Recombination in amorphous semiconductors at temperatures above 100 K

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A model of radiationless recombination is used for an exact calculation of the main exponential factor which determines the recombination flux. This factor contains strongly nonlinear temperature dependence in its argument.

1. The recombination of charge carriers determined by photoluminescence in amorphous semiconductors begins to fall off rapidly at temperatures above 70 K.[1] It is apparently governed by radiationless processes at higher temperatures. Analysis of these processes in the case of a quasicontinuous spectrum of localized states (capture centers) in the mobility gap of an amorphous semiconductor reduces to the model of Ref. 2, in which an electron tunnels successively from one capture center to another, descending along a ladder of levels from the conduction band until it recombines with the hole.

The time (τ_i) of the transition from a deep level ϵ_i to a level ϵ_{i+1} of lower energy is determined by a multiphonon "shedding" of energy:

$$\tau_i = \nu_0^{-1} \exp(\Delta\epsilon/\epsilon_0 + 2\Delta r_i/a), \quad \Delta\epsilon = \epsilon_{i+1} - \epsilon_i. \tag{1}$$

Here $\Delta r_i = |\mathbf{r}_i - \mathbf{r}_{i+1}|$ is the distance between the centers which form the levels, a is the localization length of an electron at a center, and ϵ_0 and $h\nu_0$ are quantities on the order of the characteristic phonon energy. They depend weakly on $\Delta\epsilon$ and on the temperature T (we will ignore that dependence). We also assume $\Delta\epsilon \gg \epsilon_0$. We assume that $(M+1)$ levels with energies $\epsilon_1 < \epsilon_2 < \ldots \epsilon_{M+1} < G$ (G is the width of the mobility gap) participate in the recombination.

Transitions from the free state to the bound state are described by

$$\tau_e^{-1} = n V_e \nu_0 \exp(-\epsilon_1/\epsilon_0), \quad \tau_h^{-1} = p V_h \nu_0 \exp\left(\frac{\epsilon_{M+1} - G}{\epsilon_0}\right), \tag{2}$$

where V_e and V_h are the effective interaction volumes around a deep center in which a charge carrier may be captured. The time of transitions up the energy scale is related to τ_e and τ_h by the standard equations

$$\tau_e' = \tau_e \frac{n}{N_C} \exp\left(\frac{\epsilon_1}{T}\right), \quad \tau_h' = \tau_h \frac{P}{N_V} \exp\left(\frac{G - \epsilon_{M+1}}{T}\right), \tag{3}$$

where N_C and N_V are the effective densities of states in the C and V bands. Finally, the density of states in the mobility gap, $\rho(\epsilon)$, is described under the assumption that the

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first level and the $(M+1)$-st level are in the "tails" of the distributions at the upper and lower edges of the mobility gap. The other capture centers then have a density ρ_0 which is independent of ϵ:

$$\rho(\epsilon_1)=N_1 \exp\left(-\frac{\beta\epsilon_1}{\epsilon_0}\right), \quad \rho(\epsilon_{M+1})=N_2 \exp\left[-\frac{\beta(\epsilon_{M+1}-G)}{\epsilon_0}\right], \quad \rho(\epsilon_i)=\rho_0, \tag{4}$$

$$2\leqslant i\leqslant M; \quad N_1, N_2 \gg \rho_0.$$

Relations (1)–(4) completely model the formulation of the problem. We would simply point out that the characteristic localization length generally depends strongly on the depth of the center, ϵ_i. For the comparatively shallow 1st and $(M+1)$-st centers, for example, it is considerably larger than for the other, deep capture centers. For this reason, V_e and V_h in (2) are larger than a^3, if the parameter a is assumed to characterize the deep levels. We assume $V_e \sim V_h \sim \gamma V$, where $V=\pi a^3/6 \sim 10^{-22}$ cm^{-3} and $\gamma \sim 10^2$–10^3. In precisely the same way, for transitions from the first to the second level and from the M-st to the $(M+1)$-st level we need to make the replacement $a \rightarrow a\gamma^{1/3}$ in (1).

