Loss of photocurrent efficiency in low mobility semiconductors: Analytic approach to space charge effects

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We derive an analytic expression for the photocurrent efficiency as a function of the optical excitation power within the framework of space charge limit of Mott and Gurney [Electronic Processes in Ionic Crystals (Oxford University Press, London, 1940)]. This complements the approach based on charge recombination and we show that the two give similar expressions. Namely, in low mobility and intrinsic semiconductors (as conjugated polymers) based photocell, where recombination follows Langevin’s expression, the onsets of space charge and of charge recombination coincide. The analysis shows that the onset of space charge or recombination depends only on the slow carrier mobility value and do not require imbalanced mobility values.

The importance of organic photocells is gradually rising as indicated by the steady increase in reports concerning material synthesis or material composite design which are specifically targeting photocell functionalities. However, there is still a lack of device oriented research that is aimed at modeling the device performance. In a recent paper we have shown, using extensive numerical modeling of the transport and Poisson equations, that the optical power dependence of the photocurrent efficiency can be reproduced using the charge transport equations. In that paper we used the numerical modeling results of charge concentration and electric field distributions to show that reduction in photocurrent efficiency is associated with the onset of charge recombination only (neglecting space charge effects) and provided a guideline for the target mobility values. These results showed that the recombination would reduce the efficiency to half of its low power value at a charge photogeneration rate that is equal to the space charge current \[J_{SC} = (9/8)\varepsilon \mu (V^2/d^3)\]. This suggests that the two phenomena are closely linked. To examine this link, in this letter, we derive an analytic expression for the reduction in photocurrent efficiency due to charge recombination only and provided a guideline for the target mobility values.

The operation of a photocell under low excitation power and in the current mode (i.e., no significant load or short circuit) is described by \(J = AP\). Here \(J\) is the photocurrent density flowing through the photocell, \(P\) is the incident optical power density, and \(A\) is a constant taking into account the fraction that is being absorbed and the efficiency of turning the absorbed photons into dissociated electron-hole pairs. In this low excitation density regime, the efficiency of such a photocell can be written as \((J/P)\) which is constant and equals \(A\). At high enough excitation powers the charge generation is still as efficient but the current generation (flow) is not and one can describe it by adding a factor of \(K\) which is power dependent and assumes values that are equal or smaller than 1: \(J = AK(P)\). The early model by Goodman and Rose suggested that for a space charge to form there should be a large difference between the electron and hole mobility values. In our detailed numerical simulations (see Fig. 2 in Ref. 16) we have shown that, in fact, the built in potential is sufficient to spatially separate the electron and hole populations such that space charge can be formed even where the mobility values of electrons and holes are identical. Moreover, in Ref. 14 it was shown that the predictions of this early model do not apply to current devices.

The physical picture we wish to provide analytic expression for is that of a device under (built in or external) bias where optically generated charge carriers are swept by the electric field resulting from current flow. In analogy to the treatment of space charge in light-emitting diodes (LEDs) we replace the contact injection found in LEDs with the charge generation that results from absorption of photons. Increasing the optical power (charge generation) can be viewed as improving the contact injection in LEDs (reduced barrier) and again, similar to LEDs, under intense charge generation the device switches to bulk limited conduction, which is space charge limited in the case of organic devices. This physical picture is actually similar to the one studied in Ref. 18 and hence we start with the well known Mott-Gurney expression for the single carrier current:

\[
V = \sqrt{\frac{8J}{9\varepsilon \mu}} \left( d + \frac{Je}{2N^2q^2\mu} \right)^{3/2} - \left( \frac{Je}{2N^2q^2\mu} \right)^{3/2}.
\]

Here \(V\) is the voltage, \(J\) is the current, \(d\) is the device length, \(\varepsilon\) is the permittivity, \(q\) is the unit charge, \(\mu\) is the mobility, and \(N\) is the charge density close to the contact. In their book, it is shown that this equation can be approximated in one of the following two cases.

1. Bulk limited conduction for which the charge density near the injecting contact is high such that \(d \gg Je/2N^2q^2\mu\) leading to the space charge limited (SCL) law \(J_{SC} = (9/8)\varepsilon \mu (V^2/d^3)\).
2. Contact limited conduction for which \(d \ll Je/2N^2q^2\mu\) leading to the Ohmic law \(J_{Ohm} = Nq\mu V/d\) (derived by...
expanding \([d+(Je/2N^2q^2\mu)]^{3/2}\) using the Taylor series to first order around \(d=0\).

In photocells the picture is modified by the fact that the source is no longer a single point in space (the contact interface) but is rather distributed according to the optical absorption depth. This “small” difference in the boundary conditions softens the space charge limit and the photocurrent can exceed the value of \(J_{\text{SCL}}\). To illustrate this point we present in Fig. 1 the result of a full numerical simulation (described in details in Ref. 16) which shows the photocurrent as a function of excitation power for a device characterized by: \(\mu_r=\mu_a=10^{-4}\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}\), \(d=200\ \text{nm}\), and \(V=V_{\text{appl}}-V_{\text{bi}}=-1\ \text{V}\) where \(V_{\text{appl}}\) is the applied voltage and \(V_{\text{bi}}\) is the built-in (flat-band) voltage (if \(V_{\text{bi}}=1\ \text{V}\) then \(V_{\text{appl}}=0=V_{\text{short
circuit}}\)). It shows that in the low excitation regime the response is linear and we can extract the slope as \(A=0.000\ 488\ \text{A/W}\). At higher power the line becomes sublinear but is definitely not clamped at the value of \(J_{\text{SCL}}=\frac{9}{8}\times10^{-4}\times10^{-11}\times10^{-12}/(200 \times10^{-7})=0.0037\ \text{A/cm}^2\).

