Photocurrent Transient Spectroscopy: Measurement of the Density of Localized States in a-As_2Se_3

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Measurements of transient photoinduced optical absorption in a-As_2Se_3 show that carriers thermalize within a distribution of localized states in the band gap. Photocurrent as well as photoinduced optical absorption transients are explained in a unified way with the multiple-trapping mechanism. Under such circumstances, transient photoconductivity provides a spectroscopy of the density of localized states.

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A number of models have been proposed to explain the unusual electronic properties of amorphous semiconductors. These models differ dramatically in their predictions about the density of localized states in the gap between the bands of extended states. For example, the model of Anderson[1] assumes that single-particle states extend throughout the gap with only minor variation in density; alternate models[2-4] take as their starting point a small number of structural defects with a narrow spectrum of energies in an otherwise relatively empty gap. The controversy has remained at this most basic level because of the absence of a reliable spectroscopy of the density of localized states. The purpose of this Letter is to show that transient photoconductivity (PC) provides just such a spectroscopy.

When electron-hole pairs are created by pulsed optical excitation, they give rise to an excess conductivity proportional to the product of their number density and mobility. In amorphous semiconductors, it is found that the photocurrent decreases with time even under conditions where the total number of excited charge carriers remains constant. This corresponds to a decay of the effective carrier mobility with time following pulsed photoexcitation. This phenomenon, known as dispersive transport, was first studied with use of the time-of-flight technique. The work of Pfister and Scher[5] emphasized the importance of dispersive transport as a probe of localized states in amorphous semiconductors.

The results reported here point to the usefulness of dispersive transport as a spectroscopy of the density of localized states. We have measured the optical absorption of carriers trapped after pulsed photoexcitation. The time-resolved spectra provide direct evidence that the bound carrier distribution evolves within a continuum of localized-state energies. In addition, the PC decays as a power law, $t^{-1+\alpha}$, with α proportional to temperature T. These observations can be explained in a unified manner as manifestations of multiple trapping (MT) and release from localized states. To see how the PC provides a spectroscopy of the localized level density under such circumstances, it is necessary to gain insight into the MT process.

Several authors have considered this process using analytical methods and computer simulation.[6] In particular, the treatment of Schmidlin[7] for discrete trap energies can be easily extended to give exact results[8] for the case of continuous distribution. A simplified model, which makes the results intuitive, is useful in understanding the experimental observations. Consider a density of states in the gap like that sketched in Fig. 1(a). (This diagram, which applies to electrons, can be altered in the obvious way to describe the hole transport observed in the chalcogenide glasses.) We assume that the mobility decreases rapidly below E_0 so that the motion of a bound electron is limited by the rate of thermal excitations to $E \gtrsim E_0$. If the capture cross section is independent of energy, the states below E_0 will initially be populated uniformly by carriers which become trapped following pulsed photoexcitation. However, as time goes on, carriers in shallow states will be released preferentially while the trapping process remains random. The mean occupation number will therefore evolve as shown in Fig. 1(b). A demarcation energy, $E_d(t)$, separates those states whose occupation remains uniform from those in quasithermal equilibrium. This demarcation occurs at the energy where the trap-release time $\tau(E_d)$ is equal to the delay after the laser pulse, t. Since $\tau(E) = \nu_0^{-1}\exp[(E_0 - E)/kT]$,

