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Space Charge and Recombination Limited Currents—How Different Are They?

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Space charge limits the current under single carrier injection because only approximately CV can be injected. On the other hand, under double injection one requires only that $|Q^+ - Q^-| \approx CV$. In this paper, I discuss the conditions where $Q^\pm >> CV$ and the recombination limited current is very large compared with the space charge limited current. It is shown that $Q^\pm >> CV$ can be achieved providing that the capture rate constant to neutral recombination centers is very small compared with the capture rate constant to occupied charged centers and the ratio of the extended state mobility μ to the capture rate constant to charged centers is also large.

INTRODUCTION

It is generally believed that because of the space charge neutralization possible under double injection, which is clearly not possible under single injection, that the current being recombination limited is larger than the space charge limited current. The space charge limitation comes about because only approximately CV of charge can be injected when only one contact is ohmic. On the other hand when both contacts are injecting only the difference in the charge $|Q^+ - Q^-|$ need be of order CV. We must therefore examine the conditions under which this large charge storage is possible. Further, if there are recombination centers, we must also look at the fractional population of these centers.

Lampert and Mark¹ have presented the simplest picture for analyzing the situation. They show that

$$Q^{\pm} \simeq 8CV \frac{\bar{\tau}}{I_{\text{on}} + I_{\text{op}}} \tag{1}$$

where the 8 comes from assuming that the spatial dependence of each sign of charge is linear in position, $\bar{\tau}$ is the mutual average lifetime and $\bar{\tau}_{on}$ and $\bar{\tau}_{op}$ are the average transit times of the electrons and holes. This expression resembles the well-known relationship for photoconductive gain.² (The simplification involves the approximation of a common average lifetime rather than equating the rate of loss

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of electrons to the rate of loss of holes). The analysis then involves a parameterized study of the microscopic capture rates and relates them to the transit time.

Analysis and discussion

The space charge limited and recombination limited currents are:

$$j_{SCL} \simeq \frac{\theta_s CV}{t_o}$$

$$j_{RCL} \simeq \frac{8\theta_R CV}{(\bar{t}_{o_R} + \bar{t}_{o_R})^2}$$
(2a)

where θ_s and θ_R are the fraction of the total injected charge lying above the conduction or below valence band edges. In order to calculate the values for the θ_R , we use Shockley-Read recombination where

$$f \simeq \frac{n}{p} \frac{b_n}{b_c} \tag{3}$$

where f is the fractional population of the recombination centers and b_n and b_c are the capture rate constants to the empty and filled recombination centers respectively. The value of f is important because it determines θ through

$$Q = \int_{\epsilon_f}^{\epsilon_{qf}} fg(\epsilon) d\epsilon + \int_{\epsilon_{qf}}^{\infty} f(\epsilon)g(\epsilon) d\epsilon$$
 (4)

where $f(\epsilon)$ is the fractional population of states above the quasi fermi level and $g(\epsilon)$ is the density of states. The smaller f is, the smaller is the first term, the higher E_{qf} is and therefore the larger is the number of carriers above the conduction band edge. For θ_s a similar approach is used except that since there is no recombination, f = 1 below E_{qf} .

It is not the purpose of this paper to show specific calculations for specific density of states but only to show general features. Consequently we will not concentrate on any specific density of states but focus on the effect of various microscopic capture processes. From Equation 1, the ratio of

$$\bar{\tau}/(t_{\rm on} + t_{\rm op}) = \frac{1}{b_c \left(\alpha \frac{Q}{eL}\right) \left[\frac{L^2}{V} \left(\frac{1}{\mu_n} + \frac{1}{\mu_n}\right)\right]}$$
 (5)

where α is the fraction of injected charge acting as recombination centers which simplifies to

$$Q^{\pm} = CV \left(\frac{8}{\alpha} \frac{b_L}{b_c}\right)^{1/2} \tag{6}$$

where

$$b_L = \frac{\mu_n \mu_p}{\mu_n + \mu_p} \left(\frac{e}{\epsilon} \right)$$

The term b_L resembles the Langevin field driven recombination coefficient for a coulomb center. Further from Equations 3 and 4, the quantity Q/f is important so that

$$\frac{Q_{\pm}}{f} = CV \frac{b_c}{b_n} \frac{p}{n} \left(\frac{8}{\alpha} \frac{b_L}{b_c} \right)^{1/2}$$
 (7)

assuming p/n is of order unity,

$$\frac{Q^{\pm}}{f} = CV \left(\frac{8}{\alpha} \frac{b_L b_c}{b_n^2}\right)^{1/2} \tag{8}$$

From this simple analysis, we see that the ratio $b_L b_c/b_n^2$ (and of course the density of states) determines how large Q^{\pm}/f is and therefore how large the recombination limited current is. The larger the ratio is, the larger is the current.

