Electronic Transport and Recombination in Amorphous Semiconductors at Low Temperatures

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The problem of simultaneous diffusion and recombination of electron-hole pairs, photoexcited in noncrystalline semiconductors at low temperatures, is reduced to a universal mathematical problem whose solution does not depend on the density-of-states function. We derive a general geminate-recombination function which at low light intensities describes the distribution of radiative recombination times. The low-temperature photoconductivity is found to depend only weakly on material parameters and agrees with experiments on hydrogenated amorphous silicon.

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Electronic processes in disordered materials such as noncrystalline semiconductors are very complicated because the lack of long-range order invalidates the use of the elegant theorems that are based on the periodic spatial arrangements of atoms found in crystals. As a result there are only few theories that have general validity and offer experimentally verifiable predictions.

In this paper we present a simple solution of apparently complicated phenomena, the radiative recombination, diffusive hopping motion, and photoconductivity of photo carriers in noncrystalline semiconductors at very low temperatures. Our solution is probably applicable to a variety of problems or material systems because it generally deals with the hopping motion of particles among random sites in space in the absence of thermal agitation.

In amorphous semiconductors these random sites are the tails of localized states that extend from the conduction and valence bands into the mobility gap.[1] We present here a simple treatment of the fate of electron-hole pairs in these localized tail states after photoexcitation of such pairs at or slightly below the mobility edges. This treatment is particularly simple at low temperatures where hopping can occur only to localized states lying lower in energy. We derive expressions for geminate recombination as well as for the dc photoconductivity at low temperature. We neglect nonradiative and defect recombination because they were found to be negligible in the amorphous semiconductors whose properties we shall use for comparison with our results.

After photogeneration in localized states the electron-hole pair is quite close because absorption by a distant pair of states is small due to the small value of their overlap integral. During subsequent hops through tail states the pair has a probability $\nu_r/(\nu_r+\nu_d)$ to recombine radiatively and a probability $\nu_d/(\nu_r+\nu_d)$ for each carrier to hop to the next site. Both these transitions occur by tunneling so that one finds for the recombination and diffusion rate, respectively,[2]

$$\nu_r(R)=\tau_0^{-1}\exp(-2R/a)\,, \tag{1}$$

$$\nu_d(r)=\nu_0\exp(-2r/a)\,. \tag{2}$$

Here R is the electron-hole separation, r is the distance from the carrier to the nearest tail state, and a is the localization radius. One might suppose that radiative recombination has the greatest chance at the beginning, while the electron is close to the hole. This, however, is not the case because the attempt-to-escape frequency ν_0 is typically of the order of a phonon frequency $\nu_0\sim 10^{12}\text{-}10^{13}$ s^{-1}, while the magnitude of $\tau_0^{-1}\approx 10^8$ s^{-1} is determined by the dipole matrix element. Hence at the beginning, when both r and R are small, $\nu_d \gg \nu_r$, and the pair separates by diffusive hopping.

This diffusive motion, which we call energy-loss hopping, is of a special kind because each subsequent hopping step occurs, on the average, over a larger distance than the previous one as illustrated in Fig. 1. Here the hole is considered fixed for simplicity and the motion of only the electron is shown. The progressively increasing hop distance arises from the assumption that every state at distance r having a lower energy is reached with the same probability. From this assumption it follows that the concentrations of states available for successive hops

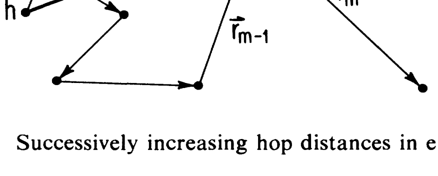

FIG. 1. Successively increasing hop distances in energy-loss hopping.

are related as

$$N_m = N_{m-1} x_m , \tag{3}$$

where x_m is a random number $0 < x_m < 1$ with the average value $\langle x_m \rangle = \frac{1}{2}$, independent of the energy dependence of the density of localized states.[3] This information together with Eqs. (1) and (2) is sufficient to obtain by a computer calculation a general function describing the diffusive motion and the probability for recombination.

