Picosecond Photoluminescence: A Probe of Band-Tail Thermalization in Amorphous Semiconductors

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We have determined that the initial photoluminescence decay in a-Si:H (at emission energies > 1.5 eV) follows an algebraic form $t^{-\alpha}$, for 50 psec $< t < 3$ nsec, with $\alpha(T) = \alpha_0 + \beta T$. These results are interpreted with a comprehensive model of nonradiative relaxation through electron band-tail thermalization. From our data we find a maximum hopping rate of 3×10^{13} sec^{-1}, an effective energy width of 20 meV for single-hop relaxation in the band tail, and that electrons have relaxed 50 meV from the conduction-band edge within 50 psec of excitation.

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Time-resolved photoluminescence (PL) measurements have contributed substantially to the understanding of carrier transport and recombination mechanisms in amorphous semiconductors. Early work[1] revealed a broad distribution of recombination rates in a-Si:H and chalcogenide glasses generally thought to arise from radiative and nonradiative tunneling processes with rates strongly dependent upon pair separation. Time-resolved spectra in these systems show a characteristic shift of the PL band to lower energy with time which has been attributed to recombination at randomly separated charged (donor-acceptor type) sites in the chalcogenides[2] and carrier thermalization within band-tail states[3] in a-Si:H. As the time resolution in PL experiments improves there is increasing opportunity to obtain more detailed information concerning the initial distribution of pair separations created by optical excitation (and the subsequent time evolution of this distribution) as well as the maximum or limiting recombination and relaxation rates. PL studies in the picosecond regime can elucidate the nature of the electronic states in the energy region between the exponential band tail and the mobility edge as well as excitonic effects involving these states.[4]

In this paper we report the results of recent picosecond PL measurements[5] in a-Si:H. An excitation energy of 2.33 eV is used, well above the optical gap (1.8 eV at 300 K), resulting in the creation of mobile carriers. Because of the time (10 psec–4 nsec) and spectral (2.1–1.5 eV) regimes associated with the streak-camera detection scheme used, our measurements select the closest pairs emitting at the highest PL energies. We find rapid PL decay with power-law behavior. A comprehensive model of nonradiative relaxation is developed in which band-tail thermalization proceeds initially via efficient electron transfer (hopping) among states within an energy bandwidth determined by $\hbar\omega$, an effective phonon frequency, and kT. The model correlates the thermalization process with radiative decay and T-dependent local diffusion and provides results in excellent agreement with experiment. Recently, subnanosecond (> 0.25 nsec) PL measurements[6] at lower PL energies (< 1.6 eV) were reported in a-Si:H. We compare those findings with the present results.

Experiments were performed with single pulses (7 psec) from a passively mode-locked, frequency-doubled Nd^{3+}:glass laser. Photoluminescence was collected and time resolved with a streak camera and optical multichannel analyzer. The maximum excitation density was $\sim 10^{17}$ photons/cm^3. Sharp-cut blocking filters at 2.1 eV were used to prevent detection of scattered light from the excitation pulse. Generally, we observed the entire PL band within the limits of the streak-camera photocathode response. From 2.1 to 1.7 eV, this response varies by $< 50\%$ but at lower energies the response drops quickly (down a factor of 10 at 1.5 eV). Therefore, our measurements select high-energy PL predominantly in the range (2.1–1.5 eV). Samples used in this study (1 μm thick) were prepared by plasma decomposition of undiluted SiH_4 at low rf power (1 W) deposited on roughened fused-silica substrates at 230 °C. The low-temperature time-integrated PL quantum efficiency of these samples is high (0.25–0.50 at 10 K). Extreme care was taken in sample cleaning prior to mounting in the sample chamber to prevent surface-contamination emission. A more detailed description of the apparatus and experimental results will appear elsewhere.[7]

Figure 1 displays the PL intensity, $I(t)$, measured at 20 K and averaged over 20 laser shots for fast (500 psec) and slow (4 nsec) streak-camera total-sweep times. In all of our measurements the PL build-up time is less than the system response time which places an upper limit of ~ 10 psec on the time for

