}_b, \mathbf{r}_a) = \gamma_{\text{eq}}(\mathbf{r}_a, \mathbf{r}_b)$ . The corresponding formula for non-equilibrium generation was found as<sup>7</sup>  $\gamma(\mathbf{r}_b, \mathbf{r}_a) = \gamma_{\text{eq}}(\mathbf{r}_b, \mathbf{r}_a) u(\mathbf{r}_a)$ . Rau<sup>7</sup> then integrated  $\gamma(\mathbf{r}_b, \mathbf{r}_a)$  to obtain the energy-independent non-equilibrium generation rate  $\kappa(\mathbf{r}_b, \mathbf{r}_a) = \int \gamma(E_\gamma, \mathbf{r}_b, \mathbf{r}_a) dE_\gamma$  and concluded that  $\kappa(\mathbf{r}_b, \mathbf{r}_a) = \kappa(\mathbf{r}_a, \mathbf{r}_b)$  because of the symmetry  $\gamma(\mathbf{r}_b, \mathbf{r}_a) = \gamma(\mathbf{r}_a, \mathbf{r}_b)$ . However,  $\gamma(\mathbf{r}_b, \mathbf{r}_a) \neq \gamma(\mathbf{r}_a, \mathbf{r}_b)$  unless  $u(\mathbf{r}_a) = u(\mathbf{r}_b)$ . In practice, an offset between  $u(\mathbf{r}_a)$  and  $u(\mathbf{r}_b)$  can be present due to different rates of increase with applied voltage at different distances from the junction edge. This error invalidates the

associated argument after Eq. (19) in Rau's original<sup>7</sup> work. [The conclusions of this work<sup>7</sup> are undoubtedly correct but, due to this error, are as yet unproved.]

In the present analysis,  $\kappa(\mathbf{r}_b, \mathbf{r}_a)$  is reformulated as the *equilibrium* generation rate at  $\mathbf{r}_b$  due to photon emission at  $\mathbf{r}_a$

$$\kappa(\mathbf{r}_b, \mathbf{r}_a) = \int \gamma_{\text{eq}}(E_\gamma, \mathbf{r}_b, \mathbf{r}_a) dE_\gamma. \quad (8)$$

It now follows the symmetry of  $\gamma_{\text{eq}}$  that  $\kappa(\mathbf{r}_b, \mathbf{r}_a) = \kappa(\mathbf{r}_a, \mathbf{r}_b)$ , i.e., the present  $\kappa$  redefined by Eq. (8) is symmetric. Also,  $\gamma(\mathbf{r}_b, \mathbf{r}_a)$  is reformulated by replacing  $u$  by the more general parameter  $\omega$ , i.e.,  $\gamma(\mathbf{r}_b, \mathbf{r}_a) = \gamma_{\text{eq}}(\mathbf{r}_b, \mathbf{r}_a) \omega(\mathbf{r}_a)$ , to accommodate radiative recombination in  $\mathcal{J}$ . Correspondingly, the energy-independent non-equilibrium generation rate becomes

$$\int \gamma(E_\gamma, \mathbf{r}_b, \mathbf{r}_a) dE_\gamma = \kappa(\mathbf{r}_b, \mathbf{r}_a) \omega(\mathbf{r}_a). \quad (9)$$

Accounting for radiative recombination within the whole volume,  $\mathbb{V}$ , of the absorber,

$$G_r(\mathbf{r}) = \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega(\mathbf{r}') dV' \quad (10)$$

with  $dV'$  being the volume element at  $\mathbf{r}'$ .

To recapitulate, Eq. (7) incorporates the effects of photon recycling and is applicable to three-dimensional geometries with arbitrary doping profile and variable band gap. On the right of Eq. (7),  $G_r(\mathbf{r})$  accounts for photon recycling and is linear with  $\omega(\mathbf{r}')$ , i.e., non-local injection levels, in the whole volume of the device. However, both terms on the left,  $\nabla \cdot \mathbf{J}_p / q$  and  $U$ , are linear with  $\omega$  only in QNRs. Such linearity is not warranted inside  $\mathcal{J}$ . Therefore, the junction depletion edge divides the absorber into linear and nonlinear domains for Eq. (7).