Before presenting this general function we derive its shape by the following simple arguments. The electron-hole separation is given by

$$\langle R_m^2 \rangle = \sum_{i=1}^{m} \langle r_i^2 \rangle , \tag{4}$$

with

$$\langle r_m^2 \rangle \approx 2^{2/3} \langle r_{m-1}^2 \rangle . \tag{5}$$

At each step radiative recombination over the separation R_m competes with diffusive hopping to the next site at a distance r_{m+1}. Defining a characteristic length R_c as[4]

$$R_c = (a/2) \ln(\nu_0 \tau_0) , \tag{6}$$

we can write

$$\nu_d(r_{m+1}) / \nu_r(R_m) = \exp(2A/a) , \tag{7}$$

where

$$A = R_c - (r_{m+1} - R_m) . \tag{8}$$

From Eq. (7) one can see that $A > 0$ favors diffusion and $A < 0$ favors radiative recombination. The sum of the geometric progression in Eq. (4) is close in magnitude to its last member. Consequently, when r_{m+1} and $R_m < R_c$ one obtains $A > 0$, whereas A fluctuates between positive and negative values when r_{m-1} and $R_m > R_c$. We can estimate the probability $\eta(R)$ for surviving to a separation $R > R_c$ as follows. The distance R is reached from R_c on the average in M steps:

$$R \sim R_c (2^{1/3})^M , \tag{9}$$

$$M \sim 3 \ln(R/R_c) / \ln 2 . \tag{10}$$

At each step there is a probability q for escape. This probability does not depend on the step number m because the problem remains self-similar for $R > R_c$ despite the change of scale. Thus

$$\eta(R) \propto q^M = \exp(-M |\ln q|) \tag{11}$$

and substituting Eq. (10) into Eq. (11) yields

$$\eta(R) \propto (R_c/R)^{3|\ln q|/\ln 2} \equiv (R_c/R)^{\beta} . \tag{12}$$

The probability density for radiative recombination, $P(R) = -d\eta/dR$, is therefore

$$P(R) \propto R_c^{-1} (R_c/R)^{\beta+1} \quad (R > R_c) . \tag{13}$$

The recombination probability density $P(R)$ is very small when $R \ll R_c$ because $A > 0$ favors diffusion. $P(R)$ reaches a maximum near R_c and then follows the power-law decrease of Eq. (13). Computer calculations have confirmed these predictions. We find

$$P(R) = R_c^{-1} f(R/R_c) , \tag{14}$$

where $f(R/R_c)$ shown in Fig. 2 is a general function independent of the distribution of localized states provided that R and $R_c \gg a$ and $N_0^{-1/3}$, where N_0 is the total concentration of localized states. The maximum occurs at $R/R_c \approx 0.8$ and $\beta = 1 \pm 0.1$ for $R > R_c$. We call $f(R/R_c)$ the geminate-recombination function and β the geminate-recombination index.

Note that the algorithm used for modeling was not exact. We assumed that states which the electron can visit at step m are randomly distributed in space; i.e., we simulated a Markovian process. Preliminary results using an exact algorithm give a slightly smaller value for the geminate-recombination index, $\beta = 0.8 \pm 0.2$ for $2R_c \leq R \leq 5R_c$.

The experimental quantity to be compared with $P(R)$ is $W(\ln \tau)$, the distribution of the logarithm of the photoluminescence decay time, where $\tau = \nu_r^{-1}$. The maximum of this distribution is observed at $\tau \sim 10^{-4}$-10^{-5} s in hydrogenated amorphous silicon (*a*-Si:H).[5,6] From the position of the maximum of $P(R)$, $R_{\max} \simeq 0.8 R_c$, and Eq. (1), one predicts

