Hopping in Exponential Band Tails

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Hopping of photoexcited carriers directly between localized, band-tail states gives rise to a new regime of energy relaxation which is manifested at low temperatures: For times shorter than a characteristic "segregation time," carriers hop directly to lower-energy states; at longer times, thermal excitation—resulting in multiple trapping—is more important. Even in the multiple-trapping regime, however, the current is carried at a transport energy *within* the band tail. We present a simple description which includes both of these processes in a single, self-consistent model, and estimate the segregation time.

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Transient measurements near room temperature in a variety of amorphous semiconductors are well described by the multiple-trapping (MT) model, in which injected carriers thermalize in a broad distribution of localized, band-tail states,[1-6] moving to deeper energies as a result of thermal activation to transport states and subsequent retrapping. Under these circumstances the time dependence of the transient photocurrent provides a spectroscopy of the density of states (DOS) in the tail[5]; a power-law time decay corresponds to an exponential DOS:

$$g(E) = N_L/kT_0 \exp(E/kT_0). \tag{1}$$

Here E (which is defined to be increasingly negative for states deeper in the gap) is the energy of a trap with respect to the mobility edge, and N_L is the total number of localized states. The temperature T_0 which characterizes the width of the exponential is typically a few hundred degrees; for example, for holes in both a-As$_2$Se$_3$ and a-Si:H, $T_0 \sim 550$ K. The power-law exponent, plotted in Fig. 1, is predicted to be $-1+T/T_0$, and this temperature dependence is confirmed for $T \gtrsim 200$ K.

At lower temperatures, however, recent measurements[7-9] have shown deviations from this simple model, in both of the materials mentioned: The photocurrent decays too rapidly at low temperatures, as indicated by the fitted power-law exponents below 200 K in Fig. 1. In addition, the induced optical absorption in a-As$_2$Se$_3$ shows a large spectral shift with time even at low temperatures[10]; this suggests that the carriers are moving to deeper states faster than would be expected from MT alone. In this Letter, we explain these observations in terms of a thermalization process in which carriers hop directly between the states in the band tail. This process is contrasted with the thermal-excitation process in Fig. 2; the key distinction is whether the rate-limiting transition is to higher or lower energy, *not* the extended or localized nature of the final state. We will show that the intuitive picture[4,5] developed for MT can be adapted to provide significant insight into the hopping case as well.

In order to provide a concrete example, we will assume the simplest form for the hopping rate which is consistent with the restriction imposed by detailed balance that the hopping rates up and down in energy differ by a Boltzmann factor:

$$\nu_{ij} = \nu_0 \exp(-2\gamma R_{ij}) \times \begin{cases} \exp(-E_{ij}/kT), & E_{ij} > 0, \\ 1, & E_{ij} < 0. \end{cases} \tag{2}$$

Here ν_{ij} is the hopping rate between occupied site i and unoccupied site j separated in energy by E_{ij} and in distance by R_{ij}. γ^{-1} is the decay length of the wave functions. The attempt-to-hop frequency ν_0 is expected to be of the order of 10^{12} s^{-1}.

Because the decreasing DOS makes it much harder to find a close neighbor at low energies, carriers in

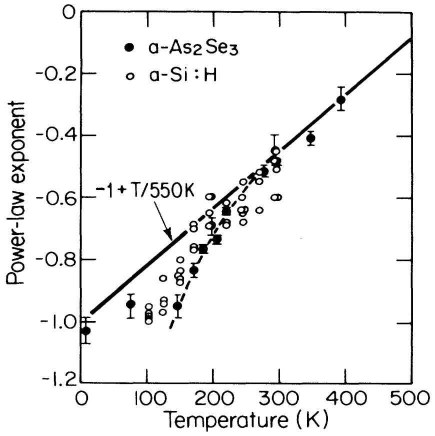

FIG. 1. Exponent of power-law fit to transient photocurrent, on a time scale of order microseconds, at different temperatures. Data are shown for holes in a-As$_2$Se$_3$ and holes in a-Si:H (Ref. 8). The straight line is the prediction of MT; the dashed line is a guide to the eye for the a-As$_2$Se$_3$ data, showing the deviations from MT at low temperatures.

