

Optical studies of thermalization mechanisms in *a*-Si:H

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Thermalization mechanisms of photoexcited carriers in *a*-Si:H have been studied by monitoring the spectral shift with delay of the main luminescence band as a function of temperature. The weak temperature dependence of the shift at early times precludes any multiple-trapping process based on thermal excitation to transport states, but is consistent with thermalization by direct hopping between localized states. A hopping model recently proposed to account for low-temperature transport phenomena is shown to provide a good description of the early-time spectral shift. This represents the first unified description of optical and transport measurements at low temperatures. The shift rates suggest that only one of the carriers is thermalizing or that excitons dominate the early-time dynamics. The acceleration of the shift rate per decade at later times is found to correlate with the onset of thermally activated recombination processes, implying that depletion of higher-energy states by recombination is responsible.

INTRODUCTION

The cw photoluminescence (PL) in plasma-deposited *a*-Si:H consists of a band at ~ 1.4 eV, referred to here as the main PL band, and a number of weaker bands attributed to coordination defects.¹⁻⁴ The main PL band, which is the subject of this paper, is generally thought to arise from the radiative recombination of electrons and holes independently trapped in band-tail states,² although evidence for exciton recombination at early times also has been reported.^{1,5} Time-resolved measurements have revealed that the PL spectrum shifts in energy with delay, and that the shift occurs in two time regimes, one early ($t < 10^{-6}$ s) and one late ($t > 10^{-4}$ s). Various sources of these shifts have been suggested, including thermalization of the carriers within the band tails,^{2,3} hopping together of carrier pairs in their mutually attractive Coulomb field,^{6,7} and correlations between the energy and lifetimes of states such that higher-energy states recombine more rapidly.^{3,6,8} Experiments utilizing sub-band-gap photoexcitation⁹ and subnanosecond time resolution⁵ have effectively ruled out the possibility of energy-lifetime correlations as the source of the early-time shift. These measurements have also suggested that the hopping together of carriers is not important in plasma-deposited *a*-Si:H, although other experiments suggest that it may play an important role in sputtered materials⁷ and oxygen- and nitrogen-based alloys.^{6,10} Thus carrier thermalization appears to be the dominant mechanism responsible for the spectral shift observed at early times in plasma-deposited *a*-Si:H.

Carrier thermalization in the band tails is also thought to underlie the dispersive transport observed in *a*-Si:H as well as in chalcogenide glasses.¹¹⁻¹³ Transport data in the room-temperature range have been successfully modeled in the multiple-trapping (MT) picture, in which carriers trapped in localized band-tail states are thermally

excited to transport states at the band edge, and subsequently retrapped. Since carriers in shallow states are released more rapidly than those in deep states, the carrier distribution gradually moves deeper into the band tail, resulting in a monotonically decreasing mobility. For an exponential band tail of arbitrary width the peak of the carrier distribution at time t and temperature T is predicted¹³ to reach an energy

$$E_d^{MT}(t, T) = E_c - kT \ln \nu_0 t, \quad (1)$$

where ν_0 is a vibrational frequency of order 10^{12} – 10^{13} s⁻¹, and E_c is the mobility edge separating extended and localized states. This simple result was found to be consistent with photoconductivity (PC) and photoinduced-absorption (PA) measurements.^{12,14} It is notably *not* consistent, however, with the low-temperature PL data in *a*-Si:H and chalcogenide glasses, which exhibit a much more rapid spectral shift^{2,15} than predicted by this model.

Recently, PC and PA experiments in *a*-Si:H and chalcogenide glasses have been extended to lower temperatures.¹⁶⁻¹⁸ Consistent with the PL data, these results have also indicated that at low temperatures ($T < 150$ K) carriers thermalize more rapidly than expected from the MT model. Apparently some other mechanism dominates in this regime where the MT rate becomes exceedingly small. A natural candidate is direct hopping within the band tails, a mechanism which has been demonstrated¹⁹ to produce dispersion analogous to MT effects, and which was, in fact, originally proposed²⁰ as the basis of all dispersive transport. Recently, Monroe²¹ developed an intuitive, but quantitative, model describing the dynamics of thermalization by direct hopping to deeper band-tail states. For an exponential band tail of width kT_0 , the energy of the thermalizing carrier packet is given by