$$E_0 - E_d(t) = kT\ln\nu_0 t, \tag{1}$$

where ν_0 is a vibrational frequency, of order

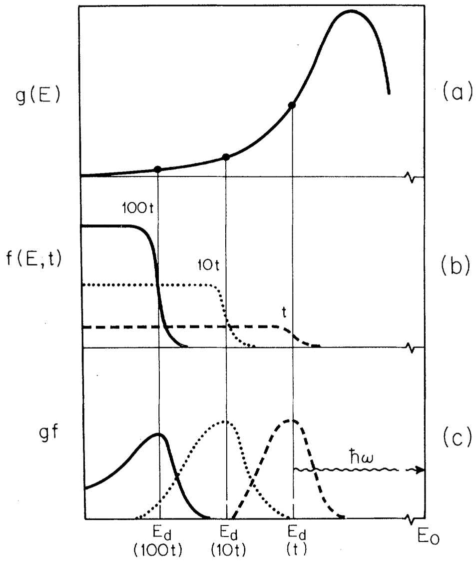

FIG. 1. (a) Sketch of continuum of bound states in the gap which rapidly trap electrons after photoexcitation. Carriers empty out of shallow states and are retrapped uniformly so that the mean occupation number evolves as in (b). For a density of states which decays steeply away from E_0 the carriers are distributed in a packet, shown in (c), localized near $E_d(t)$. The arrow indicates the threshold energy for the PA transition which increases as the carriers thermalize.

10^{12}–10^{13} s^{-1}. Thus E_d moves away from E_0 with time as depicted in Fig. 1(b). The thermalizing carriers will be distributed according to the product of the mean occupation number and the density of states. For cases where the density of states decreases rapidly with energy away from E_0, most of the photoexcited carriers reside near $E_d(t)$. These bound carriers form a packet, localized in energy, whose evolution in time is shown in Fig. 1(c).

The conducting carriers (those with $E > E_0$) lie in the Boltzmann tail of the carrier packet in Fig. 1(c); they constitute a fraction, θ, given by

$$\theta(t, T) \simeq [g(E_0)/g(E)] \exp[-(E_0 - E)/kT]\Big|_{E=E_d(t)}. \quad (2)$$

With use of Eq. (1),

$$\theta(t, T) \simeq [g(E_0)/g(E_0 - kT\ln\nu_0 t)]/\nu_0 t. \quad (3)$$

Therefore, θ probes the density of localized states at the instantaneous position of the thermalizing carrier packet.[9] If the MT interpretation is correct, the PC, which measures θ, provides a spectroscopy of the gap states for the many cases where space-charge methods (field-effect, capacitance-voltage, deep level transient spectroscopy) are either ambiguous, or simply impossible.

The most direct evidence for MT comes from the time-resolved photoinduced-absorption (PA) spectra. The optical absorption is by carriers which have become trapped in localized states after photoexcitation. Figure 2(a) shows the time evolution of the PA spectrum following pulsed

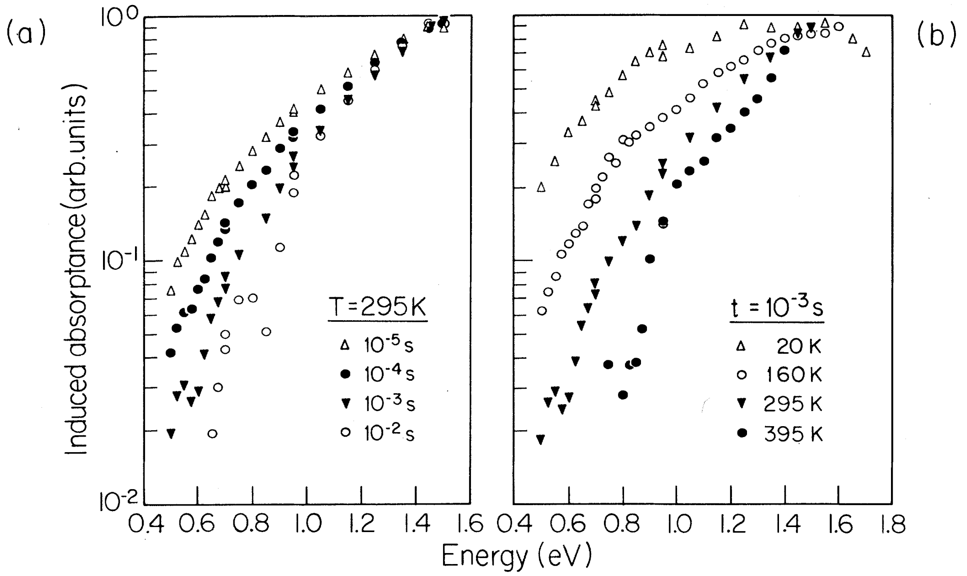

FIG. 2. The PA spectrum, (a) for several time delays following pulsed excitation, and (b) at $t = 10^{-3}$ s for various temperatures. In both cases the shift to higher energies is in qualitative agreement with the MT process described by Eq. (1).