The n-type QNR is bounded by three different types of surface regions, namely the junction depletion edge, contact regions, and the remaining exposed surface regions that may include features such as internal voids.<sup>17</sup> Inside  $\mathcal{J}$ ,  $E_{fn}$  and  $E_{fp}$  remain relatively constant in all but the poorest quality materials and their separation is controlled by the junction voltage,<sup>20</sup>  $V_J$ , giving

$$\omega_J = \exp[qV_J/(kT)] - 1. \quad (11)$$

Assuming negligible voltage drop along the junction depletion edge,  $\omega_J$  is constant with position in the junction region under a certain bias. Non-junction regions are under the assumed low-injection condition with surface regions able to be described in terms of a surface recombination velocity,  $S_{p0}$ , that can be position-dependent but is also assumed independent of  $\omega$

$$\mathbf{J}_p \cdot \hat{\mathbf{n}} = q p_0(\mathbf{r}) S_{p0}(\mathbf{r}) \omega(\mathbf{r}), \quad (12)$$

where  $\hat{\mathbf{n}}$  is a unit vector in the outward normal direction at the boundary point.

With these formulations, the whole system is linear in  $\omega$  in the QNR, i.e., if  $\omega_1$  and  $\omega_2$  are solutions under junction boundary conditions  $\omega_{J1}$  and  $\omega_{J2}$ , and external generation profiles  $G_{e1}$  and  $G_{e2}$ ,  $\omega_1 + \lambda\omega_2$  will be a solution under junction boundary condition  $\omega_{J1} + \lambda\omega_{J2}$  and external generation profile  $G_{e1} + \lambda G_{e2}$ , where  $\lambda$  is an arbitrary constant.

### III. DERIVATION OF RESULTS

In shorthand form, following Green,<sup>17</sup> the left-hand side of Eq. (7) is written as  $\mathcal{L}(\omega)$ . Consider two distinct solutions: (i)  $\omega_D$  for the dark diode under arbitrary  $V_{DJ}$ ; (ii)  $\omega_L$  for the illuminated diode under arbitrary  $V_{LJ}$ . The assumed narrow width of the junction depletion region in assumption (A2) implies negligible effects of junction edge movement under different bias. In the n-type QNR where  $\mathbf{J}_p$  is given by Eq. (6), forming the unusual product below allows the second term on the left of Eq. (7) to be eliminated

$$\begin{aligned}\omega_D \mathcal{L}(\omega_L) - \omega_L \mathcal{L}(\omega_D) &= -\nabla \cdot [Dp_0(\omega_D \nabla \omega_L - \omega_L \nabla \omega_D)] \\ &= \nabla \cdot (\omega_D \mathbf{J}_{pL} - \omega_L \mathbf{J}_{pD})/q.\end{aligned}\quad (13a)$$

Inside the n-type junction depletion region,  $\omega_D \nabla \cdot \mathbf{J}_{pL} = \nabla \cdot (\omega_D \mathbf{J}_{pL})$  as  $\omega_D = \omega_{DJ}$ , a constant,  $\omega_D U_L = \omega_D (U_{iL} + \beta_b \omega_L) = \omega_D U_{iL} + \omega_L U_{bD}$  and  $\mathcal{L}(\omega_D) = G_r$ , giving within this region

$$\begin{aligned}\omega_D \mathcal{L}(\omega_L) - \omega_L \mathcal{L}(\omega_D) &= \nabla \cdot (\omega_D \mathbf{J}_{pL})/q + \omega_D U_{iL} + \omega_L U_{bD} \\ &\quad - \omega_L \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_D(\mathbf{r}') \partial V' dV'.\end{aligned}\quad (13b)$$

