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## GENERALIZED RECIPROcity RELATION IN P-I-N JUNCTION SOLAR CELLS

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**ABSTRACT:** The reciprocity relation, whose original version is not applicable to solar cells with wide depletion regions, is investigated and generalized to apply to p-i-n junction solar cells. By linearizing the transport equation in the i-region, we have derived the general form of reciprocity relation between electroluminescence and quantum efficiency at forward bias, not short circuit. This generalized reciprocity relation has been experimentally confirmed by comparing the electroluminescence and the voltage-dependent quantum efficiency of p-i-n multiple quantum well solar cells.

**Keywords:** Electroluminescence, p-i-n junction, Reciprocity relation, Quantum efficiency, Quantum Well, Voltage dependence

## 1. INTRODUCTION

The photovoltaic reciprocity relation [1] connecting electroluminescence ( $\Phi_{EL}$ ) spectrum and short-circuit external quantum efficiency (EQE) of solar cells (Fig. 1(a)) is a well-known theorem which helps enhance our understanding of the fundamental operation of solar cells and develops several new cell evaluation techniques based on electroluminescence measurements [2,3]. It is expressed by

$$\Phi_{EL}(\varepsilon, V) = \text{EQE}^{(sc)}(\varepsilon) \Phi_{bb}(\varepsilon) \left( e^{qV/kT} - 1 \right), \quad (1)$$

where  $\varepsilon$  is photon energy,  $\Phi_{bb}$  is the blackbody photon flux spectrum,  $V$  is the applied voltage at the device terminal,  $q$  is the elementary charge,  $k$  is Boltzmann's constant,  $T$  is the temperature and, the (sc) subscript denotes the short-circuit operation. It has also been used to derive the well-known relation between the open-circuit voltage  $V_{oc}$  and the luminescence efficiency  $\eta_{ext}$  [1]:

$$V_{oc} = V_{oc}^{(rad)} + \frac{kT}{q} \ln \eta_{ext}, \quad (2)$$

where  $V_{oc}^{(rad)}$  is the open-circuit voltage at the radiative limit (i.e.  $\eta_{ext} = 1$ ). The reciprocity relation, however, is valid only if the deviation of device operation, e.g. carrier transport and recombination, from the thermal equilibrium is linear. The non-linearity of the system and consequently the failure of the original reciprocity relation in p-i-n junction solar cells (Fig. 1(b)) have been discussed [1,4] as the carrier dynamics in the i-region cannot be considered linear with the excess minority-carrier density. This leads to the limitation of cell evaluation methods that are based on the reciprocity relation in p-i-n junction solar cells. In this study, we examine how to modify the original reciprocity relation to account for the carrier dynamics in the i-region.

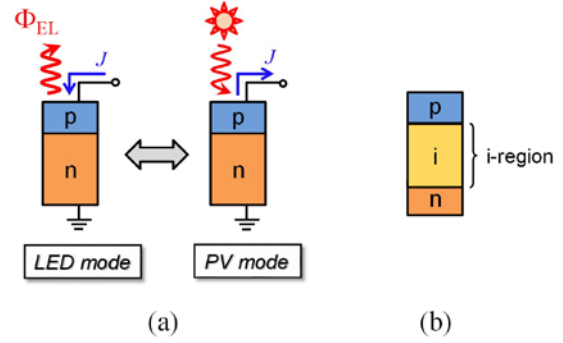


Fig. 1. (a) Reciprocity relation describing the connection of the two device modes: the electroluminescence in the LED mode and the EQE in the photovoltaic mode. (b) p-i-n junction solar cells. Carrier dynamics in the i-region is not simply linear with the excess minority-carrier density, violating the assumptions in the previously proposed Donolato's theorem and reciprocity relation.

## 2. THEORETICAL APPROACH

By considering the carrier transport equation (current continuity equation), it can be confirmed that carrier transport and recombination in the i-region is not linear with the excess minority-carrier density as addressed in [1,4]. For instance, the equation for electron current continuity in the p-region can be written by

$$G = -\nabla \cdot (q\mu_n n \mathbf{E} + qD_n \nabla n) + q \left( n - \frac{n_i^2}{p} \right) \left( \frac{1}{\tau_n} + Bp + C_p p^2 \right), \quad (3)$$

where  $G$  is the photogeneration rate,  $n$ ,  $p$ , and  $n_i$  are the electron, hole, and intrinsic carrier densities, respectively,  $\mu_n$  is the electron mobility,  $D_n$  is the electron diffusion coefficient,  $\tau_n$  is the electron non-radiative lifetime,  $B$  is the radiative recombination coefficient, and  $C_p$  is the 2-hole Auger recombination coefficient. In the p-region,  $p$  can be considered constant and Eq. (3) becomes linear

relation. In the i-region, however, both  $p$  and  $n$  have spatial dependence as well as voltage dependence and thus Eq. (3) is not linear with the excess minority-carrier density  $n - n_{V=0}$ .