$$E_d^H(t, T_0) = E_0 - 3kT_0 \ln(\ln \nu_0 t), \quad (2)$$

where E_0 is an energy close to E_c and the difference ($E_c - E_0$) is proportional to kT_0 . This expression, first given by Kastner²² in another context, results in very different characteristics than for the MT model. While the MT thermalization rate is constant in $\ln t$ and is independent of band-tail width, the hopping rate smoothly decreases in $\ln t$ and is linear in kT_0 . The temperature dependences are also notably different: the MT model predicts a linear temperature dependence, but the hopping-down rate increases much more weakly through thermal broadening of the band tails. Thus at low enough temperatures direct hopping to lower-energy states will dominate at early times. Monroe has noted that even at late times transport should occur by a modified MT process in which carriers are excited to a band of localized states for which hopping rates start to compete favorably with activation to E_c .²¹ Thermalization by excitation to these transport states should take over after a time

$$t_s = \nu_0^{-1} \exp(3T_0/T), \quad (3)$$

with MT behavior observed at later times. This crossover time, which increases exponentially as the temperature is lowered, correctly predicts the times and temperatures that mark the borders of good agreement of the MT model with PC measurements. The model also accounts for a number of other previously unexplained transport phenomena.²¹

Since the transport experiments do not directly measure the carrier energies, a detailed comparison with these predictions of the hopping model is not straightforward. PL, on the other hand, provides a direct measure of the combined electron and hole (or exciton) energy states at the time of radiative recombination. By monitoring the position of the spectral peak as a function of time and temperature, a detailed, quantitative comparison is possible. In this paper we present new data on the temperature-dependent peak position of time-resolved spectra coupled with absorption spectra and spectrally integrated decay measurements of the main PL band, which allow us to evaluate the ability of the various models to describe the thermalization characteristics in the early-time regime. The results suggest that direct hopping is indeed the mechanism responsible for the early-time spectral shift, leading to a unified description of optical and transport data.

EXPERIMENTAL TECHNIQUES

The sample studied in detail was plasma-deposited at 250°C on roughened fused silica in a gas mixture of 30 mol % SiH_4 –68 mol % Ar–2 mol % Kr. The deposition was carried out at a pressure of 0.36 Torr and 5 W of rf power. This 2.0- μm -thick film is the same as sample 1 in Refs. 5 and 23, and subnanosecond results from that investigation are included in the data presented here. Other samples grown at different gas ratios exhibited similar behavior.

The samples were placed in a flowing-He-gas temperature-controlled cryostat for optical measurements. Absorption spectra were measured as the ratio of transmitted light from a tungsten-halogen lamp through

the substrates with and without the α -Si:H film. A doubled Nd:YAG laser (where YAG is yttrium aluminum garnet) was used for pulsed photoexcitation, with power densities $\sim 10^{15}$ photons/cm² in 25-ns pulses impinging on the samples at a repetition rate of 10 cps. For time-resolved spectra the PL was dispersed through a spectrometer and detected with an S1 photomultiplier. For consistency, a fixed ratio of gate width to delay of 20% was maintained, with the earliest delay set at 100 ns to avoid artificial spectral broadening⁹ due to the 25-ns laser-pulse width. Spectra at 500 ps and 2.5 ns were obtained previously²³ using a high-power picosecond laser system for excitation, and a fast GE photodiode and a set of calibrated interference filters for detection of the time-resolved spectra. All spectra were calibrated for the response of the detection system, including a normalization to intensity per unit energy range. We used fits to Gaussian line shapes to determine the peak positions. Decay curves of the spectrally integrated PL intensity were measured with a 25-ns-resolution Ge photodiode system, using interference filters to isolate the main PL band.

RESULTS AND DISCUSSION

Absorption data shown in Fig. 1 reveal typical thermal narrowing of the effective band gap with temperature. We determine the band gaps from the intercepts of $\sqrt{\alpha E}$ versus the photon energy E , where α is the absorption length. The narrowing is a relatively small effect: 13 ± 3 meV between 15 and 90 K, and 18 ± 3 meV between 15 and 120 K. Plots of $\ln \alpha$ versus E do not exhibit an extended exponential-tail region needed for a reliable determination of the band-tail width, kT_0 . In the region where $\alpha = 10^3$ – 10^4 cm⁻¹, the slopes lie in the range 85–150 meV. These are rather large values for kT_0 in good α -Si:H material, and may in fact not represent a true measure of the absorption edge. As recently shown in the case of polyacetylene, inhomogeneous materials can diffusively scatter a non-negligible portion of the incident light.²⁴