(10 ns) excitation from a dye laser, for several delay times in the range 10 μs–10 ms. The sample, a 1-mm-thick polished platelet of high-purity a-As_2Se_3, is excited to a depth of 10^{-3} cm by the (20 μJ) laser pulse. The induced absorptance (6.5×10^{-4} at 1.5 eV, for $t=10^{-5}$ s) decays due to carrier recombination, but the spectra at longer delay have been adjusted (by factors 1.6, 2.7, and 9.3) for ease of comparison. It is apparent from Fig. 2(a) that the induced absorption edge shifts to higher energy with increasing delay.

The fact that the spectra evolve with time indicates that there is a distribution of localized-state energies within the gap. Furthermore, the occupancy of these levels is changing throughout the time range of the measurement. Note that the energy shift is roughly equal for exponentially increasing intervals of time. This is consistent with the optical transition, depicted in Fig. 1(c), of a carrier in the packet moving in accordance with Eq. (1). A further prediction of Eq. (1) is that the effect of increasing T in constant steps at fixed delay should mimic the effect of increasing the delay exponentially at fixed T, namely the carrier packet will shift uniformly to lower energies. This is borne out by Fig. 2(b), which shows normalized PA spectra at various temperatures for a fixed time delay of 1 ms.

Although the PA data give convincing evidence for the MT model, the spectra themselves are not sensitive to the shape of the density of states. The reason is that the homogeneous width of the spectrum is too large to reveal any structure due to the precise shape of the carrier packet of Fig. 1(c). However, the transient photocurrent is directly proportional to θ of Eq. (3) allowing the spectrum of binding energies to be determined.

To measure the PC the same sample used for PA was prepared with two coplanar electrodes of spacing 2.5 mm. As described earlier[10] the photocurrent, Δi_p, is proportional through known factors to the product $\theta(t, T)\mathfrak{N}(t)\mu_0$, where $\mathfrak{N}(t)$ is the areal density of photoexcited carriers and μ_0 is the mobility of states with $E \gtrsim E_0$. In general, $\mathfrak{N}$ will change during the time of the measurement because of recombination between photoexcited electrons and holes. However, this bimolecular recombination can be made negligible during the time scale of the measurement (10^{-8} s $< t < 10^{-2}$ s) by reducing the excitation intensity.[11] The photocurrent transients shown in Fig. 3 were measured in this manner and are proportional to $\theta(t, T)$.

In agreement with previous measurements, we obtain an accurate power-law decay at each temperature, $\theta(t) \sim t^{-1+\alpha}$. Inspection of Eq. (3) shows that this is consistent only with a density of states that decreases exponentially below E_0, $g(E) = g_0 \exp[-(E_0 - E)/kT_0]$ for $E < E_0$, where kT_0 is the energy scale of the distribution. With this form of $g(E)$, Eq. (3) becomes

$$\theta(t, T) \simeq [g(E_0)/g_0](1/\nu_0 t)^{1-\alpha} \tag{4}$$

with $\alpha = T/T_0$. The inset of Fig. 3 shows that α is consistent with this prediction and that the slope of a linear fit yields $kT_0 \simeq 50$ meV.

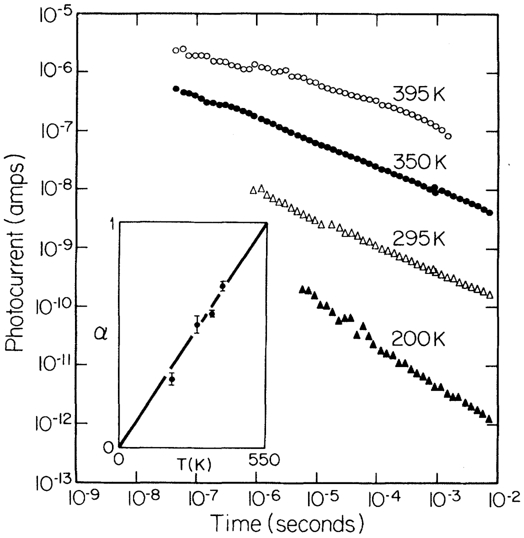

FIG. 3. Time decay of photocurrent after pulsed excitation with band-gap light at several temperatures. At each temperature the decay of the current is accurately described by $\Delta i_p \sim t^{-1+\alpha}$. The temperature dependence of α is shown in the inset.