Integrating the unusual product over the entire n-type region,  $\mathbb{V}_N$ , including its QNR,  $\mathcal{D}_N$ , and its junction depletion region,  $\mathcal{J}_N$ , and utilizing the divergence theorem gives

$$\begin{aligned}q \int_{\mathbb{V}_N} [\omega_D \mathcal{L}(\omega_L) - \omega_L \mathcal{L}(\omega_D)] dV &= \int_{\mathcal{D}_N + \mathcal{J}_N} \nabla \cdot (\omega_D \mathbf{J}_{pL}) dV - \int_{\mathcal{D}_N} \nabla \cdot (\omega_L \mathbf{J}_{pD}) dV + q \int_{\mathcal{J}_N} [\omega_D U_{iL} + \omega_L U_{bD} \\ &\quad - \omega_L \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_D(\mathbf{r}') \partial V' dV'] dV \\ &= \omega_{DJ} \int_{S_0} \mathbf{J}_{pL} \cdot \hat{\mathbf{n}} ds - \omega_{LJ} \int_{S_N} \mathbf{J}_{pD} \cdot \hat{\mathbf{n}} ds + q \omega_{LJ} \int_{\mathcal{J}_N} [U_{bD} \\ &\quad - \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_D(\mathbf{r}') \partial V' dV] dV + q \omega_{DJ} \int_{\mathcal{J}_N} U_{iL} dV,\end{aligned}\quad (14)$$

where  $S_0$  is the boundary where  $n = p$  lying within  $\mathcal{J}$  and  $S_N$  is the n-type junction depletion edge. Note that, in Eq. (14), surface integrals of  $\omega_D \mathbf{J}_{pL}$  and  $\omega_L \mathbf{J}_{pD}$  over non-junction regions annihilate each other because each term equals  $qp_0 S_{p0} \omega_D \omega_L$  by invoking Eq. (12). As surface states can be treated similarly to bulk defects, extra surface integral contributions from integrating  $\omega_D \mathbf{J}_{pL}$  over exposed junction regions can be incorporated into  $q \omega_{DJ} \int_{\mathcal{J}_N} U_{iL} dV$ .

Since  $\mathcal{L}(\omega_L) = G_e + G_r(\omega_L)$  and  $\mathcal{L}(\omega_D) = G_r(\omega_D)$ , the volume integral on the left can be alternatively written as

$$q \int_{\mathbb{V}_N} [\omega_D \mathcal{L}(\omega_L) - \omega_L \mathcal{L}(\omega_D)] dV = q \int_{\mathbb{V}_N} \omega_D G_e dV + q \mathcal{K}_N, \quad (15a)$$

where

$$\begin{aligned}\mathcal{K}_N &= \int_{\mathbb{V}_N} (\omega_D(\mathbf{r}) \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_L(\mathbf{r}') \partial V' dV' \\ &\quad - \omega_L(\mathbf{r}) \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_D(\mathbf{r}') \partial V' dV') dV.\end{aligned}\quad (15b)$$

Combining Eqs. (14) and (15a),

$$\begin{aligned}q \int_{\mathbb{V}_N} (\omega_D / \omega_{DJ}) G_e dV + (q / \omega_{DJ}) \mathcal{K}_N &= \int_{S_0} \mathbf{J}_{pL} \cdot \hat{\mathbf{n}} ds - (\omega_{LJ} / \omega_{DJ}) \int_{S_N} \mathbf{J}_{pD} \cdot \hat{\mathbf{n}} ds \\ &\quad + q (\omega_{LJ} / \omega_{DJ}) \int_{\mathcal{J}_N} [U_{bD} - \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_D(\mathbf{r}') \partial V' dV] dV + q \int_{\mathcal{J}_N} U_{iL} dV.\end{aligned}\quad (16)$$

In Eq. (16),  $\mathbf{J}_{pD} / \omega_{DJ}$  is constant with varying  $\omega_{DJ}$  due to the linearity of the governing equations in the QNR. Its value can be found by considering the case where  $\omega_{DJ} = -1$ , i.e.,

the diode is in the dark under a large reverse bias. The current flowing into the junction in this case is the dark saturation current density contribution from the n-type QNR,  $I_{oN}$ .