In organic crystals where the recombination is likely to be bi-molecular f becomes unimportant and

$$Q^{\pm} = CV \left(8 \frac{b_L}{b_c}\right)^{1/2}. \tag{9}$$

We will discuss this case separately later because b_c can be very small when μ is large.

The quantum mechanical calculations for the recombination processes have not yet been made satisfactorily. As a consequence, our only recourse is to estimate the capture radius and the decay rate at the center.

Nevertheless, it can easily be shown that the capture rate constant can be limited by a) the rate of encounter between the capturing site and the recombining particle and b) the rate of decay at the center for example due to slow phonon emission. There are two cases associated with a): when capture is diffusion limited, e.g., $\lambda_x << (1/N_R)^{1/3}$ and when the capture is ballistic, e.g., $\lambda_s >> (1/N_R)^{1/3}$ where λ_s is the m.f.p. for momentum exchange scattering of the moving particle. It is easily shown that these three cases can be put in simplified form.³

a)
$$b = \frac{4 \pi D R}{1 + \frac{3D}{R^2 k}}$$
 $\lambda_s \ll (1/N_R)^{1/3}$ (10)

b)
$$b = \frac{4 \pi R^2 v_o}{1 + \frac{3v_o}{R k}}$$
 $\lambda_s >> \left(\frac{1}{N_R}\right)^{1/3}$

and

c)
$$b = \frac{4}{3} \pi R^3 k$$

where k is the inverse lifetime at the center, v_o is the random velocity of the moving particle and b is the generic symbol for the capture rate constant, case c, obviously is the limit of $k \ll 3v_o/R$ or $3D/R^2$. Therefore, we can consider case a) to be $b \simeq 4\pi DR$ and case b) to be $b \simeq 4\pi R^2 v_o$.

We are now in a position to estimate the relative magnitudes of Q^{\pm} as given by Equation 8. Perhaps the simplest case to evaluate is when capture is diffusion limited. Here $b_n \simeq 4\pi D_n R_n$ and $b_c \simeq \mu_n e/\epsilon$ assuming $\mu_n >> \mu_p$. In this case $b_L b_c/b_n^2 \simeq \mu_p/\mu_n \ R_c^2/R_n^2$ where R_c is the radius of a coulomb and R_n is the radius of a neutral center. With the assumption that $\mu_p << \mu_n \ Q^{\pm} \simeq CV$ and the recombination limited current will be about the same magnitude as the space charge limited current.

The ballistic case where the μ 's are large can also be approximated and $b_c b_L/b_n^2$ is of order $R_c^3 \lambda R_n^4$. Since λ is assumed to be very large $[\lambda >> (1/N_R)^{1/3}] b_c b_L/b_n^2$ is large and the recombination limited current is very large compared with the space charge limited current.

When capture is phonon emission limited one can make some guesses. One might expect b_n to be small and b_c to be large and therefore, the recombination limited current might again be large compared with the space charge limited value. However, this case requires a detailed knowledge of the quantum mechanics of the capture process.

Finally, let us consider a true bi-molecular process in which p directly recombines with n. In this case f is irrelevant and

$$Q^{\pm} \simeq CV \left(8 \frac{b_L}{b_c}\right)^{1/2}.$$

For low mobility material or high T where $b_L \propto (\mu_n \mu_p)/(\mu_n + \mu_p)$ and $b_c \propto (\mu_n + \mu_p)$, and consider the easy case where $\mu_n = \mu_p$, then

$$Q^{\pm} \simeq CV/2 \tag{11}$$

and the space charge and recombination limited current are approximately equal. However, at low T where μ is large b_c may be considerably smaller because the recombination may be phonon or photon emission limited. In this case, the recombination limited current may be considerably larger than the space charge limited value. Considering the sharp mobility rise as the temperature is lowered in naphthalene, looking a d.c. double injection vs. T could be very profitable since it would not require temporal resolution as does time of flight.

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