It is clear that MT explains both the PA and PC results in a consistent way. The PC experiment should provide the same information as the time-of-flight (TOF) experiment for times shorter than the transit time, t_T. To compare the two experiments, Eq. (4) can be used to calculate the MT prediction for t_T. A photoinjected hole drifts with speed $\mu_0\mathcal{E}$ except when immobilized in a trap. Since $\theta(t)$ is the fraction of carriers in the mobile states, the mean displacement between times t and $t+dt$ is $\mu_0\theta(t)\mathcal{E}\,dt$. The time to traverse the sample is given by

$$L = \int_0^{t_T} \mu_0\theta(t)\mathcal{E}\,dt \quad \text{or} \quad t_T = \nu_0^{-1}\exp(\Delta/kT),$$

where $\Delta = kT_0 \ln\{\alpha[g_0/g(E_0)](\nu_0 L/\mu_0\mathcal{E})\}$, and L and $\mathcal{E}$ are the sample thickness and applied electric field, respectively.[12] It is interesting that the exponential distribution of trapping levels yields a single activation energy for t_T.

Pfister and Scher (PS) did, indeed, observe a thermally activated transit time in their TOF experiment. Reasonable[13] values of $\nu_0 \approx 10^{12}$ s^{-1} and $\mu_0 g_0(E)/g_0 \simeq 0.2$ cm^2/V s account for the large activation energy 0.6 eV. However, a central result of the work of PS was that α was found to be independent of temperature, in direct conflict with the results of Fig. 3. As we have seen, a temperature-dependent α is required by the MT model and PS argued that because they saw no such dependence, the time-dependent mobility is the result of hopping among isoenergetic localized states with a random distribution of separations. To account for the temperature dependence of t_T, they proposed a discrete set of deep traps which limits the number of hopping carriers.

We can see no reason why the two experiments should probe different phenomena. They are carried out at comparable excess carrier concentrations and electric fields. Of course, in the TOF experiment a net charge is transported across the sample whereas in PC the separation of charge is negligible, but since the carrier densities are so small, it is unlikely that this can be the origin of the different results. Since the dispersive transport provides a spectroscopy of the density of states only if it originates from MT, it is very important that this inconsistency be resolved and new experiments are planned which will make this possible.

Assuming for the present that MT is the origin of the dispersion in the PC experiment, we find a continuous spectrum of binding energies from at least ~0.3 to ~0.7 eV above the valence band corresponding to the range of $kT\ln\nu_0 t$ examined thus far.[14] However, the distribution is not nearly uniform as in the Anderson[1] picture but has an energy scale which is very small compared with the band gap. The observation that $T_0 \simeq 550$ K points to the role of disorder characteristic of thermal equilibrium at T_g (glass transition temperature). Within this view, the experiment indicates that the binding energy of a carrier in a localized state is the same to within an additive constant as the energy required to create the state at T_g. In a forthcoming article[8] we show that this is expected for interacting pairs of oppositely charge structural defects.

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[9] If the capture cross section is not constant, then the analysis is more complicated since ν_0 must also depend on the energy, by detailed balance. For $\sigma(E)$ slowly varying compared with $g(E)$, Eq. (1) remains valid, and the measurement yields an effective density of states proportional to $\sigma(E)\, g(E)$.

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[11] Reduction of the density of photoexcited carriers to $\sim 10^{13}$ cm^{-3} was sufficient. The monomolecular recombination, discernible in the upper curve of Fig. 3, cuts off the measurement at ~1 ms for $T = 395$ K.

[12] A similar picture of MT was arrived at independently by T. Tiedje and A. Rose, to be published.

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[14] Experiments to be published put a lower bound on the prefactor $kT_0 g_0 > 10^{20}$ cm^{-3}.