$$\tau_{\max} = \tau_0 (\nu_0 \tau_0)^{0.8} \tag{15}$$

or $\tau_{\max} \simeq 10^{-5}$ s using the values of τ_0 and ν_0 mentioned at the beginning of this paper, in good agreement with experiment. On the other hand, the experimental curve $W(\ln \tau)$ decreases as $(\ln \tau)^{-\alpha}$ with $3 < \alpha < 4$ at long times.[5,6] According to Eq. (13) we should expect $\alpha = \beta + 1 \simeq 2$. We suggest that this discrepancy is due to the large concentration n_0 of photoexcited pairs per excitation pulse used in the experiment. It can be shown that the long-time decay follows $P(R) \propto 1/n_0 R^4$ when saturation of the occupancy of the tail states becomes

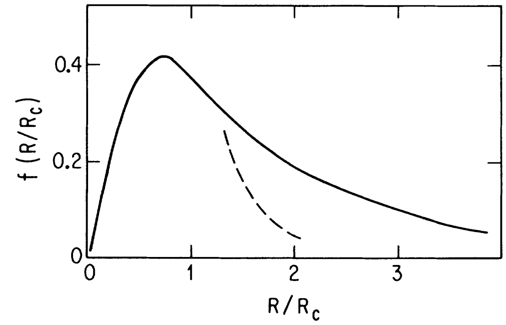

FIG. 2. Geminate-recombination function $f(R/R_c)$ as a function of geminate pair separation R in units of the critical length scale R_c.

important. This decay, sketched by the dashed line in Fig. 2, agrees quite well with the experiments.

We used for the photoluminescence decay time $\tau = \nu_r^{-1}$. One can suspect, however, that for some electrons the time of the longest hop $\nu_d^{-1}(r_{\max})$ may be longer than $\nu_r^{-1}(R)$ and therefore $\tau = \nu_d^{-1}(r_{\max})$. We have computed $P(\ln\tau)$, where $\tau = \max\{\nu_r^{-1}(R), \nu_d^{-1}(r_{\max})\}$, and have found it to be indistinguishable from $P(\ln\nu_r^{-1}(R))$ within the accuracy of the simulation. That justifies the use of $P(R)$ and $\tau = \nu_r^{-1}$ for the comparison with luminescence experiments.

We now turn to the question of the steady-state carrier concentration n and the photoconductivity σ_P under a constant pair generation rate G.

Electrons that reach a distance $n^{-1/3}$ find themselves at equal distance to their own and to other holes. At that point nongeminate recombination becomes important. An estimate of n is obtained by equating the concentration reaching $n^{-1/3}$ per unit time with the rate of recombination over that distance:

$$G\eta(n^{-1/3}) = (n/\tau_0)\exp(-2n^{-1/3}/a)\,. \tag{16}$$

When the generation rate G is increased such that $n^{-1/3} < R_c$, recombination occurs predominantly via close nongeminate electron-hole pairs as discussed earlier.[7]

A pair that recombines geminately cannot contribute to dc photoconductivity because the dipole moment produced by spatial diffusion is canceled by the recombination process. Hence we write the photocurrent density as a product of the rate of nongeminate recombination $G\eta(n^{-1/3})$ and the average dipole moment p of a geminate pair at the moment of nongeminate recombination

$$j = G\eta(n^{-1/3})p\,. \tag{17}$$

In order to obtain p one should take into account the spatial asymmetry of hopping due to an electric field E. To estimate this we have to use for the first time a density-of-states function $g(\epsilon)$. For simplicity we assume

$$g(\epsilon) = (N_0/\epsilon_0)\exp(-\epsilon/\epsilon_0)\,, \tag{18}$$

where the energy ϵ is measured from the mobility edge into the gap. The average dipole moment arising from a hop over a length r is

$$p(r) = (er)\frac{1}{3}\frac{eEr}{\epsilon_0}\,. \tag{19}$$

This equation is obtained by considering that the concentration of final hopping sites depends on the coordinate x along the field direction as