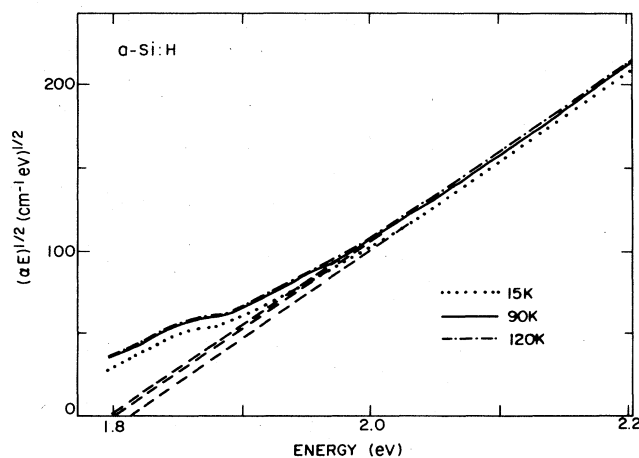


FIG. 1. Absorption data plotted as $(\alpha E)^{1/2}$ versus energy. Dashed lines show the extrapolations used to determine the optical band gaps.

Since transmission measurements do not distinguish between scattered and absorbed light in the weakly absorbing region below the optical gap, the spectrum obtained from transmission data is dominated by spurious effects due to scattering. Similarly, diffusive scattering from internal microstructure may be the source of the broadened absorption edge and low-energy shoulder frequently observed in *a*-Si:H samples prepared in our laboratory. A comparison of transmission data with photo-thermal deflection measurements, such as reported in polyacetylene, would be useful to clarify this point.

The peak positions of the time-resolved PL spectra are plotted versus $\ln t$ in Fig. 2 for 15, 90, and 120 K. In the early-time regime ($10^{-10} < t < 10^{-6}$ s) for each temperature, the peak positions fall monotonically with delay, the rate of fall with $\ln t$ gradually decreasing. The curves at different temperatures are approximately parallel, but offset by ~ 33 meV between 15 and 90 K, and by ~ 70 meV between 15 and 120 K. Similar data on other samples in the very-early-time regime have recently been reported.²⁵ These characteristics in no way match those expected from the multiple-trapping picture. The MT model predicts a constant rate of shift with $\ln t$, and a linear dependence of the rate on temperature. The latter corresponds to a sixfold increase in the thermalization rate between 15 and 90 K. For electrons and holes thermalizing independently, the MT model predicts a net rate of $2kT/t$, or 6 meV per decade at 15 K, much smaller than the observed 15–20 meV per decade. On the other hand, by 90 K the calculated MT rate for the carriers increases to 36 meV per decade, considerably larger than that observed. This implies not only that the combined MT rate for the two carriers does not dominate the thermalization, but also that this process is actually inhibited in some way in this time and temperature regime. A number of possibilities come to mind. First, the carriers could be thermalizing as excitons, as suggested by sub-

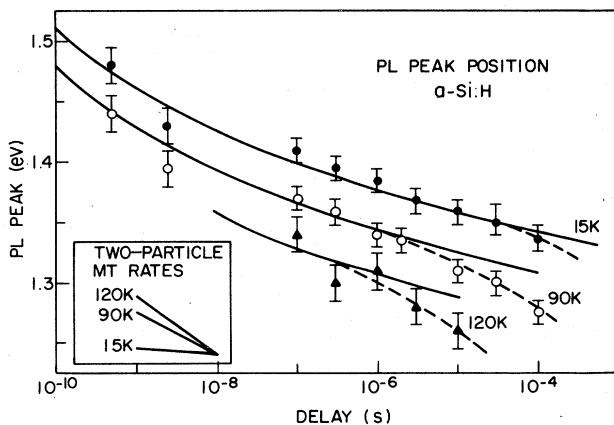


FIG. 2. Peak positions of the main PL band as a function of delay for 15, 90, and 120 K. The solid lines are fits to a model of thermalization by direct hopping between localized states. The dashed lines drawn through the data points are guides to the eye highlighting the departure of the data from this model at late times. Calculated shift rates for both carriers thermalizing by a multiple-trapping process are shown in the inset.

nanosecond experiments.^{5,23} Second, if one of the carriers were to be immediately trapped in a relatively deep state, the other carrier would be left to thermalize by itself through shallow states. Either mechanism would reduce the effective MT rate to that for a single particle, kT/t , which would not exceed the observed rates. A sizable Stokes shift or a gap in the density of tail states would also reduce the MT rate at early times. A final resolution of this question must await further work such as time-resolved spectra on picosecond time scales. In any case, it is clear that the MT model is totally unable to account for any of the major characteristics of the thermalization at early times.