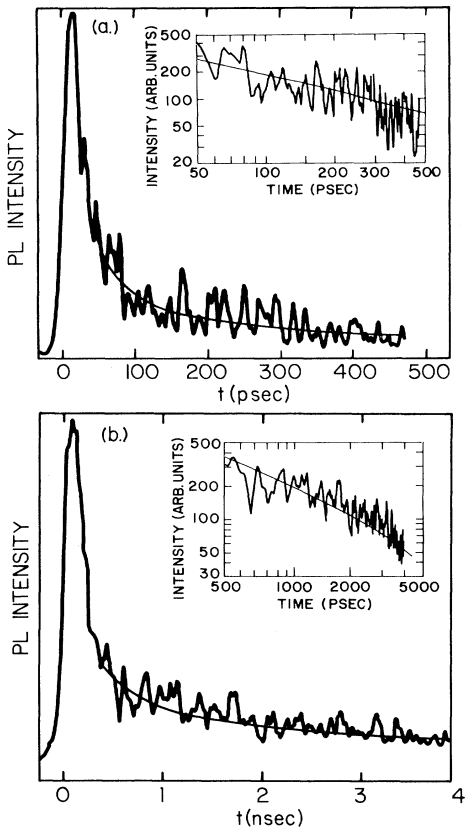

FIG. 1. Measured buildup and decay of PL (2.1–1.5 eV) in a-Si:H at 20 K. Also shown are least-squares fits for a power law, $t^{-\alpha}$, decay. The insets show log$I$ vs log$t$ plots of the data and fits obtained with use of the model described in the text.

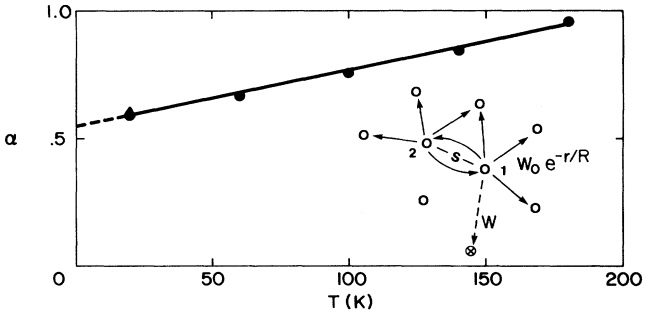

FIG. 2. Temperature dependence (filled circles) of the power-law exponent, α, for the initial PL decay in a-Si:H and the fit (solid line) with use of the model described in the text. The inset illustrates the mechanism for rapid PL decay involving competition between electron band-tail hopping (among a cluster of sites, O) at a rate $W_0 e^{-r/R}$ with radiative recombination at a maximum rate, W. The hole is taken to be immobile at site ⊗ .

photoexcited carriers to relax into states emitting within our spectral observation window (2.1–1.5 eV). Since the exponential optical-absorption edge (Urbach edge) in a-Si:H extends to ~ 1.85 eV at 20 K,[3,8] and the fastest radiative lifetimes are ~ 8 nsec,[6] these experiments probe the closest pairs emitting at the highest PL energies as they thermalize within the manifold of band-tail states. This thermalization process, which manifests itself as a PL spectral shift, represents relaxation of carriers to lower-energy states and *not* recombination. Recent experiments[6] have shown that at 15 K the PL spectrum at 500 psec following excitation is quite broad with appreciable intensity at energies > 1.6 eV. Using a high-energy cutoff filter at 1.8 eV we examined the PL buildup and decay characteristics and, within experimental accuracy, found no variation in these times, although the peak PL intensity decreased about a factor of 3 with the reduced spectral bandwidth. This indicates that the PL spectrum extends to energies > 1.8 eV for $t < 100$ psec.

The PL decay data at 20 K are best fitted by a power law, $t^{-\alpha}$, for 50 psec $< t < 3$ nsec. At earlier times the decay is convoluted with the system response. From the least-squares fits in Fig. 1, we find for the fast sweep $\alpha = 0.59 \pm 0.03$ and for the slow sweep $\alpha = 0.61 \pm 0.03$. Thus, within experimental uncertainty the decay at 20 K is characterized from 50 psec to 3 nsec by $\alpha = 0.60$. Attempts at fitting the data to an exponential decay over the same time range gave poorer fits in all cases.

Measurements of the temperature dependence of the initial PL decay were performed over the range 20 to 180 K. We find that the power-law exponent, α, is temperature dependent taking the form $\alpha(T) = \alpha_0 + \beta T$. Shown in Fig. 2 is a plot of α vs T where we find from the intercept a value of $\alpha_0 = 0.55 \pm 0.03$ and from the slope a value of $\beta = 0.0022 \pm 0.0003$ K^{-1}. No change in the initial (maximum) PL intensity is found up to 100 K where it begins to decrease gradually, down a factor of 2 at 140 K. At 180 K the initial PL intensity is down a factor of 4 from that at 20 K. Although the power-law decay behavior seen in these experiments differs from the exponential decay reported in Ref. 6 for the spectral regime below 1.6 eV, the temperature dependence of the initial intensity does agree. As emphasized earlier, our measurements use PL as a probe of thermalization processes which are much faster than the fastest radiative recombination rates. We now present a model which accounts for the observed power-law behavior of the initial PL decay in a-Si:H in terms of electron band-tail thermalization.

