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BASIC EQUATIONS FOR STATISTICS, RECOMBINATION PROCESSES, AND PHOTOCONDUCTIVITY IN AMORPHOUS INSULATORS AND SEMICONDUCTORS

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The original work of Shockley and Read, which described the statistic of a single trapping level in terms of four simple processes, is applied to insulators and semiconductors containing an arbitrary distribution of trapping levels. These statistics formerly involved solving an arbitrary number of rate equations; however, by the use of a mathematical artifice, a simple formal solution is obtained. The solution is also shown to be generally valid for an arbitrary dependence in energy of the cross sections $\sigma_n(E)$ and $\sigma_p(E)$ and to be independent of the effects of band to band recombination. Using the statistics, expressions are derived for the rate of recombination and the lifetimes of free carriers in such systems. Also, the ground rules for photoconductivity in amorphous materials are presented; these rules are summarized by two general equations. The first is the steady-state rate equation giving the total net rate of recombination of photoexcited carriers via all the trapping levels in the energy gap. The second is a general statement of charge neutrality, which shows that the excess charge contained in trapping levels above E_{F0} (the equilibrium Fermi level) is equal to the charge that has been removed from trapping levels below E_{F0}.

1. Introduction

Shockley–Read statistics[1]) have been extremely successful in describing non-equilibrium steady-state processes in crystalline semiconductors. The work was concerned with four generation–recombination processes occurring through a single trapping level. Our object here is to apply these processes to semiconductors and insulators containing an *arbitrary* distribution of trapping levels in their energy gaps, and to determine the recombination statistics and the ground rules for photoconductivity in such systems.

2. Kinetic processes

The four kinetic processes for a particular trapping level are illustrated in the fig. 1. G represents the rate of generation of electron–hole pairs, which we assume is directly proportional to the light intensity.

The four processes are described in terms of the free carrier densities n and p, the parameters of the trapping level, and the non-equilibrium occupancy

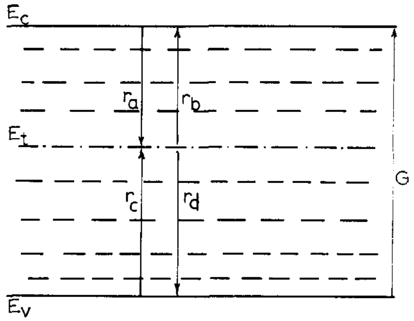

Fig. 1. Kinetic processes associated with a particular trapping level of a distribution of trapping levels.

function f. The rate, r_a, of capture of electrons by the trapping level is given by

$$r_a = \bar{n}\, N_t(1 - f), \tag{1}$$

where $\bar{n} = v\sigma_n n$, n is the free electron density, v is the thermal velocity, σ_n is the capture cross section for electrons, N_t is the trapping density of the level and $N_t(1-f)$ is the number of empty states in the trapping level. The rate of emission r_b of electrons from the trap is given by

$$r_b = e_n N_t f, \tag{2}$$

where $N_t f$ is the fullness of the trap, and e_n is the rate of emission of electrons from the trap. From detailed balance considerations $e_n = v\sigma_n N_c \exp[(E_t - E_c)/kT]$, where N_c is the effective density of states in the conduction band, and E_t is the energy of the trap level. Equations analogous to (1) and to (2) for the emission and capture of holes are given by

$$r_c = \bar{p} N_t f \quad \text{and} \quad r_d = e_p N_t(1 - f), \tag{3}$$

respectively, where

$$\bar{p} = v\sigma_p p \quad \text{and} \quad e_p = v\sigma_p N_v \exp[(E_v - E_t)/kT].$$

3. Non-equilibrium steady state-statistics

Let us now consider an arbitrary distribution of trapping levels in the band gap as shown in fig. 1. The rate of change, dn/dt, of free electrons in the conduction band is

$$\frac{dn}{dt} = G - \int_{E_v}^{E_c} \bar{n} N(E)(1 - f)\, dE + \int_{E_v}^{E_c} e_n\, N(E)\, f\, dE - \beta np. \tag{4}$$

The term βnp is the rate at which free electrons and free holes recombine directly across the band gap, a process which is normally referred to as bimolecular recombination. Analogous expressions hold for the rate of change, $\mathrm{d}p/\mathrm{d}t$, of free holes in the valence band; that is

$$\frac{\mathrm{d}p}{\mathrm{d}t} = G - \int_{E_v}^{E_c} \bar{p}\, N(E)\, f\, \mathrm{d}E + \int_{E_v}^{E_c} e_p\, N(E)\, (1-f)\, \mathrm{d}E - \beta np \tag{5}$$