The gradual decrease of the thermalization rate with $\ln t$ and its weak temperature dependence are, on the other hand, precisely the characteristics expected for the hopping model.²¹ Fits of this model to the data also yield physically realistic values for the associated parameters. The 15-K data, for example, are best modeled with $E_0 = 1.7$ eV, $kT_0 = 40.9$ meV, and $\nu_0 \sim 10^{12}$ s⁻¹, shown as a solid line in Fig. 2. Our measurements of other samples at 15 K consistently yield values of $E_0 \sim 1.6$ –1.8 eV and $kT_0 \sim 40$ –50 meV. The values of E_0 are consistent with experiments on similar samples using sub-band-gap excitation.⁹ In that study little change was noted in the spectra in this time regime until the excitation energy fell below about 1.75 eV, implying that thermalization above this threshold is much faster. While, as mentioned earlier, we cannot obtain reliable values of kT_0 for these samples from our absorption data, Cody *et al.*²⁶ have measured the absorption edge in a variety of samples and report $kT_0 = 50$ –55 meV in all their good samples at low temperature. These values are thought to represent the broader valence-band tail, with the conduction-band tail being only about one-third to one-half as broad. If both carriers were thermalizing independently, the two hopping-down rates would add, and the value of kT_0 measured would be the sum of both band-tail widths. Thus the smaller values of kT_0 obtained from the fits are consistent with the earlier arguments that the thermalization observed here involves either excitons or only one of the two carriers. During this time, therefore, luminescence is dominated either by exciton recombination or by diffusion-limited recombination in which the mobile, thermalizing carrier hops into the vicinity of, and recombines with, its deeply trapped counterpart. Diffusion-limited recombination, however, might be expected to involve energy-lifetime correlations, at odds with the interpretation of time-resolved sub-band-gap excitation data.⁹ Further theoretical analysis will be needed to resolve this point.

Analysis of the early-time data at higher temperatures in terms of the hopping model also yields reasonable values for kT_0 , which appears to increase only slowly with temperature, consistent with expectations from absorption measurements.²⁶ Best fits shown as solid lines in Fig. 2 yield $kT_0(90 \text{ K}) \cong 41$ meV, $kT_0(120 \text{ K}) \cong 42$ meV. On the other hand, the large parallel shift between the 15- and 90-K curves indicates substantial changes in E_0 which cannot be accounted for by the small band-gap shrinkage observed in absorption data. The two thermali-

zation curves are separated by ~ 33 meV, while the absorption edge narrows by only ~ 13 meV. The source of the additional 20-meV shift in E_0 is not clear. We note that since $(E_c - E_0)$ is proportional to kT_0 in this model, if a much higher value of E_c is postulated, then relatively small changes in kT_0 could be responsible for shifts of this magnitude. In particular, if we use the 2.2-eV gap suggested by the interpretation of absorption data by Cody *et al.*,²⁶ the early-time data at all three temperatures can be fitted consistently and with little loss in accuracy. While this approach explains the large parallel shifts in a self-consistent way, the values of kT_0 for good fits increase more rapidly with temperature than observed in the referenced absorption measurements,²⁶ and correspond to a rather unphysically low Debye temperature of 300 K. Given that one of the most striking features of the data is the essentially parallel shift of the curves at different temperatures, it may be more reasonable to invoke some shift of the total-energy scale which does not rely on an increase in T_0 . It is interesting to note that sub-band-gap excitation⁹ also reduces the energy scale for recombination on all timescales, manifested again as parallel shifts of the peak positions once the initial thermalization regime is passed.

The agreement of the hopping-down model with the data ends with the onset of the mechanism responsible for the late-time shift. The break point moves to earlier times as a function of temperature and, for the 90- and 120-K data, is not far from the time t_s of Eq. (3), where the single-particle MT process was expected to take over from the hopping-down mechanism. This agreement, however, appears to be fortuitous. To start with, at 90 K the shift rate after the break point is at least as large as the two-particle MT rate, but the equivalent t_s for the crossover to the *two-particle* rate should have occurred much earlier. In addition, at 15 K with a kT_0 of 40.9 meV, t_s should be $\sim 10^{29}$ s, while it is well known that at low temperatures the shift rate breaks from the plateau region after a delay of only ~ 100 μ s. Meanwhile, the subsequent rate of shift at low temperatures far exceeds even the two-carrier MT rate. Finally, the crossover from the hopping mechanism to the thermally activated MT process should occur as an asymptotic approach to the linear (in $\ln t$) MT rate, not as an *acceleration* of the thermalization rate per decade.

