Model for surface recombination

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A model is proposed for radiationless recombination in a system with a continuous spectrum of localized states, e.g., at a surface. The saturation recombination flux and the rate of surface recombination are estimated on the basis of recombination channels: ladders of levels of closely spaced states.

The recombination of nonequilibrium carriers in semiconductors is hindered by the circumstance that the probability for the simultaneous emission of a large number of phonons with a total energy equal to the gap width E is usually very small. At low temperatures, $kT \ll \hbar\omega$, the transition frequency can be described in order of magnitude by

$$\nu = \omega\gamma^{E/\hbar\omega} \simeq \omega e^{-E/\epsilon_0} , \tag{1}$$

where ω is a frequency on the order of Debye frequency, $\gamma < 1$ is a dimensionless constant which is a measure of the coupling of electrons with phonons, and $\epsilon_0 \simeq \hbar\omega/\ln\gamma^{-1}$. If $E = 1$ eV and $\epsilon_0 = 0.03$ eV, we have $\nu \ll 1$ Hz, which could of course in no way correspond to experiment. Recombination is facilitated by impurity states in the energy gap, which make it possible to reduce the number of phonons scattered in one event. A particularly rapid recombination occurs at a surface, where the energy gap contains surface states with a finite density $g(\epsilon)$.

Our purpose in the present letter is to estimate the low-temperature rate of surface recombination as a functional of $g(\epsilon)$, under the assumption that all the surface states are formed by short-range potential wells which are distributed randomly over the surface, and each of which can trap a single electron. With an eye on high carrier densities, we ignore band-curvature effects near the surface. We write the frequency of tunneling of an electron accompanied by the emission of an energy $\Delta\epsilon$ between two localized states, separated from each other by a distance r, as follows:

$$\nu = \omega e^{-\Delta\epsilon/\epsilon_0} e^{-2r/a} , \tag{2}$$

where a is the localization length. We treat the surface as consisting of a set of recombination channels connected in parallel, each consisting of a "ladder" of levels created by states which are close together on the surface (Fig. 1). We characterize each channel by the number M, which is the number of successive "rungs" of average height E/M, by the scatter in the heights of the rungs ($\delta\epsilon$), and by the typical distance (R) an electron jumps along the surface. We begin by calculating j_s: the maximum number of pairs which can recombine per second per square centimeter of the surface. In other words, this is the saturation value of the recombination flux density. We write j_s as

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$$j_s = \sum_i N_i \tau_i^{-1}, \tag{3}$$

where

$$N_i = \frac{1}{R^2} (gR^2 \delta\epsilon)^M \tag{4}$$

is the number of channels of "type"

$$\tau_i^{-1} = \omega e^{-E/M\epsilon_0} e^{-\delta\epsilon/\epsilon_0} e^{-2R/a} \tag{5}$$

(this is the reciprocal of the scale time for descent along such channels). Because of the pronounced scatter in the frequencies in (2), τ_i is determined by the slowest jump along the ladder. The product $N_i \tau_i$ has a sharp maximum as a function of M, R, and $\delta\epsilon$ at

$$M_m = \left(\frac{E}{\epsilon_0} \Big/ \ln \frac{1}{gR_m^2 \delta\epsilon_m} \right)^{1/2}, \quad R_m = M_m a, \quad \delta\epsilon_m = \epsilon_0 M_m , \tag{6}$$

We see that the condition $\delta\epsilon_m \ll E/M_m$ holds; i.e., the levels of a channel are essentially equidistant. Substituting (6) into (4), (5), and (3), we find

$$j_s = \frac{\omega \epsilon_0 L}{a^2 E} \exp\left\{ -2\sqrt{\frac{EL}{\epsilon_0}} \right\}, \quad L \equiv \ln \frac{\epsilon_0^{1/2}}{ga^2 E^{3/2}} . \tag{7}$$

In this derivation we have assumed that g and a are independent of the energy ϵ ($\epsilon = 0$ at the center of the energy gap). It is easy to show that even for an exponential functional dependence $g(\epsilon)$ the levels of the channel remain essentially equidistant, and the logarithm in (7) should be replaced by its average value over the energy gap:

$$\frac{1}{E} \int_{-E/2}^{E/2} d\epsilon \ln \frac{\epsilon_0^{1/2}}{g(\epsilon) a^2(\epsilon) E^{3/2}} . \tag{8}$$

Let us assume, for example, that $g(\epsilon)$ at $-E/2 < \epsilon < E/2$ is described by

$$g(\epsilon) = g_0 e^{-(E/2\epsilon_1)} \mathrm{ch}(\epsilon/\epsilon_1) , \tag{9}$$

where $E \gg \epsilon_1/\epsilon_0$. Substituting (9) into (8) and (7), and assuming $\ln(\epsilon_0^{1/2}/g_0 a^2 E^{3/2}) \ll \sqrt{E/4\epsilon_1}$, we find the approximate result

$$j_s \simeq \frac{\omega \epsilon_0}{a^2 \epsilon_1} \exp\left\{ -\frac{E}{\sqrt{\epsilon_0 \epsilon_1}} \right\} . \tag{10}$$

We see that under the condition $\epsilon_1 > \epsilon_0$ the exponential function in (10) is considerably larger than that in (1). To find an estimate, we assume $\omega = 10^{13}\ \mathrm{s}^{-1}$, $a = 15$ Å, $E = 1$ eV, $\epsilon_0 = 0.03$ eV, and $\epsilon_1 = 0.15$ eV; we find $j_s = 3 \times 10^{19}\ \mathrm{cm}^{-2} \cdot \mathrm{s}^{-1}$. This calcu-