In the steady-state condition we have $\mathrm{d}n/\mathrm{d}t=0$ and $\mathrm{d}p/\mathrm{d}t=0$. The problem at hand is to extract the occupancy function f from (4) and (5). This is accomplished[2]) by subtracting (5) from (4) and using the steady-state conditions, to obtain

$$\int_{E_v}^{E_c} N(E)\,[e_n f - e_p(1-f) - \bar{n}(1-f) + \bar{p}f]\,\mathrm{d}E = 0. \tag{6}$$

Since this integral is equal to zero for an *arbitrary* distribution of traps $N(E)$, then it follows that the factor in the square brackets must be identically equal to zero; from this relation we obtain the statistic

$$f = \frac{\bar{n} + e_p}{\bar{n} + \bar{p} + e_n + e_p}, \tag{7}$$

which is simply the statistic originally derived by Shockley and Read for a single trap level. However, we have shown that the same statistic is valid for an arbitrary distribution of trapping levels. It is of some interest now to discuss several salient features of this statistic, which up until now, have not been recognized. Let us assume that the capture cross sections σ_n and σ_p are either constant in energy or their ratio σ_n/σ_p is equal to a constant, say R. This condition will define a species of traps. In this case we may define an energy E_{tn} by the condition $e_n = \bar{n} + \bar{p}$, or

$$E_{tn} = E_{F0} + kT \ln\left[\frac{\sigma_p p + \sigma_n n}{\sigma_n n_0}\right], \tag{8}$$

where E_{F0} is the equilibrium Fermi level and n_0 and p_0 are the dark carrier concentrations. It then follows from (7) and (8) that for levels above E_{F0} ($e_p \ll \bar{n}, \bar{p}, e_n$), the electron occupancy is given by the modulated Fermi–Dirac function

$$f = \frac{Rn}{Rn + p}\left\{\frac{1}{1 + \exp[(E_t - E_{tn})/kT]}\right\}, \tag{9}$$

centered about the energy E_{tn}, as shown in fig. 2. E_{tn} is designated the quasi-Fermi level for *trapped* electrons; this is because below E_{tn} the occupancy of the levels is essentially constant and equal to $Rn/(Rn+p)$. (Note that E_{tn} never coincides with the quasi-Fermi level for free electrons and also that the levels are never *fully* occupied; for example, if $R=1$ and $n=p$ the occupancy of the levels is $\frac{1}{2}$). On the other hand, traps above E_{tn} are occupied according to Boltzmann statistics. Thus the occupancy is quite low and decays exponentially with increasing energy above E_{tn}. Similar considerations hold in the lower half of the band gap ($e_n \ll \bar{n}, \bar{p}, e_p$) for trapped holes. In this case it can

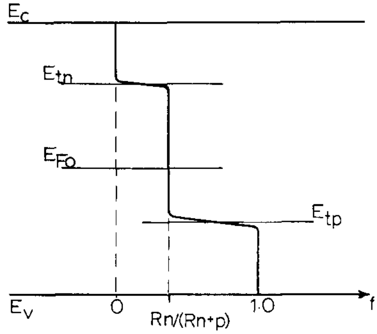

Fig. 2. Non-equilibrium statistics of occupancy for an arbitrary distribution of trapping levels belonging to a particular species $R=\sigma_n(E)/\sigma_p(E)$.

be shown that the occupancy of the levels with holes $(1-f)$ is given by a modulated Fermi–Dirac function

$$1-f=\frac{p}{Rn+p}\left\{\frac{1}{1+\exp\left[(E_{tp}-E_t)/kT\right]}\right\}, \tag{10}$$

centered about the energy E_{tp} (quasi-Fermi level for trapped holes) defined by $e_p=\bar{n}+\bar{p}$, or

$$E_{tp}=E_{F0}-kT\ln\left[\frac{\sigma_n n+\sigma_p p}{\sigma_p p_0}\right]. \tag{11}$$

The significant feature of the statistic is that between the energy levels E_{tn} and E_{tp} the occupancy of the levels with electrons is constant and equal to $Rn/(Rn+p)$. Furthermore, it will be apparent from (8) and (11) that with increasing light intensity the energies E_{tn} and E_{tp} approach the band edges E_c and E_v respectively.

4. Charge neutrality considerations

The condition for charge neutrality is

$$\Delta p - \Delta n = \int_{E_v}^{E_c} N(E)\left[\frac{\bar{n}+e_p}{\bar{n}+\bar{p}+e_n+e_p}\right]\mathrm{d}E - \int_{E_v}^{E_c} N(E)\{1+\exp[(E_{F0}-E_t)/kT]\}^{-1}\,\mathrm{d}E, \qquad (12)$$

where $\Delta n = n - n_0$ and $\Delta p = p - p_0$. The first term on the right in (12) is the number of electrons in traps in the steady state; the second term is the number of electrons in traps in thermal equilibrium. Generally speaking, in insulators and amorphous semiconductors the excess free electrons are many orders of magnitude less than the trapped electrons. Thus the two terms on the right side may be equated and with appropriate manipulation we have

$$\int_{E_{F0}}^{E_{tn}} N(E)\left(\frac{\bar{n}}{\bar{n}+\bar{p}}\right)\mathrm{d}E = \int_{E_{tp}}^{E_{F0}} N(E)\left(\frac{\bar{p}}{\bar{p}+\bar{n}}\right)\mathrm{d}E. \qquad (13)$$

This equation is the statement of charge neutrality for amorphous semiconductors and insulators.