Dunstan and Boulitrop²⁷ have recently fitted similar spectral-shift data with a model that relies solely on hopping thermalization across both early- and late-time regimes. While it is conceptually simpler, this approach fails to reproduce the plateau region and accelerated late-time shift. These features—which are consistently reported—would seem to require the presence of an additional mechanism beyond hopping thermalization alone. Street has suggested⁶ that the increased shift rate at late times is the result of radiative tunneling recombination, which preferentially depletes higher-energy states. The onset of significant redistribution of the carrier energies by radiative tunneling or other recombination processes with energy-dependent rates appears a much more likely source of the increased shift rate per decade than any late-time acceleration of the thermalization rate itself.

To test whether recombination processes are indeed in-

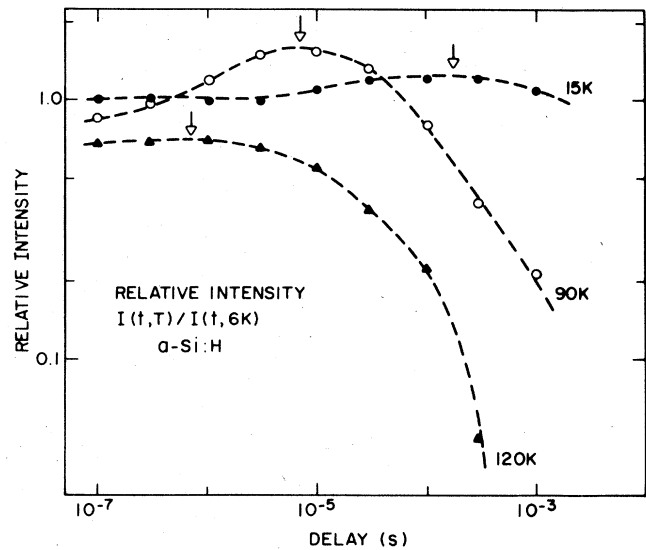


FIG. 3. Relative intensities in the spectrally integrated PL band as a function of delay for 15, 90, and 120 K compared to 6-K data. The dashed lines are guides to the eye. The arrows indicate the delay times at which the intensity ratios start to drop from their maximum values.

involved in the increased rate of shift at later times, we have examined the dynamics of the spectrally integrated intensity in the main PL band as a function of temperature. In order to highlight temperature-related effects, the data are displayed in Fig. 3 as ratios of intensities with respect to values at 6 K. After the initial intensity drop, which occurs on much faster time scales,⁵ we observe a slight absolute increase in the intensity at intermediate times, followed by a strong subsequent decrease. The increase in intensity is consistent with previous time-resolved data interpreted as indicating an increase in radiative recombination rates² up to about 60 K. The subsequent decrease may reflect both a depletion of longer-lived states by this shift of the radiative processes to earlier times, as well as an increase in the nonradiative (NR) recombination rates. The latter appears to be the dominant effect, at least by 90 K. Note that we use NR recombination here to describe any process that depletes the radiative population whether or not subsequent nonradiative recombination occurs rapidly. Since energy-lifetime correlations may occur for both radiative and NR recombination processes, either or both could, in general, be responsible for the accelerated spectral shift. We note that the times marked with arrows in Fig. 3 at which the relative intensities start to drop correspond approximately to the break points in the spectral shifts seen in Fig. 2. This agreement further strengthens the hypothesis that the late-time shift is caused by depletion of the higher-energy states through recombination, and suggests that, at least by 90 K and above, the relevant recombination processes are nonradiative.

SUMMARY

In this paper we have examined the thermalization rate of photoexcited carriers in *a*-Si:H as a function of tem-

perature by monitoring the spectral shift of the main PL band. A model of direct hopping between localized band-tail states offers the best account of the rapid thermalization at early times, thus providing a unified description of optical and transport data in these materials. The source of the parallel offset between peak positions at different temperature remains an intriguing puzzle. Models based on thermal activation to transport states followed by retrapping in deeper states are incapable of accounting for any of the significant characteristics reported here. The measured rates suggest that the early-time shift is the result of thermalization by a single particle. This could be an exciton, or possibly one of the carriers with its counterpart held stationary after initial capture in a deep trap.

Spectrally integrated intensity measurements presented here show a correlation between thermally activated

changes in recombination rates and the onset of the late-time shift. These results strongly support the idea that the late-time shift is the result of NR recombination events that preferentially deplete states of higher energy. In the temperature range of these experiments, this additional shift mechanism becomes significant at or before the time where the crossover from direct hopping to MT thermalization is expected to occur. Thus higher-temperature, earlier-time data will be needed to observe directly the regime where the MT mechanism is expected to dominate the thermalization process in these materials.

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