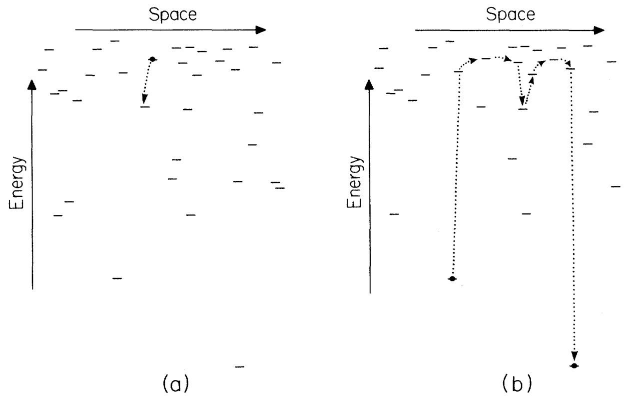

FIG. 2. Illustration of two thermalization mechanisms. (a) Hopping directly to deeper states. (b) Thermal excitation to shallower states (transport states), transport, and subsequent retrapping at deeper states.

deep states will move by thermal excitation to shallower states, while carriers in shallow states will move by hopping to other shallow states. In either case, the typical rate at which carriers hop away from a state is much smaller for deeper initial energies, because of the exponential dependence of the rate on energy difference (important for deep states) and the exponential dependence of density and thus wave function overlap on energy (important for shallow states).

We can therefore divide states into fast and slow (compared to the observation time) on the basis of their energy. Shallower states have fast rates, and carriers will leave as fast as they arrive. They accumulate in deeper states, which have slow leaving rates and still contain all carriers which have hopped into them. The energy separating fast and slow states is the (time and temperature-dependent) demarcation energy E_d defined as the energy at which the typical hopping-away rate ν_{typ} is equal to the reciprocal of the observation time. Because of the rapidly decreasing DOS, most of the carriers are near the demarcation energy, which gets deeper as time progresses.

At short times, when the demarcation energy is shallow, the carriers are in a high DOS, and the resulting large overlap between states means that carriers move primarily by hopping directly to lower energies. The number of states available below the initial energy E is just $N_L \exp(E/kT_0)$, so the typical rate is the rate for hopping a typical distance to a lower state:

$$\nu_{\mathrm{typ}}(E) = \nu_0 \exp[-2\gamma N_L^{-1/3} \exp(-E/3kT_0)], \quad (3)$$

and the demarcation energy (at which $\nu_{\mathrm{typ}} t = 1$) is

$$E_d(t) = kT_0 \ln(8\gamma^3/N_L) - 3kT_0 \ln[\ln(\nu_0 t)]. \quad (4)$$

We expect that the first term of Eq. (4) represents an energy not too far from the mobility edge, since the localized wave functions should just overlap at the mobility edge.

This form was derived by Kastner[11] to describe the change of peak luminescence energy with time in chalcogenide glasses; it also seems to apply to a-Si:H quite well.[12] The hopping-down process may well be as ubiquitous in low-temperature transient measurements as the multiple-trapping phenomenon is at high temperatures.

The current observed in the hopping-down regime arises from the bias the electric field causes in the hopping-down process itself; this current will be proportional to the number of carriers hopping down per unit time. Since the rate-limiting step for the redistribution of carriers is hopping out of states which have rates of order $1/t$, the total current will thus be $1/t$ times the downfield charge displacement per hop. Since the typical distance hopped depends only logarithmically on time, the overall time dependence of the current will be roughly $1/t$, with $\ln(\nu_0 t)$ corrections. This is consistent with the data for a-$\mathrm{As_2Se_3}$ shown in Fig. 1, which seem to reach a constant slope of -1 at low temperature (the lowest-temperature data in Ref. 7 were in error).

As the carriers continue to lose energy, the hopping-down process becomes slower because of the rapidly decreasing DOS. The rate at which carriers lose energy per logarithmic time increment is just the derivative with respect to $\ln t$ of the demarcation energy. From Eq. (4) this is $3kT_0/\ln(\nu_0 t)$. In contrast, if activation to higher energies limits the thermalization, the carriers move deeper at a constant rate of kT per logarithmic time interval, since the Boltzmann factor changes the rate by a factor of e for a change of kT in energy. Setting these two rates equal, we find that hopping down becomes slower than thermal activation after a time

$$\tau_s = \nu_0^{-1} \exp(3T_0/T). \quad (5)$$

Using $\nu_0 \sim 10^{12}\ \mathrm{s}^{-1}$, and $T_0 = 550$ K, we expect τ_s to reach the microsecond time scale at around 125 K. Considering the simplicity of the model, this is in good agreement with the observed temperature at which the data of Fig. 1 deviate from the MT predictions. The model also predicts that the deviations should occur for all materials at the same fraction $3/\ln(\nu_0 t)$ of T_0. The similarity of the behavior of holes in materials as different as a-$\mathrm{As_2Se_3}$ and a-Si:H supports this idea. Indeed, similar effects have been observed for *electrons* in a-Si:H[9]; although the temperature at which they occur is smaller by a factor of 2, as is T_0.