$$N(x) = N(0)\left[1 + \frac{eEx}{\epsilon_0}\right], \tag{20}$$

with the origin $x = 0$ at the initial state. The average value $\langle x\rangle$ for a nearest neighbor among all these states is

$$\langle x\rangle = \frac{1}{3}\frac{eE\langle r^2\rangle}{\epsilon_0}\,, \tag{21}$$

where $\langle r^2\rangle$ is the average square nearest-neighbor distance and the factor $\frac{1}{3}$ comes from directional averaging. Since $\langle r_m^2\rangle$ increases with m according to Eq. (5), the dipole moment is determined by the last hop before nongeminate recombination

$$p = p(n^{-1/3})\,. \tag{22}$$

With $\sigma = j/E$ we obtain the dc photoconductivity

$$\sigma_P = G\eta(n^{-1/3})\frac{e^2}{3}\frac{n^{-2/3}}{\epsilon_0} \quad (n^{-1/3} > R_c)\,. \tag{23}$$

Substituting the steady-state concentration n from Eq. (16) and $\eta(R)$ from Eq. (12) with $\beta = 1$ we find

$$\sigma_P = G\frac{e^2a^2}{12\epsilon_0}\ln(\nu_0\tau_0)L\,, \tag{24}$$

where L represents $2n^{-1/3}/a$ and is the solution of the equation $L = \ln[G\tau_0(a/2)^3L^2\ln(\nu_0\tau_0)]^{-1}$. The photoconductivity depends on G as $\sigma_P \propto G^{\gamma}$ with

$$\gamma = -1 - L^{-1}\,. \tag{25}$$

Substituting values appropriate to a-Si:H,[1,2] $a = 1$ nm, $\epsilon_0 = 0.025$ eV, $\nu_0\tau_0 = 10^4$, and $G = 10^{20}\ \mathrm{cm}^{-3}\mathrm{s}^{-1}$, we obtain from Eqs. (23) and (24) $L \simeq 15$, $\sigma_P/eG = 5\times10^{-12}$ cm^2/V, and $\gamma = 0.93$ which agree reasonably well with the experimental observations[8,9] $\sigma_P/eG = (5\times10^{-12})$–$(3\times10^{-11})$ cm^2/V and $\gamma = 0.97 \pm 0.03$. Since the localization radius a and the decay parameter ϵ_0 which characterizes the tails of localized states do not vary by more than a factor of order 2 we expect the value of σ_P/eG to be of the same order of magnitude for many amorphous semiconductors.

Let us briefly discuss the effect of the Coulomb interaction of geminate carriers on the function $P(R)$. Being born typically at a short distance ($\approx a$) from the hole, the electron has a binding energy $\epsilon_b \approx e^2/\kappa a$, with κ the dielectric constant. Using $g(\epsilon)$ of Eq. (18) we obtain for the average length of the first hop down in energy

$$R(\epsilon_b) = N_0^{-1/3}\exp\left[\frac{e^2}{3\epsilon_0\kappa a}\right]. \tag{26}$$

If $R(\epsilon_b) < R_c$, then $P(R)$ is not significantly affected by the Coulomb interaction. In the unlikely event that $R(\epsilon_b) > R_c$, most electrons recombine before the first step and the whole function $P(R)$ at $R > N_0^{-1/3}$ thereby receives a small normalization factor.

We conclude by noting that the problem of simultaneous diffusion and recombination of electron-hole pairs at low temperatures is reduced to a universal mathematical problem whose solution does not depend on the density-of-states function. It is shown that the survival probability $\eta(R)$ decreases with R according to a power law whose exponent β is a new critical index characteristic only of the property of a random distribution of points in 3D space. In order to observe the manifestations of the large-R tail of the geminate-recombination function $P(R)$ one should use small excitation intensities. A theory of the stationary-state carrier concentration and of the dc photoconductivity is presented.

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[9] In these experiments photocarriers were excited to extended states above the mobility edge. Part of the observed σ_P may therefore arise during thermalization of the photocarriers in the extended states.