Analysis of the carrier transport equation (the detailed analysis and derivation will be published elsewhere [5]) provides a new finding that the carrier transport equation can be linearized in terms of  $u$ , which corresponds to quasi-Fermi level splitting  $\Delta\varepsilon_F$

$$G = \mathcal{L}_V u, \quad (4)$$

$$u \equiv e^{\Delta\varepsilon_F/kT} - 1. \quad (5)$$

Here,  $\mathcal{L}_V$  is a linear operator that has voltage  $V$  dependence. The carrier transport equation in Eq. (4) implies that carrier transport is therefore linear with variable  $u$  but not linear with voltage  $V$ . Mathematical treatment on Eq. (4) and (5) provides the new relation between the carrier injection efficiency  $f_i(V)$  under voltage  $V$  and the *voltage-dependent* photocarrier collection efficiency  $f_c(V)$  through [5]

$$f_i(V) = f_c(V), \quad (6)$$

which is the generalized form of Donolato's theorem. Note that the original Donolato's theorem claimed the relation between  $f_i(V)$  and the photocarrier collection efficiency  $f_c^{(sc)}$  at short circuit:  $f_i(V) = f_c^{(sc)}$  [6]. In other words, it has been assumed in the original theorem that  $f_i$  and  $f_c$  are independent of voltage  $V$ .

The generalized Donolato's theorem in Eq. (6) can be confirmed by the agreement between the simulated  $f_i(V)$  and  $f_c(V)$  in a p-i-n junction solar cell at various operating voltages  $V$  shown in Fig. 2. Even though both  $f_i(V)$  and  $f_c(V)$  have clear voltage dependence in p-i-n junction solar cells,  $f_i(V) = f_c(V)$  still holds, which has not been predicted by the original theorem.

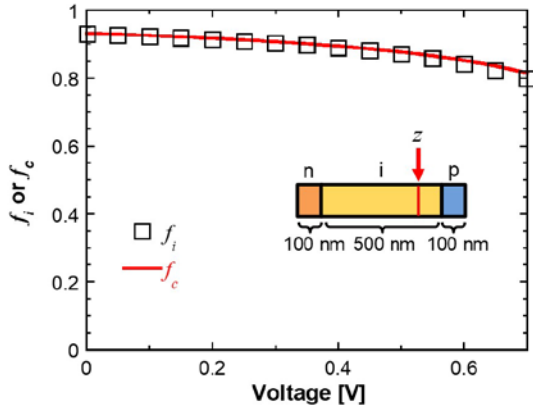


Fig. 2. Simulated dark-carrier injection efficiency  $f_i$  and photocarrier collection efficiency  $f_c$  of a p-i-n junction solar cell as a function of applied voltage  $V$ . The p-i-n junction solar cell simulated here had 100-nm p-region, 500-nm i-region, and 100-nm n-region. The simulated  $f_c$  here is the collection efficiency of carriers photogenerated at the position  $z$  (see the inset;  $z$  is at 100 nm from the p-region) and  $f_i$  is the efficiency of carrier injection to the position  $z$ . A mobility  $\mu$  of  $0.1 \text{ cm}^2/\text{Vs}$  and a lifetime  $\tau$  of 100 ns have been assumed.

### 3. PHOTOVOLTAIC RECIPROcity AND EXPERIMENTAL RESULTS

The original version of the photovoltaic reciprocity relation in Eq. (1) has employed the original version of Donolato's theorem [6] as one main assumption; therefore it becomes invalid if Donolato's theorem is modified. Fortunately, the modification of the photovoltaic reciprocity relation is straightforward: the voltage-dependent photocarrier collection  $f_c(V)$  in Eq. (6) directly links to the voltage-dependent EQE. This leads to the general form of the photovoltaic reciprocity relation

$$\Phi_{\text{EL}}(\varepsilon, V) = \text{EQE}(\varepsilon, V) \Phi_{\text{bb}}(\varepsilon) \left( e^{qV/kT} - 1 \right) \quad (7)$$

connecting electroluminescence spectrum with *voltage-dependent* EQE (NOT short-circuit EQE in Eq. (1)).

The theoretical investigation described above has been experimentally confirmed by the electroluminescence measurement on p-i-n junction InGaAs/GaAsP multiple quantum well (MQW) solar cells with the same absorption spectrum but with different carrier non-radiative lifetime as shown in Fig. 3. The device preparation has been explained in [7]. The measured electroluminescence and voltage-dependent EQE are shown in Figs. 4(a)-(d), respectively. The generalized reciprocity relation in Eq. (7) were used to estimate electroluminescence from the measured EQE, which is plotted as open circles in Fig. 4(a). The agreement between the measured electroluminescence and the electroluminescence estimated from voltage-dependent EQE using Eq. (7) justifies the theoretical investigation on the reciprocity relation made in this study.