We assume, along with a number of authors,[1] that the higher-energy luminescence is due to a band-tail electron recombining with a band-tail hole. A typical configuration for this interaction is shown in the inset of Fig. 2. The arrows indicate the possible electron transfer steps [among a random distribution (energy, separation) of sites, O] and the hole is taken to be im-

mobile (at site ⊗). As discussed above, these experiments select the closest pairs emitting at the highest PL energies. The pair can be geminal, a localized exciton, or randomly separated as a result of relaxation of an electron with as much as 0.4-eV energy above the optical gap.

The single (fastest) radiative recombination rate is designated as W. Competing with W are the electron transfers away from the hole offset by the back transfers. One can readily assume that the back transfer occurs preferentially from a small number of nearby sites. This local diffusion involving interaction among a cluster of sites imbedded in a fixed random background of additional sites is solved exactly. The electron can hop back and forth an arbitrary number of times to the sites within the cluster and, from each of these, hop once to the fixed random background of sites. The time to return to the cluster after leaving is on the order of a large sampling time of all the other sites. The configuration average over these latter site positions and energies is then carried out exactly, retaining *all* the correlations between the cluster geometry and the background. Referring again to Fig. 2, we are interested in determining the (averaged) probability $\langle P(1,t)\rangle$ for the electron to be found at site 1 at time t if it started there at $t=0$. The luminescence intensity is then $I(t)=W\langle P(1,t)\rangle$. Since we are considering one (i.e., the maximum) radiative rate, $I(t)$ is proportional to the probability and *not* the rate of change of the probability. The latter case applies when all the decay channels are radiative. Hence $I(t)\sim t^{-\alpha}$ (as we will show) and not $t^{-1-\alpha}$. We specialize the cluster to two sites $\{1,2\}$ separated by s and obtain[9]

$$W\langle P(1,t)\rangle = W\exp[-t(W_{21}+W)]\Phi_1(t) + W(W_{12}W_{21})^{1/2} \times \int_0^t d\tau \exp[-(t-\tau)W_{12}-\tau(W_{21}+W)]\tau^{1/2}(t-\tau)^{-1/2}I_1(\sigma)\Phi_2(t-\tau,\tau), \quad (1)$$

$$\Phi_1(t)=\exp\left[-\int d^3r\, d\epsilon\, p(r,\epsilon)\{1-\exp[-tW(r-r_1)]\}\right], \quad (2)$$

$$\Phi_2(t-\tau,\tau)=\exp\left[-\int d^3r\, d\epsilon\, p(r,\epsilon)\{1-\exp[-(t-\tau)W(r-r_2)-\tau W(r-r_1)]\}\right]. \quad (3)$$

Here, $p(r,\epsilon)$ is the probability of finding a site at r with energy difference ϵ and $W(r)$ is the transition rate to this site (the ϵ dependence is implicit). $I_1(\sigma)$ is the modified Bessel function of order unity and $\sigma\equiv[4W_{12}W_{21}(t-\tau)\tau]^{1/2}$, where W_{12} and W_{21} are the transition rates between sites $\{1,2\}$. The function Φ_2 is a generalization (to two sites) of the more familiar[10] Φ_1, the configuration average probability to remain on a single site in a random distribution of sites.

In order to calculate $I(t)$ from Eqs. (1)–(3) we must specify $W(r)$ and $p(r,\epsilon)$. To initially simplify the calculation of Φ_1 and Φ_2 we consider the transition rate to be nonzero and a function of r only in an energy width $\hbar\omega$, an effective phonon energy, for $\epsilon<0$ (hopping down) and kT for $\epsilon>0$ (hopping up). The basic parameters can now be defined as

$$W(r)=W_0\exp(-r/R), \quad (4)$$

$$p(r,\epsilon)=g(\epsilon_1-\epsilon)\equiv g_0\exp[-(\epsilon_1-\epsilon)/kT_0], \quad (5)$$