We can show that in our model the recombination flux (the number of recombining pairs per unit time per unit volume) can be calculated analytically within a factor on the order of unity, provided that the condition

$$g^{5/2}\delta \lesssim 1 \tag{5}$$

holds, where $g=G/\epsilon_0$ and $\delta=V\rho_0\epsilon_0$.

2. The "stepping onto" the ladder of levels and also the "stepping off" should incorporate the possibility of an inverse activation-law transition. The effective time of the "stepping on" is then $\tau_e(1+\tau^*/\tau_e')$, where τ^* is the time it takes the electron to travel the M steps between localized states. The ratio τ^*/τ_e' characterizes the effective increase in time which occurs because there is a probability that an electron captured in level ϵ_1 will go back into the C band instead of recombining. The quantity τ^* is evidently determined by the largest of the M times in (1). Estimating the effective time for "stepping off" into the V band in the corresponding way, we find the total "descent" time to be

$$\tau=\tau_e+\tau_h+\tau^*(1+\tau_e/\tau_e'+\tau_h/\tau_h'). \tag{6}$$

The time τ^* is determined by the largest of the M times in (1), which characterize transitions between levels which are neighbors along the energy scale. The problem is primarily one of integrating the microcurrent

$$\tau^{-1}\prod_{i=1}^{M+1}\rho(\epsilon_i)$$

over the M spatial variables Δr_i. In the approximation which we are considering, this integration can be carried out easily. The dependence of τ_i on Δr_i is strong, so the quantity τ, thought of as a function of Δr_i, is simply $\tau_e+\tau_h$ for Δr_i values smaller than

$$\frac{a}{2}R_i=\frac{a}{2}\left[L(u,v)-(\epsilon_{i+1}-\epsilon_i)/\epsilon_o\right], \quad \epsilon_{i+1}>\epsilon_i,$$

where

$$L(u,v)=\lambda+(t+1)u+\ln\frac{\cosh(v)}{\cosh(vt+\alpha)}, \tag{7}$$

$$\alpha=1/2\ln(N_V/N_C),\quad \lambda=-\alpha-\ln(N_CV),\quad t=\epsilon_0/T,$$

$$u=(\epsilon_1+G-\epsilon_{M+1})/2\epsilon_0,\quad v=(\epsilon_1+\epsilon_{M+1}-G)/2\epsilon_0.$$

In writing expression (7), we used $n\sim p<N_{C,V}\exp(-tu)$; i.e., we allowed for the circumstance that the temperature is assumed to be high or the pair generation rate low (we are taking n to be on the order of $10^{13}-10^{14}\,\text{cm}^{-3}$). As a result, we obtain a linear dependence of the recombination flux on n, so n is proportional to the optical emission flux. This result is of course valid if the optical load is sufficiently low. We also assume $L\gg 1$. For values $\Delta r_i-aR_i/2>a$, the time τ increases exponentially with increasing Δr_i, so the corresponding microcurrents become negligible. Consequently, under the condition $R_i\gg 1$ the spatial integration reduces to a multiplication by the volume of the region of the M-dimensional space in which the condition $\Delta r_i<aR_i/2$ holds. The result is

$$J_M=\gamma^2V^M(\tau_e+\tau_h)^{-1}\prod_{i=1}^{M}\rho(\epsilon_i)R_i^3\theta(R_i), \tag{8}$$

where $\theta(x)$ is the unit step function.

3. At fixed energies ϵ_1 and ϵ_{M+1}, the product of the R_i in (8) is the product of quantities whose sum is fixed. The maximum of this product is thus reached at R_i values of $L-(g-2u)/M$, i.e., in the case of an equidistant chain of levels. If a finite number of levels deviate from this equidistant arrangement, there is no sharp decrease in J_M. In this sense, the assertion that the ϵ_i are equidistant in optimum chains[2] is valid only under the condition that not only is M large but also a large number of levels participate in the deviations.