Furthermore, it has been shown in [8] that the open-circuit voltage  $V_{\text{oc}}$  for solar cells with voltage-dependent carrier injection and collection can be generalized and written by

$$V_{\text{oc}} = V_{\text{oc}}^{(\text{rad})} + \frac{kT}{q} \ln \eta_{\text{ext}} + \frac{kT}{q} \ln \frac{F_c(V_{\text{oc}})}{F_i(V_{\text{oc}})}, \quad (8)$$

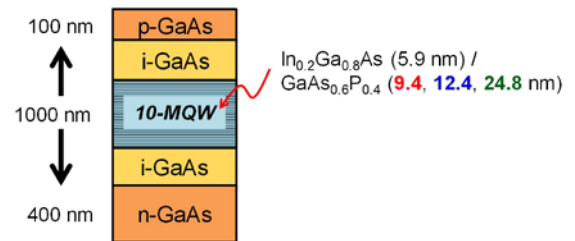


Fig. 3. InGaAs/GaAsP MQW solar cells with the same light absorption but different non-radiative lifetime [7]. Different thicknesses of GaAsP layers on GaAs substrates result in different net strains, which in turn varies the carrier lifetimes. On the other hand, the thickness variation of GaAsP, which has much larger bandgap than InGaAs, has negligible effect on light absorption near the absorption edge, resulting in the similar light absorption among samples. This can be confirmed by the similar reverse-bias EQE in Figs. 4(b)-(d).

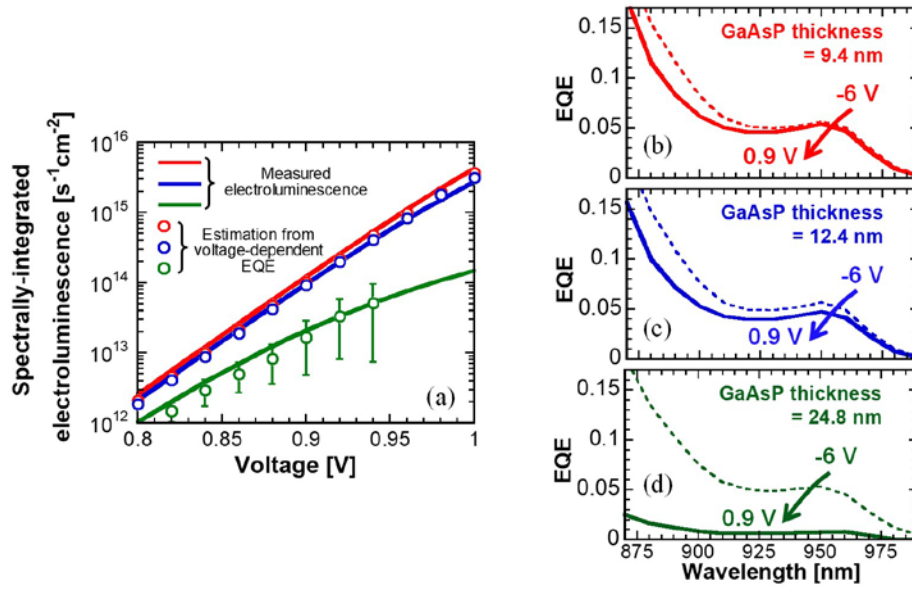


Fig. 4. (a) Measured (lines) and estimated (open circles) electroluminescence of InGaAs/GaAsP MQW solar cells, which have different carrier lifetimes but similar light absorption. The generalized reciprocity relation in Eq. (7) was used to estimate the electroluminescence from voltage-dependent EQE. Reverse-bias and forward-bias EQEs of MQWs with GaAsP thicknesses of (b) 9.4 nm, (c) 12.4 nm, and (d) 24.8 nm. The low signal-to-noise ratio of EQE in MQW cells with 24.5-nm-thick GaAsP results in large error bars for the estimated electroluminescence intensity from this EQE spectra.

where  $F_i$  and  $F_c$  are the spatial averages of the carrier injection efficiency  $f_i$  and the photocarrier collection efficiency  $f_c$ . Note that  $f_i$  and  $f_c$  are defined by the injection and collection of carriers at the specific position as one example is shown in Fig. 2. The third term comes from the fact that the total current  $J$  is not simply given by the so-called superposition of dark current  $J_{\text{dark}}$  and short-circuit current  $J_{\text{sc}}$  if the photocurrent has voltage dependence. Under the condition that the generalized Donolato's theorem in Eq. (6) holds, we obtain  $F_i(V) = F_c(V)$  and thus

$$V_{\text{oc}} = V_{\text{oc}}^{(\text{rad})} + \frac{kT}{q} \ln \eta_{\text{ext}}, \quad (9)$$

implying that the  $V_{\text{oc}}-\eta_{\text{ext}}$  relation in Eq. (2) also holds in p-i-n junction solar cells regardless of the failure of the superposition principle.

#### 4. CONCLUSION

In conclusion, we have investigated the validity of the reciprocity relation in p-i-n junction solar cells, where the device operation is not linear with the excess minority-carrier density. By properly linearizing the carrier transport equation, we propose the general form of the reciprocity relation which holds in p-i-n junction solar cells. The cell evaluation techniques based on electroluminescence measurement are found to be available in p-i-n junction solar cells as well, provided that voltage-dependent EQE must be used instead of short-circuit EQE to interpret the measured electroluminescence data. The generalized  $\Phi_{\text{EL}}$ -EQE reciprocity relation is used to confirm that the well-known formula for  $V_{\text{oc}}-\eta_{\text{ext}}$  relation is still applicable in

p-i-n junction solar cells regardless of their voltage-dependent EQE.

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