Therefore, in this letter we are interested in a regime that is between the two limits found in LEDs [see cases (1) and (2) above] where the space charge affects the current flow but do not clamp it. In other words, we seek to derive an expression for the regime where the current is not entirely injection limited but is not bulk limited either. To do so we expand \([d+(Je/2N^2q^2\mu)]^{3/2}\) using Taylor series to one more (second) order around \(d=0\) and rewrite Eq. (1) as

\[
V = \sqrt{\frac{8J}{9e\mu}} \left[ \left( \frac{Je}{2N^2q^2\mu} \right)^{3/2} + \frac{3}{2} \left( \frac{Je}{2N^2q^2\mu} \right)^{1/2} \right]^{1/2} + \frac{3}{8} \left( \frac{Je}{2N^2q^2\mu} \right)^{1/2} d^2 - \left( \frac{Je}{2N^2q^2\mu} \right)^{3/2}.
\] (2)

After rearranging the terms in Eq. (2):

\[
V = \frac{J}{Nq\mu} d + \frac{27Nq}{128e} d^2,
\] (3)

and finally,

\[
J = Nq\mu d \left[ 1 - \frac{27 \times 9}{128 \times 8} \frac{Nq(V/d)}{(9\mu eV^2/8d^3)} \right] = J_{\text{Ohm}} \left( 1 - 0.2373 \frac{J_{\text{Ohm}}}{J_{\text{SCL}}} \right).
\] (4)

We note that in the Mott and Gurney treatment the value of \(N\) (charge density) is determined by the boundary conditions at the contact interface. In our treatment it is determined by the photons flux. To be able to estimate \(N\) we need to make another approximation. Let us assume that the excitation is not very high and use the low power relation \(J_{\text{Ohm}} = J = Gdz = AP\). This leads to our central result

\[
\text{Eff} = \frac{J}{A \cdot P} = \frac{J}{J_{\text{Ohm}}} = 1 - 0.2373 \frac{AP}{J_{\text{SCL}}}. \tag{5}
\]

Equation (5) describes the photocurrent efficiency at low to moderate optical powers and is based on space charge considerations only. In the analysis leading to Eq. (5) we did not explicitly include the charge recombination process. However, the reduced extraction current efficiency implies that charges are “lost” and the only mechanism available is that of charge recombination. Namely, from Eq. (5) we can derive the recombination current \(J_{\text{R}}=J_{\text{G}}-J = 0.2373[(AP)^{2}/J_{\text{SCL}}]\) which has the proper bimolecular form.

To examine the validity of the approximations made above we plot in Fig. 2 the normalized photocurrent efficiency as derived from the full numerical simulations [16] (filled circles), the recombination model [14] (dashed line, Eq. (6)), and the present model (full line, Eq. (5)). We note that the approximate expression (5) is reasonable up to and slightly above the onset of the reduction in efficiency and hence it predicts well the onset point.

Finally, we try to answer whether it is the recombination process that primarily limits the efficiency or is it the space charge (that enhances the recombination). For this we need to compare Eq. (5) with that derived in Ref. 14 for the charge recombination scheme

\[
\text{Eff}_2 \cong 1 - \frac{[-1 + \sqrt{1 + (AP/J_{\text{SCL}})(9/8)}]^2}{(AP/J_{\text{SCL}})(9/8)}. \tag{6}
\]

To bring the expression in Ref. 14 to a form that is comparable to the small signal analysis described here we use \(\sqrt{1+x} = 1 + 0.5x\) (for \(x \ll 1\)) and simplify Eq. (6)

\[
\text{Eff}_2 \cong 1 - \frac{9AP}{32J_{\text{SCL}}}. \tag{7}
\]

We note that 9/32=0.28 compares well with the 0.24 that appears in Eq. (5). Namely, it is not possible to assign the...
reduction in photocurrent efficiency at high power to a single process.

To conclude, we have presented an analytic expression for the photocurrent efficiency as a function of the optical excitation density which was derived using the space charge limited framework set by Mott and Gurney. The analysis shows that at low to moderate powers the increase in optical density resembles a current driven device where the contact barrier is gradually being reduced thus taking it out of the injection limited regime towards the space charge limited one. As the onset of reduced efficiency, at practical powers, is associated with the space charge limit this onset power scales with $V^2$ and $d^{-3}$ (note that $V = V_{\text{appl}} - V_{\text{bi}}$). We have compared the results with those obtained using the recombination scheme only and found that the two expressions are practically similar. Namely, in a low mobility and intrinsic semiconductor, where the recombination follows Langevin’s expression, the onsets of space charge effects and of charge recombination coincide. We note that in the analysis presented here and in Refs. 14 and 16 it is the mobility of the slow charge carrier that determines the onset of efficiency loss and imbalanced mobility values are not essential for this effect to take place. Finally, the inclusion of the mobility spatial distribution function effect in the above analysis is not expected to affect the general conclusion drawn above.

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