We integrate over the "internal" variables $\epsilon_2, \epsilon_3, \ldots, \epsilon_M$:

$$I_M(u,v)=\int J_M d\epsilon_2 d\epsilon_3 \ldots d\epsilon_M=\frac{\gamma^2 N_1 N_2\exp(-2\beta u)}{(\tau_e+\tau_h)\rho_0\epsilon_0}[\delta(g-2u)^4]^M K_M(u,v). \tag{9}$$

The integral in (9) vanishes if $M<1/l$, where $l=L/(g-2u)$. If, on the other hand, $M=[1/l]+1$, then by fixing $\epsilon_3, \epsilon_5, \ldots, \epsilon_{M-1}$, we can integrate over $\epsilon_2, \epsilon_4, \ldots, \epsilon_M$. In other words, we can reduce the multiplicity of the integral by a factor of 2 (we are assuming that M is even). Repeating this procedure, we see that the integral in (9) can be written in algebraic form for any finite M which is a power of 2. For larger values of M, the result is

$$K_M=(l-1/M)^{4M-1}(\pi/2)^{(M-1)/2}M^{-1/2},\quad M\gg 1. \tag{10}$$

Analysis shows that the error ΔK_M which arises from the use of expression (10) in cases with $M>[1/l]+1$ depends on the value of the parameter $q=Ml$. It is also found that the following is a valid estimate of an upper bound on this error:

$$\Delta K_M/K_M < l^{-1}\exp[-4/(q-1)]. \tag{11}$$

We see that for the parameter values of interest here the right side of (11) must be smaller than or on the order of unity. Using (10), we can now find the optimum value of M. Substituting $M=q/l$ into (10) and (9), and assuming $\delta g^4 \gg 1$ and $u \ll g$, we find that I_M reaches a maximum if q satisfies the equation

$$(q-1)^{-1}=\ln\left[\frac{q(2)/\pi)^{1/8}}{(q-1)L\delta^{1/4}}\right]+0(l),\quad l\ll 1. \tag{12}$$

The summation over M reduces to an integration of I_M near q/l. We then integrate over ϵ_1 and ϵ_{M+1}, assuming that the function $q(u, v)$ is given by Eq. (12):

$$R\sim\frac{\gamma^2 VN_1N_2nGv_0}{\rho_0}\int_0^{g/2}du\int_{-u}^{u}dv\,\frac{\exp(-\Phi)}{L\cosh v},\quad \Phi=(1+2\beta)u+\frac{4q(g-2u)}{L(q-1)}. \tag{13}$$

This integral is determined primarily by the region of values of the variables near the maximum of $\Phi+\ln(\cosh v)$, which is realized at the value of u which corresponds to the value

$$L\approx\lambda+(t+1)u=L_0,\quad \text{where } L_0=2q\left[\frac{g(t+1)+2\lambda}{(1+2\beta)(q-1)}\right]^{1/2}\gg 1. \tag{14}$$

The characteristic values of v must be smaller than u provided that the condition $t>t_0=\beta/(1+\beta)$ holds (this condition holds at temperatures below the melting point). Substituting (14) into (12), we find the equation

$$(q-1)^{-1}=\frac{1}{2}\ln(q-1)^{-1}+\frac{1}{2}\ln\frac{(1+2\beta)(2/\pi)^{1/4}}{4\delta^{1/2}[g(1+t)+2\lambda]}, \tag{15}$$

which has a solution if

$$\frac{\delta^{1/2}[g(1+t)+2\lambda]}{1+2\beta}<\frac{1}{8e}\left(\frac{2}{\pi}\right)^{1/4}=0.0412\ldots. \tag{16}$$

We are interested in the smaller of the two roots of (15), such that $1<q<3$. The other root, which is larger than 3, corresponds to a maximum of Φ. Integrating over u and v near the extremum, we finally find

$$R\sim\frac{\gamma^2 N_1N_2nV\epsilon_0 v_0 g^{3/4}(q-1)^{1/4}}{\rho_0(t-t_0+1/L_0)(3-q+1/L_0)^{1/2}}\exp(-\Phi), \tag{17}$$

$$\Phi=2(q+1)\sqrt{\frac{(1+2\beta)\left[\frac{g}{(t+1)}+\frac{2\lambda}{(t+1)^2}\right]}{q-1}}-\frac{8q}{(q-1)(1+t)}-\frac{(1+2\beta)\lambda}{t+1}+O(1). \tag{18}$$

Here we have retained only those terms in the argument of the exponential function which could in principle turn out to be large.