Similarly, the third term on the right equals  $\omega_{LJ}$  multiplied by a constant. In more detail,  $q[U_{bD} - G_r(\omega_D)]/\omega_{DJ} = q\beta_b - qG_r(\omega_D)/\omega_{DJ}$  and inside  $G_r(\omega_D)$ ,  $\omega_D(\mathbf{r}')$  is linear with the boundary condition  $\omega_{DJ}$  in QNRs and equals  $\omega_{DJ}$  inside  $\mathcal{J}$ . Its integral over  $\mathcal{J}_N$  represents the often minor change in  $I_{oN}$  in traversing  $\mathcal{J}_N$ ,  $\delta I_{oN}^B$ , which is due to band-to-band recombination reduced by internal photo-generation inside  $\mathcal{J}_N$ . Hence,

$$q \int_{\mathbb{V}_N} (\omega_D/\omega_{DJ}) G_e dV + (q/\omega_{DJ}) \mathcal{K}_N \\ = I_{pN} + (I_{oN} + \delta I_{oN}^B) \{ \exp [qV_{LJ}/(kT)] - 1 \} + q \int_{\mathcal{J}_N} U_{tL} dV, \quad (17)$$

where  $I_{pN}$  is the illuminated hole current flowing exactly at  $\mathcal{S}_0$  from the entire n-type region,  $\mathbb{V}_N$ .

Applying similar reasoning to the entire p-type region,  $\mathbb{V}_P$ , an equation similar to Eq. (17) can be derived with all terms replaced by those for the p-type region. In particular, the integral,  $\mathcal{K}_P$ , accounting for the effects of photon recycling on  $\mathbb{V}_P$ , is given by Eq. (15b) with  $\mathbb{V}_N$  replaced by  $\mathbb{V}_P$ . Hence, the sum of  $\mathcal{K}_N$  and  $\mathcal{K}_P$  is given by Eq. (15b) with  $\mathbb{V}_N$  replaced by  $\mathbb{V}_N + \mathbb{V}_P = \mathbb{V}$ . By the symmetry of  $\kappa$  and reversing the order of integration,

$$\int_{\mathbb{V}} \omega_D(\mathbf{r}) \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_L(\mathbf{r}') \partial V' \partial V \\ = \int_{\mathbb{V}} \int_{\mathbb{V}} \omega_D(\mathbf{r}) \kappa(\mathbf{r}', \mathbf{r}) \omega_L(\mathbf{r}') \partial V' \partial V \\ = \int_{\mathbb{V}} \omega_L(\mathbf{r}') \int_{\mathbb{V}} \kappa(\mathbf{r}', \mathbf{r}) \omega_D(\mathbf{r}) \partial V \partial V' \\ = \int_{\mathbb{V}} \omega_L(\mathbf{r}) \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_D(\mathbf{r}') \partial V' \partial V, \quad (18)$$

which means  $\mathcal{K}_N + \mathcal{K}_P = 0$ . Therefore, adding up Eq. (17) and its duplication for the p-type region gives

$$q \int_{\mathbb{V}} (\omega_D/\omega_{DJ}) G_e dV = (I_{pN} + I_{pP}) + (I_{oN} + \delta I_{oN}^B + I_{oP}) \\ \times \{ \exp [qV_{LJ}/(kT)] - 1 \} + q \int_{\mathcal{J}} U_{tL} dV, \quad (19a)$$

where  $I_{pP}$  is the illuminated electron current flowing exactly at  $\mathcal{S}_0$  from the entire p-type region,  $\mathbb{V}_P$ ,  $I_{oP}$  is the dark saturation current contribution from the p-type QNR, and  $\delta I_{oN}^B$  is defined as for  $\delta I_{oN}^B$  with the domain  $\mathcal{J}_N$  extended to  $\mathcal{J}$

$$\delta I_{oN}^B = (q/\omega_{DJ}) \int_{\mathcal{J}} [U_{bD} - \int_{\mathbb{V}} \kappa(\mathbf{r}, \mathbf{r}') \omega_D(\mathbf{r}') \partial V'] dV. \quad (19b)$$

One particular case of interest is when the illuminated diode is at short circuit, i.e.,  $V_{LJ} = 0$ , which leads to  $\omega_{LJ} = 0$  and hence  $U_{tL} = 0$  inside  $\mathcal{J}$ . Then, Eq. (19a) reduces to

$$q \int_{\mathbb{V}} (\omega_D/\omega_{DJ}) G_e dV = I_{pN} + I_{pP}. \quad (20)$$