5. Net rate of recombination

The net rate of recombination U of electron–hole pairs in the steady state is equal to the generation rate of electron–hole pairs G. Thus, substituting (7) into (4) we obtain the net recombination rate,

$$U = G = \int_{E_v}^{E_c} \frac{N(E)\,\bar{n}\bar{p}\,\mathrm{d}E}{(\bar{n}+\bar{p}+e_n+e_p)}. \qquad (14)$$

In obtaining (14) we have neglected the contribution of bimolecular recombination, which is important only at extremely high levels of illumination.

The factor $N(E)\,\bar{n}\bar{p}/(\bar{n}+\bar{p}+e_n+e_p)$ [the integrand of (14)] represents the *efficacy* of a particular level in the recombination process. For the case of a slowly varying distribution of trapping levels, fig. 3 shows the efficacy of the recombination process as a function of energy for constant values of σ_n and σ_p. The interesting feature of this curve is that it is only those levels positioned between the E_{tn} and E_{tp} that are effective in the recombination process. In

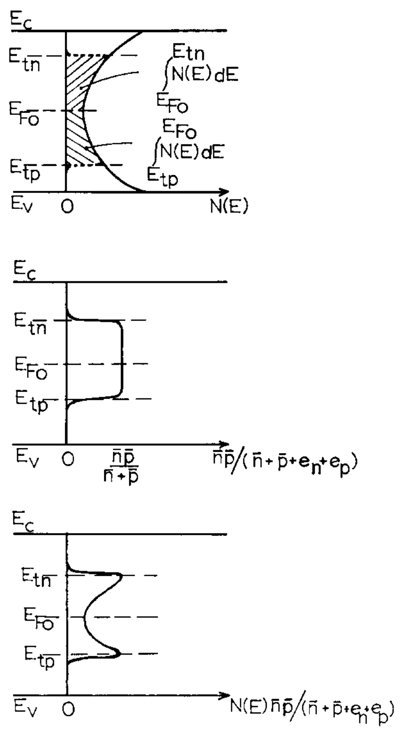

Fig. 3. Efficacy of recombination for a slowly varying distribution of trapping levels with constant values of σ_n and σ_p for all levels.

this region the efficacy is *constant* and given by $\bar{n}\bar{p}/(\bar{n}+\bar{p})$. Hence (14) may be written as

$$G = \frac{\bar{n}\bar{p}}{\bar{n}+\bar{p}} \int_{E_{tp}}^{E_{tn}} N(E)\,\mathrm{d}E. \tag{15}$$

6. Free carrier lifetimes

The lifetimes for electrons and holes are defined by $\tau_n = \Delta n/G$ and $\tau_p = \Delta p/G$ respectively. Under the steady state conditions in insulators $n \gg n_0$ and $p \gg p_0$. Thus by solving (13), (15) and (16) the case of *constant* capture cross sections σ_n and σ_p yields the following simple expressions for the lifetimes:

$$\tau_n = \left(v\sigma_n \int_{E_{F0}}^{E_{tn}} N(E)\,\mathrm{d}E\right)^{-1}, \qquad \tau_p = \left(v\sigma_p \int_{E_{tp}}^{E_{F0}} N(E)\,\mathrm{d}E\right)^{-1}. \tag{17}$$

The interesting features of (17) is that the integral in (17) are just the number of traps between E_{F0} and E_{tn} and between E_{tp} and E_{F0} respectively, as shown in fig. 3.

7. Photocurrent

The photocurrent I_p is defined by

$$I_p = q\,(\mu \Delta n + \mu_p \Delta p)\,\mathscr{E}\,, \tag{18}$$

where q is the unit of electronic charge, μ_n and μ_p are the mobilities of the excess electron and holes respectively, and $\mathscr{E}$ is the electric field strength. Substituting (21) and (22) into (27), and using (17), we have, for *constant* capture cross sections

$$I_p = \frac{qG\mathscr{E}}{v}\left\{\mu_n\left[\sigma_n \int_{E_{F0}}^{E_{tn}} N(E)\,\mathrm{d}E\right]^{-1} + \mu_p\left[\sigma_p \int_{E_{tp}}^{E_{F0}} N(E)\,\mathrm{d}E\right]^{-1}\right\}. \tag{19}$$

References

1) W. Shockley and W. T. Read, Phys. Rev. **87** (1952) 835.
2) J. G. Simmons and G. W. Taylor, Phys. Rev. B **4** (1971) 502.