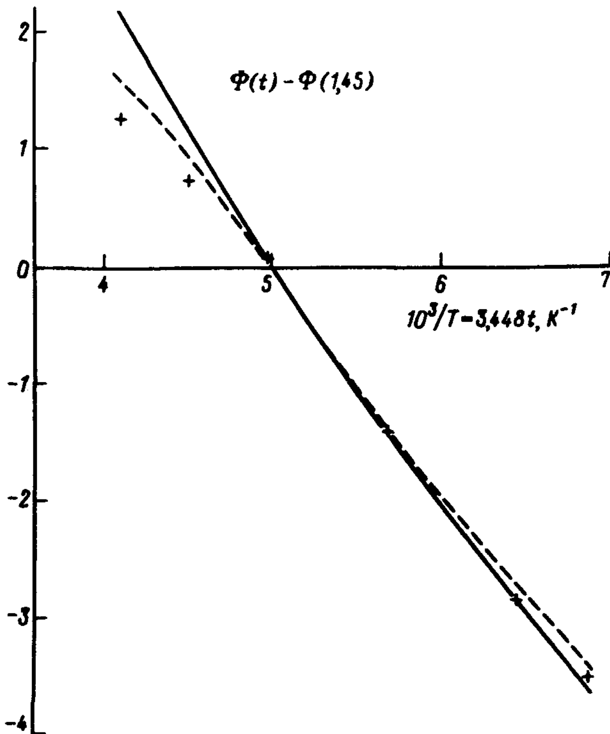

FIG. 1.

4. Assuming $\lambda \ll g$, we find the temperature dependence, which is governed by the leading term

$$\Phi_0 \approx 2(q+1)\sqrt{\frac{(1+2\beta)g}{(q-1)(t+1)}}.$$

This expression reduces to $\Phi_0 \propto \sqrt{T/(T+\epsilon_0)}$ if we ignore the comparatively weak T dependence of the factor in (18) which contains q. The result is thus quite different from the result given in Ref. 2 for the low-temperature case, $\ln R \propto -T$, and also from the activation-law dependence $\ln R \propto 1/T$ which arises in a natural way in the single-level recombination model. Figure 1 demonstrates a more accurate calculation based on the complete equation, (18), which incorporates the $q(t)$ dependence in accordance with (15). In the calculations we used the following realistic parameter values: $G=1.7$ eV, $\epsilon_0=0.025$ eV, $\rho_0=5\times 10^{16}$ $\text{cm}^{-1}\cdot\text{eV}^{-1}$, $V=10^{-22}$ cm^{-3}, $\beta=0.5$, and $\lambda=3$. For simplicity, the plot is made against the quantity $1/T$. The value $t=1.45$ corresponds to a temperature of 200 K. Shown for comparison in the same figure, by the plus signs, are experimental points showing the temperature dependence of the electron drift mobility $\mu(T)$ in amorphous hydrogenated silicon.[3] Values of $\ln[\mu(T)/\mu(200\text{ K})]$ are plotted in this figure. We see that for the given choice of

parameter values of the material it is possible to reach a good agreement with experiment at low temperatures. At room temperature and above ($t<1$), on other hand, the temperature dependence of the preexponential factor in (17) is important; this is basically a $1/(t-t_0)$ dependence. Adding the quantity $\ln[Q(t)/Q(1.45)]$ to the value of $\Phi(t)$, where Q is the preexponential factor in (17), we can achieve good agreement with experiment. The result is shown by the dashed line in Fig. 1.

In principle, we could also work from (17) to find a valid numerical estimate of the carrier lifetime n/R. This estimate is very sensitive to changes in the parameter values of the material, but the experimental values[4] $10^{-3}-10^{-6}$ s for α-Si:H are in complete agreement with the calculations.

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