The term on the left, which is independent of  $\omega_{LJ}$ , equals the total illuminated current flowing through  $\mathbb{V}$  at short circuit and hence can be identified as the light-generated current,  $I_L$ . This means that  $\omega_D/\omega_{DJ}$  must identically equal the collection probability,  $f_C(\mathbf{r})$ , for a carrier photo-generated by external illumination at point  $\mathbf{r}$

$$f_C(\mathbf{r}) = \omega_D(\mathbf{r})/\omega_{DJ}. \quad (21)$$

The proof of the validity of the charge collection theorem in the presence of photon recycling is now completed, with the inclusion of  $\mathcal{J}$  neglected by previous<sup>7,13–17</sup> relevant work. Consequently, the relationship<sup>7</sup> between photovoltaic external quantum efficiency and electroluminescent emission of solar cells is validated, with the inclusion of  $\mathcal{J}$ .

Returning to arbitrary  $V_{LJ}$ , Eq. (19a) gives a solar cell equation in the presence of photon recycling

$$I_L = I + I_o \{ \exp [qV_{LJ}/(kT)] - 1 \} + q \int_{\mathcal{J}} U_{tL} dV, \quad (22)$$

where  $I = I_{pN} + I_{pP}$  is total current flowing through the device under arbitrary  $V_{LJ}$  under illumination.  $I_o = I_{oN} + \delta I_{oN}^B + I_{oP}$  is the dark saturation current accounting for the diffusion components from the n-type and p-type QNRs as well as the junction component due to band-to-band recombination reduced by internal photo-generation inside  $\mathcal{J}$ . The last term on the far right accounts for enhanced recombination through defect levels inside  $\mathcal{J}$ , where  $U_{tL} = \beta_t(\omega_{LJ}) \times \omega_{LJ}$ . For recombination through a single defect state,  $U_{tL}$  can be described by Shockley-Read-Hall statistics<sup>22,23</sup> giving

$$\beta_t = n_i^2 / [\tau_{p0}(n + n_1) + \tau_{n0}(p + p_1)], \quad (23)$$

where  $n_1$  and  $p_1$  are parameters associated with the energy of the defect level,  $n_1 p_1 = n_i^2$  with  $n_i$  being the intrinsic carrier concentration,  $\tau_{p0}$  and  $\tau_{n0}$  are the hole and electron defect lifetimes in n-type and p-type QNRs under low injection, respectively. From Eq. (23),  $\beta_t$  is approximately constant with  $\omega_{LJ}$  in QNRs under assumption (A4) but decreases with  $\omega_{LJ}$  in  $\mathcal{J}$ . Inside  $\mathcal{J}$  for approximately constant lifetime parameters,  $U_{tL}$  will have a peak value of

$$U_{tL}^M = n_i^2 \omega_{LJ} / (2n_i \sqrt{\tau_{p0} \tau_{n0}} \exp [qV_{LJ}/(2kT)] + \tau_{p0} n_1 + \tau_{n0} p_1), \quad (24)$$

when  $n = p\tau_{n0}/\tau_{p0}$ .  $U_{tL}^M$  falls exponentially with distance on either side of the plane  $\mathcal{S}_M$  where this peak occurs with a characteristic length of  $kT/(qE)$  where  $E$  is the electric field at  $\mathcal{S}_M$ .<sup>10</sup> For multiple-level defects,  $U_{tL}$  have similar gross qualitative features to the single-level case.<sup>20</sup> When  $V_{LJ} \gg (2kT/q) \ln [\int_{\mathcal{S}_M} \pi n_i kT / (2I_o E \sqrt{\tau_{p0} \tau_{n0}}) ds]$ , the last term is negligible compared with the others in Eq. (22). In an ideal case when either  $\mathcal{J}$  is negligibly small or  $\tau_{p0,n0} \rightarrow \infty$  (the defect density approaches 0) in  $\mathcal{J}$ , the last term in Eq. (22) vanishes and Eq. (22) reduces to an ideal solar cell equation in the presence of photon recycling, applicable to arbitrary



three-dimensional geometries with arbitrary doping profile and variable band gap. On the other hand, Eq. (24) explains how recombination through defects in the junction causes deviation from the ideal equation in reality.