$$n=\int_{-\hbar\omega}^{kT} d\epsilon\, p(r,\epsilon)$$

$$=kT_0 g(\epsilon_1)[\exp(T/T_0)-\exp(-\hbar\omega/kT_0)]. \quad (6)$$

Here ϵ_1 is the energy, measured from the conduction-band edge, of the electron at 1 and kT_0 is the width of the exponential density of band-tail states (~ 30 meV in a-Si:H).[11] The estimates for the parameters are $R\simeq 7$ Å for $\epsilon_1<0.1$ eV, $W_0\simeq 10^{13}$ sec^{-1} (order-of-magnitude estimate obtained from donor-state calculations[10] in crystalline Si), and $g_0\sim 4\times 10^{20}$ eV^{-1} cm^{-3}.

Now, using the large-argument asymptotic form for $I_1(\sigma)\sim\exp(\sigma)(2\pi\sigma)^{-1/2}$ and the Laplace method one can evaluate the expression in Eq. (1) analytically as a function of $\eta\equiv 4\pi nR^3$ and W_0t and compare with the PL $I(t)$ in Fig. 1. One obtains a power-law decay $I(t)\sim t^{-\alpha}$ for nearly two decades of W_0t with a departure toward increasing α at large W_0t. An excellent fit of the theory to the PL $I(t)$ over the entire experimental range (50 psec $<t<$ 4 nsec) is obtained with $\eta=5\times10^{-3}$ and $W_0=3\times10^{13}$ sec^{-1} as shown in the log$I$ vs log$t$ plots in the insets to Figs. 1(a) and 1(b).

The theoretical values for α show a linear dependence on η over the range of α values shown in Fig. 2. Using Eq. (6) one can obtain the *relative* change in η as a function of T for various values of $\hbar\omega$, and therefore $\alpha(T)$. The linear relation (solid line) show in Fig. 2 corresponds to $\hbar\omega=20$ meV. Thus 20 meV is an *effective* measure of the energy width for relaxation involving single hops in the band tail. Since there is a peak in the acoustic-phonon density of states in a-Si at 20 meV,[12] it is tempting to ascribe the relaxation we probe to interaction with acoustic phonons.

One can now determine the electron position (energy) in the band tail by again using Eq. (6) with the value of $\hbar\omega$ obtained from the $\alpha(T)$ data and the above value of η at $T=20$ K. We obtain $\epsilon_1=50$ meV. The nearest-neighbor hopping time at ϵ_1 (with width $\hbar\omega$) is 60 psec. This time is consistent with the notion that the electron relaxes, by hopping down, to a level

where the hopping time is on the order of the observation time of the experiment (~ 100 psec). At ϵ_1 the release time to the conduction-band edge at $T = 20$ K is 10 sec. Only at $T = 180$ K is the release time comparable to the observation time. Therefore, multiple trapping is unlikely to play any role in the nonradiative transitions (via local diffusion) in the temperature range of Fig. 2. With the model presented here, one can obtain a linear $\alpha(T)$ with a nonzero $T = 0$ value simply by considering relaxation via electron hopping.

If the initial fast relaxation of the electrons in the band tail produces an occupation proportional to $g(\epsilon)$ then it can be presumed that the distribution is peaked at ϵ_1 (with a width $T_0 + T$) where ϵ_1 is relatively independent of T ($\Delta\epsilon_1 < kT_0$) for $T < 180$ K. An important additional measurement would be the time-resolved PL buildup at lower energy.

In this paper we have attributed the observed power-law nature of the initial PL decay in a-Si:H to nonradiative relaxation processes which bring electrons to lower-energy states within the band-tail manifold and have developed a comprehensive model of nonradiative relaxation which correlates the thermalization process with radiative decay and T-dependent local diffusion. The model incorporates both the site energy and position in determining the electron transfer efficiency. By considering hopping down to states within an effective phonon energy, $\hbar\omega$, and hopping up to states within kT, the model can explain the power-law nature of the PL decay and the linear temperature dependence of the power-law exponent as well as its $T = 0$ intercept. Applying this new model to all of our PL data, we conclude the following about the initial PL decay dynamics in a-Si:H: (1) Within 50 psec, electrons have moved down the band tail 50 meV from the conduction-band edge; (2) the maximum hopping rate, W_0, is 3×10^{13} sec^{-1}; and (3) the effective energy width for relaxation involving single hops in the band tail is ~ 20 meV which is close to the peak in the acoustic-phonon density of states for a-Si.

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