It is important to note that when thermal activation predominates, carriers do not hop all the way up to the mobility edge, but only to the energy at which the variation of the wave function overlap becomes too small to compete with the Boltzmann factor. This is just the energy at which thermal activation began to predominate, which is, using Eq. (5) in Eq. (4),

$$E_t = kT_0 \ln(8\gamma^3/27N_L) - 3T_0 \ln(T_0/T). \qquad (6)$$

This *transport* energy plays a role similar to the mobility edge: At long times, carriers in deeper states (traps) move by thermal activation to E_t. Furthermore, current is carried in the quasiequilibrium distribution in the transport states, which are those at E_t and shallower. The *kinetic* distinction between traps and transport states is due to Schmidlin[13]; here we have extended it to a distinction in *energy*. As T becomes smaller, the transport energy becomes significantly deeper.

We call τ_s the segregation time because only for times longer than this do the shallower states act as transport states and the deeper states as traps. In addition, since $\nu_{\rm typ}(E_d) = 1/\tau_s$, τ_s^{-1} is a representative hopping rate for carriers in the transport states. The dramatically longer τ_s at low temperature may therefore be manifested in steady-state measurements, for example ac conductivity.

For all times longer than the segregation time, thermal activation is the mechanism for thermalization:

$$\nu_{\rm typ}(E) = \tau_s^{-1} \exp[-(E_t - E)/kT] \qquad (7)$$

which differs from MT only in that carriers are activated to E_t rather than to the mobility edge. In addition, since the number of available states is smaller at the transport energy than at higher energies, the prefactor is reduced from ν_0 to τ_s^{-1}, which is the hopping rate for $E = E_t$.

This hopping-up regime is identical to MT except for the interpretation of the microscopic parameters, as was first indicated by the work of Schmidlin[13] and in numerical simulations by Silver, Schoenherr, and Baessler.[14] For example, the current is proportional to the number of carriers $n(t)$ in transport states (near E_t). This differs from the total number of carriers N (which are mostly at E_d) by a Boltzmann factor $\exp[-(E_t - E_d)/kT]$ and a degeneracy factor $\exp[(E_t - E_d)/kT_0]$, so that $n(t) \sim N(t/\tau_s)^{-1+T/T_0}$.

To compare the *magnitude* of the photoconductivity at different temperatures, $n(t)$ should be multiplied by the effective microscopic mobility of carriers near E_t, which scales with the characteristic hopping rate τ_s^{-1}. Because this rate is activated [Eq. (5)], the power-law transients for different temperatures, plotted on a double logarithmic plot, should focus at a time of order ν_0^{-1}, just as they do for activation to the mobility edge. Experimentally, however, the magnitude of the mobility to which such plots focus is ~ 0.2 cm^2/V·s in a-As$_2$Se$_3$,[15,6] which would be rather too small for extended-state conduction (assuming a degeneracy factor $N_c/N_L \sim 1$) but is very reasonable for conduction by hopping.

In the long-time regime, the current results from hopping of those carriers in states near the transport energy, which have quasiequilibrium occupation; the same set of states and the same occupation (except for overall magnitude) determine the dc transport properties. While space does not permit a discussion of the dc properties of this model,[16] we note that the hopping nature of the transport provides a natural explanation of the many anomalous features of transport in amorphous semiconductors, as reflected for example in the field-dependent conductivity,[17] the difference between the thermopower slope and the conductivity activation energy,[18] and the Hall effect.[19] The hopping process also lowers the activation energy of the dark conductivity by several kT_0 below the energy difference between the Fermi level and the mobility edge.

The simple formulas given in this Letter were obtained by using the average hopping distance to determine the typical rate, rather than averaging over rates directly. This approach, introduced by Mott,[20] has the virtue that exponentially fast rates (corresponding to rare, small separations) are not allowed to dominate the averages, which would be unphysical since only a small fraction of carriers are on centers with such rates. Furthermore, since for an exponential DOS the *average* separation varies very strongly with energy, *statistical fluctuations* in separation are of even less importance. Nonetheless, although the present description can be justified more completely,[16] it is fundamentally approximate and descriptive, and thus complementary to more rigorous approaches,[21] which treat the many complex issues much more carefully than we have done here. It is therefore gratifying to note that the approach of Grünewald, Pohlmann, Movaghar, and Würtz, when applied to transient photocurrent in an exponential DOS, agrees quite well with both the data and our simple predictions.[22]

In summary, we have presented a simple description of the behavior of carriers in a band tail when hopping in addition to thermal excitation to the band edge is included. The hopping manifests itself *directly* through hopping-down thermalization only at low temperatures. Even at high temperatures, however, current is carried by hopping at the transport energy within the band tail; the hopping nature of the transport may manifest itself in various dc measurements. The transport energy provides a means of reconciling observations indicating hopping transport with those suggesting the existence of a well-defined energy similar to the mobility edge.

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