#### IV. FURTHER DISCUSSION

Although photon recycling has no impact on the form of Eq. (22), the values of  $I_o$  and  $I_L$  are modified. Integrating  $\mathcal{L}(\omega_D) = G_r(\omega_D)$  on both sides and utilizing the divergence theorem,

$$\begin{aligned} I_{oN} &= -1/\omega_{DJ} \int_{S_N} \mathbf{J}_{pD} \cdot \hat{\mathbf{n}} ds \\ &= q \int_{S_N} p_0 S_{p0}(\omega_D/\omega_{DJ}) ds + q \int_{\mathcal{D}_N} [(\beta_b + \beta_t)\omega_D/\omega_{DJ} \\ &\quad - \int_V \kappa(\mathbf{r}, \mathbf{r}')\omega_D(\mathbf{r}')/\omega_{DJ} \partial V'] dV, \end{aligned} \quad (25)$$

where  $S'_N$  represents the non-junction surface regions of  $\mathcal{D}_N$  and  $\omega_D/\omega_{DJ}$  is constant with injection level by linearity of the governing equations for the QNR under assumption (A4). Therefore,  $I_{oN}$  is reduced by  $G_r(\omega_D)$  as is  $\delta I_{oJ}^B$ . As similar arguments also apply to  $I_{oP}$ ,  $I_o$  reduces in the presence of photon recycling. From Eq. (5), the reduction of  $I_{oN}$  and  $I_{oP}$  implies a smoother gradient,  $\nabla\omega_D$ , due to redistribution of dark minority-carriers by photon recycling, and hence an increased collection probability,  $f_C$ . Therefore,  $I_L$  increases in the presence of photon recycling. Hence, neglecting  $G_r(\omega_D)$  gives a conservative bound on both  $I_o$  and  $I_L$ . On the other hand, ignoring radiative recombination entirely and just taking non-radiative recombination within the absorber into account gives an optimistic bound on both  $I_o$  and  $I_L$ . Noticeably, the constancies of material parameters and  $\omega_D/\omega_{DJ}$  with the injection level suggest that the dark saturation current is still independent of injection level (and hence is illumination intensity independent) in the presence of photon recycling under assumption (A4).

The present formulation parameterized in terms of  $\omega$  not only proves the validity of the charge collection theorem and the solar cell equation in the presence of photon recycling but also includes the junction region which previous formulations<sup>7,13–17</sup> of the charge collection theorem using the parameter  $u$  cannot accommodate. Under assumption (A4),  $u$  equals  $\exp[qV_J/(kT)] - 1$  near the junction depletion edge. At low  $V_J$ , this relation can be extended into  $\mathcal{J}$  where low-injection condition applies and  $n \neq p$ , but  $u$  reduces to  $\exp[qV_J/(2kT)] - 1$  near  $S_0$  where  $n = p$ , inconsistent with  $f_C(\mathbf{r}) = 1$  for  $\mathbf{r} \in \mathcal{J}$ . The inclusion of  $\delta I_{oJ}^B$  in  $I_o$  also suggests that assumption (A2) can be slightly less restrictive: a non-negligible generation-recombination current in a slightly

wider  $\mathcal{J}$  with negligible junction edge movement may still allow validation of the ideal diode law provided that Eq. (11) applies and defect recombination is negligible inside  $\mathcal{J}$ . However, the present approach does require assumptions (A1), (A3), (A4), and (A5) as in Shockley's original<sup>1</sup> work.

#### V. CONCLUSIONS

In summary, the ideal solar cell equation retains its traditional form in the presence of photon recycling and is applicable to arbitrary three-dimensional geometries with arbitrary doping profile and variable band gap as is the reciprocal theorem for charge collection. However, photon recycling improves the dark saturation and light-generated currents in the equation. Recombination through defect levels inside the junction depletion region causes deviation of the current-voltage characteristic from the ideal one. The present formulation can accommodate the junction depletion region with the assumption of negligible junction edge movement.

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