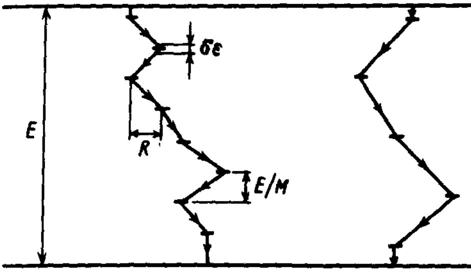

FIG. 1. Energy gap at the surface of a semiconductor. Two recombination channels are shown; that at the left is the faster.

lation has much in common with the theory of the hopping electrical conductivity across a thin film.[1,2]

We now consider the problem of calculating the steady-state density of carrier pairs, n, near a surface if G pairs are generated per second per square centimeter of the surface and if nearly all pairs recombine at the surface. This density can be measured, for example, with the help of the weak radiative recombination. In the theory, n is found from the equality $j(n) = G$, where $j(n) = sn$ is the recombination flux density, and s is the rate of surface recombination, which is ordinarily assumed to be independent of n. As we will see below, the "clogging" of the channels in our model makes s a strong function of n. To calculate $j(n)$, we need an expression for the rate at which free carriers are captured into the channel:

$$\nu_c = n\sigma_c v = n\sigma v \frac{\tau_f}{\tau_c} = \frac{n\sigma^{3/2}}{\tau_c} \equiv \frac{n}{n_0\tau_c}. \qquad (11)$$

Here σ_c is the capture cross section, v is the velocity of the electron, $\sigma \equiv n_0^{2/3}$ is the cross-sectional area of the region in which an electron can be captured while emitting phonons, τ_f is the transit time through this region, and τ_c is the scale time of capture from it. For $j(n)$ we have

$$j(n) = \sum_i N_i \left(\tau_i + \frac{\tau_{ci} n_0}{n} \right)^{-1} \qquad (12)$$

If we assume that we have $\tau_{ci} = \tau_i$ for all the channels, we find $j(n) = j_s n/(n_0 + n)$. Actually, for many of the channels the probability for the first rung to be lower than the others will be appreciable, so that there will be a rapid capture into the channel ($\tau_{ci} \ll \tau_i$). We therefore assume that all the channels have the identical value $\tau_{ci} = \tau_c$, which is shorter than the time (τ_m) of the descent through a channel with the parameters in (6). With $n > n_s \equiv n_0\tau_c/\tau_m$, it then follows from (12) that we have $j(n) = j_s$. Under the condition $n \ll n_s$, the sum in (12) is dominated by channels with $\tau_i \simeq \tau_c n_0/n \gg \tau_m$, i.e., according to (5), by channels with

$$M \simeq M_0(n) \equiv \frac{E}{\epsilon_0} \left(\ln \frac{\omega \tau_c n_0}{n} \right)^{-1} \qquad (13)$$

Roughly speaking, these channels are half-filled and separate the clogged slow chan-

nels from the empty fast ones. After an estimate of the typical values R and $\delta\epsilon$, a calculation of the number of working channels yields

$$j(n) = \frac{1}{a^2M_1^2}(M_1^3 g a^2 \epsilon_0)^{M_0}\frac{n}{n_0\tau_c} \qquad \left(M_1 \equiv \frac{\ln(\omega\tau_c n_0/n)}{\ln(M_1^3 g a^2\epsilon_0)^{-1}}\right) \tag{14}$$

which is a weaker than linear function of n. Correspondingly, $s(n)$ falls off with increasing n. This is a consequence of the progressive clogging of channels which are encountered comparatively frequently but which are slow. It follows from a substitution of (6) into (4) that only a fraction $\exp\{-\sqrt{EL/\epsilon_0}\}$ of the entire number of channels is working at saturation. Consequently, as n is increased to n_s, the value of s decreases by a factor of $\exp\{\sqrt{EL/\epsilon_0}\} = 10^3$ (we used the parameter values listed above for this estimate). If we assume $n_0 \approx R_m^{-3} \approx 3\times10^{18}$ cm^{-3}, and if we set $\tau_c = \tau_m$ for definiteness, we find that as n increases to n_s, the rate s decreases from 10^4 to 10 cm/s. These estimates agree with the observed decrease in s in germanium at the transition from the recombination of excitons to the recombination of electron-hole droplets.[3]

Solving the equation $j(n) = G$ for $n(G)$ under the condition $G \ll j_s$, we find

$$n = n_0\sqrt{\omega G}\,\tau_c a M_1 \exp\left\{\sqrt{\frac{1}{4}\ln^2(Ga^2M_1^2/\omega) - \frac{E}{\epsilon_0}\ln(ga^2\epsilon_0 M_1^3)^{-1}}\right\} \tag{15}$$

There is no steady-state solution at $G > j_s$. In this case j_s can be measured on the basis of the dependence $n(t)$ after an excitation pulse which creates a density $n_1 \gg n_s$. This dependence should be of the form $n(t) = n_1 - j_s t/d$, where d is the thickness of the sample.

Although we have been talking about a surface here, it is clear that we could take a similar approach to evaluate the rate of radiationless recombination in three-dimensional systems with a finite state density in an energy quasigap, e.g., in amorphous semiconductors.

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