Recombination in organic solar cells

1) Langevin recombination

Recombination in low mobility semiconductors can be described by Langevin recombination in the form R=knp, where k is the recombination pre-factor and n/p are the free carrier concentrations.

a) Derive the Langevin prefactor k – show all the steps of your derivation and write one sentence for each step describing the physical meaning of the step.

Answer:

$j_{electron}=qn\mu E$ The electron density due to drift across the capture radius.

$j_{electron}=qn\mu\frac{q}{4\pi\epsilon r^2}$ The electric field at the capture radius is described as a point charge.

$j_{electron}=\frac{q^2\mu n}{\epsilon}$ Multiply by the area of a sphere.

$j_{electron}=\frac{q}{\epsilon}(\frac{\mu_n+\mu_p}{2})np$ We have p holes so multiply by p and take the average of the mobilities as both electrons and holes are moving.

b) The value of k measured in P3HT:PCBM is often up to 1000 times smaller than that predicted by pure Langevin recombination. What other evidence is there that the simple Langevin recombination model may not be a good model for recombination in P3HT:PCBM? (Please cite the paper which contains the information in your answer)

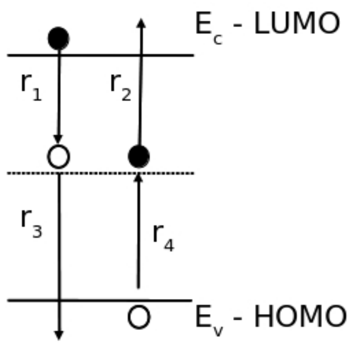
Answer:

There is a carrier density dependence of the pre factor k on carrier density. Paper: Shuttle et al. Phys. Rev. B 78, 113201 2008

2) Shockley-Read-Hall (SRH) recombination

a) Draw and label a diagram depicting SRH recombination for a single trap level.

Answer:



b) Write the equation for free electron capture into the electron trap state and name each term.

Answer:

$$r_1 = n \cdot v_{th} \sigma_n N_t (1 - f)$$

n: Free carrier density.
v_{th}: Thermal velocity of free carriers.
σ_n: capture radius
1-f: 1 minus the occupation function

c) Write the equation for trapped electrons escaping into the free carrier population and name each term.

Answer:

$$r_2 = e_n N_t f$$

e_n: carrier escape probability
N_t: Density of trapped states at the trap level.
f: the occupation function.

b) Due to the principle of detailed balance, in thermal equilibrium each carrier trapping and de-trapping process must balance. By setting the electron capture rate into an electron trap equal to the electron escape rate from the electron trap (r_1=r_2), by using the Fermi-Dirac distribution

$$f = \frac{1}{1 + \exp\left(\frac{E_t - E_f}{kT}\right)}$$

and the Maxwell-Boltzmann expression for free electrons, show that the escape rate is given as

$$e_n = v_{tv} \sigma_n N_c \exp\left(\frac{E_t - E_c}{kT}\right)$$, where E_c is the band edge and E_t is the trap level.

Answer:

$$r_1 = n \cdot v_{th} \sigma_n N_t (1-f)$$

$$r_2 = e_n N_t f$$

therefore:

$$e_n N_t f = n \cdot v_{th} \sigma_n N_t (1-f)$$

therefore,

$$e_n f = n \cdot v_{th} \sigma_n (1-f)$$

$$e_n \frac{1}{1+\exp\left(\frac{E_t - E_f}{kT}\right)} = n \cdot v_{th} \sigma_n (1 - \frac{1}{1+\exp\left(\frac{E_t - E_f}{kT}\right)})$$

multiply by through $1+\exp\left(\frac{E_t - E_f}{kT}\right)$

$$e_n = n \cdot v_{th} \sigma_n \exp\left(\frac{E_t - E_f}{kT}\right)$$

Substitute in

$$n = N_c \exp\left(\frac{E_f - E_c}{kT}\right)$$

and obtain

$$e_n = n \cdot v_{th} \sigma_n \exp\left(\frac{E_t - E_c}{kT}\right)$$

c) Both carrier dependent Langevin recombination (MacKenzie et al. *J. Phys. Chem. C,* 2011, 115 (19), pp 9806–9813) and SRH recombination (Kirchartz et al. Phys. Rev. B 83, 115209 (2011)) can be used to describe recombination in OPV devices. In SRH recombination carrier recombine via a trap state, thus recombination can be though of as free carrier to trapped carrier recombination. Show that carrier density dependent Langevin recombination is equivalent to free-carrier to trapped-carrier recombination.

Answer:

Carrier dependent electron and hole mobilities can be written as:

$$\mu_e(E_f)=\mu_e^0\frac{n_{free}}{n_{total}} \qquad \mu_h(E_f)=\mu_h^0\frac{p_{free}}{p_{total}}$$

We can write mobility dependent Langevin recombination as

$$R=\frac{q}{\epsilon_0\epsilon_r}(\mu_e^0(n)+\mu_h^0(p))n_{total}p_{total}$$

therefore substituting the expressions for mobility in to the above equation:

$$R=\frac{q}{\epsilon_0\epsilon_r}(\mu_e^0 n_{free}p_{total}+\mu_h^0 p_{free}n_{total})$$

if the number of free carriers is small we can write:

$$R=\frac{q}{\epsilon_0\epsilon_r}(\mu_e^0 n_{free}p_{trap}+\mu_h^0 p_{free}n_{trap})$$

d) Carrier dependent Langevin recombination assumes that all the carriers have had time to thermalise and thus assumes one quasi-Fermi level can describe both free and trapped carriers. Under which circumstances may this not be a good approximation?

When there the device is not at steady state.

Dr. Roderick MacKenzie 8/2011