PHYSICAL REVIEW B VOLUME 25, NUMBER 8 15 APRIL 1982

Time-resolved photoluminescence in a-Si:H: Sub-band-gap excitation

B. A. Wilson and T. P. Kerwin
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 13 November 1981)

We present a comprehensive investigation of the evolution of the photoluminescence band at ~ 1.3 eV in plasma-deposited a-Si:H as a function of excitation frequency $\tilde{\nu}_{\text{ex}}$, where $\tilde{\nu}_{\text{ex}}$ has been extended well into the band-tail region. When $\tilde{\nu}_{\text{ex}}$ is lowered below the optical-absorption gap, the early time shift is diminished and eventually lost. No corresponding change is observed in the time decay. The most frequently cited models for the photoluminescence behavior are reexamined in the light of these new results. Models of the early time spectral shift based on a correlation between recombination energy and lifetime are ruled out, and we attribute the shift to slow-electron thermalization within the conduction-band tail. The results are consistent with recombination by radiative tunneling, providing that either the electron or the hole is trapped at a charged site. A value of 0.39 eV is obtained for the sum of the Stokes shift and hole-trap binding energy.

I. INTRODUCTION

Photoluminescence (PL) studies of a-Si:H (Refs. 1–8) have typically used optical excitation frequencies $\tilde{\nu}_{\text{ex}}$ in the visible region—well above the optical gap. This practice has the advantage of producing spectra that are essentially independent of $\tilde{\nu}_{\text{ex}}$, but it may also create excited states that are highly mobile and likely to sample many different sites in the material. As a result, the PL band at ~ 1.3 eV may be a superposition of the spectra from the individual sites and it has been difficult to resolve questions of homogeneous versus inhomogeneous contributions to the width of the cw spectrum. The use of pulsed excitation and time-resolved detection has provided substantially more detailed information and has aided in clarifying the situation to some extent. At "zero delay" the PL spectrum peaks some 0.3–0.5 eV below the absorption gap and subsequently shifts to lower energy at longer delays. (In general "zero delay" corresponds to 5–20 ns resolution, an important point frequently overlooked.) This shift occurs in two stages, exhibiting rather different time scales. The first phase tails off by about 1-μs delay after a shift on the order of 0.05 eV from the zero-delay position. The second starts at about 10 μs and continues beyond the 10-ms range of available data. Time-resolved detection has also revealed a highly nonexponential decay characterized by a distribution of lifetimes spanning many decades.[5] Chalcogenide glasses exhibit very similar behavior.[9–14] Not only is there a shift of the spectrum following pulsed excitation but the shift occurs in two segments and on identical time scales.

As there is no direct counterpart to this behavior among crystalline systems it has been natural to consider models that depend directly on the amorphous (or glassy) nature of the material. Such ideas include the presence of long tails in the density of states extending far into the gap,[5] strong electron coupling to the softer amorphous lattice resulting in "negative U" centers[15] or self-trapping,[16] specific types of bonding or coordination defects,[17,18] and topological models of internal microvoid structures.[19]

Regardless of the specific nature of the centers, there is a general consensus that the carriers are trapped in localized states and that recombination in these materials is by radiative tunneling. The radiative tunneling rate

$$\nu \sim \nu_0 e^{-2R/R_0} \tag{1}$$

depends exponentially on the electron-hole separation, and can easily account for the broad distribution of lifetimes with physically reasonable values of R. The scale parameter R_0 is the extent of the larger of the electron and hole wave functions, and ν_0 is the maximum radiative rate expected to be $\sim 10^8$ Hz.

Examples of radiative tunneling between localized states are well known in crystalline semiconductors,[20] and may be grouped into three classes. The sites at which the electron and hole are

©1982 The American Physical Society

trapped can be: (i) both charged, (ii) both neutral, or (iii) one charged and one neutral. Although examples of all three have been identified, class (i), referred to as donor-acceptor pair recombination, is by far the most common, and has been modeled in detail.[21] The normally ionized donors and acceptors are neutralized in the excited state, having trapped the oppositely charged carriers. After recombination they are returned to their charged ground state, leading to a Coulomb contribution to the recombination energy which depends on the pair separation:

$$E_c = \frac{e^2}{\epsilon R} \; . \tag{2}$$

Close pairs which luminesce at higher energy also decay faster according to Eq. (1) and this correlation between energy and recombination rate leads to a shift of the PL spectrum to lower energy at longer delays. The total light decay is highly nonexponential due to the tremendous range of lifetimes and appears closer to a power law, with an exponent slightly less than one.

To first approximation, class (ii) and (iii) processes are predicted to follow the same decay statistics but to differ in their Coulomb contribution. Recombination at sites which are both neutral, i.e., class (ii), introduces a Coulomb energy equal to that of the charged defect case, but of the opposite sign, resulting in a spectral shift to *higher* energy. When only one site is charged, i.e., class (iii), there is no first-order Coulomb term and thus no shift. In fact such transitions in crystals are somewhat more complex. Neutral-neutral recombinations involve extensive excitonic contributions which alter the decay statistics, and charged-neutral spectra exhibit a very small shift to higher energy consistent with second-order polarization effects.[20]

A further complication arises for pair recombination in amorphous materials. Not only is there this range of intersite Coulomb energies, there is an even larger range of electronic binding energies within the extended band tails. Energy-lifetime correlations occurring within the range of trap depths can lead to spectral shifts, just as in the case of intersite Coulomb energies. Localization theory[22] predicts a correlation between trap depth and wave-function extent R_0, which in turn determines the radiative tunneling rate. As a result lower energy states should decay more slowly causing a spectral shift to lower energy.

Evolution of state populations is not, of course, limited to energy-lifetime correlation effects. A more direct mechanism is nonresonant energy transfer, which leads to a redistribution of the population. At low temperatures one expects highly excited carriers predominantly to lose energy by emitting phonons. In extended states, this thermalization process probably occurs rapidly, on a $1-10$-ps time scale.[23] Relaxation at a given site also occurs on this time scale. Within the band tail of localized states, however, further thermalization can also occur by tunneling from one site to another of lower energy. As the population packet moves down through the band tail, this process will become progressively slower due to the exponentially decreasing density of available states. Recombination that occurs before thermalization is complete will reflect this shift of the population to lower energy. There is also the possibility of thermalization via thermal emission to the conduction band. Although such processes are thought to be involved in dispersive transport at higher temperatures, they play a negligible role at the low temperatures of most optical experiments. Depending on the charge states of the recombination sites, the electron and hole might also be induced to tunnel to states with different Coulomb interactions, changing the distribution of Coulomb energies and recombination rates. In summary, there are a number of possible mechanisms that can be (and have been) invoked to explain the observed spectral evolution in a-Si:H and chalcogenide glasses.

Photoluminescence in a-Si:H has been modeled as the recombination of electrons in shallow-band-tail states and deeply trapped holes, with both carriers trapped at neutral sites.[5] The strong lattice coupling to the deeply trapped (possibly self-trapped) holes accounts for the Stokes shift and accompanying breadth without requiring unreasonably broad band-tail widths, which would be at odds with other measurements.[24–26] The holes are thought to trap out very rapidly, and the observable PL shift to lower energy occurring on the 10-ns to 1-μs time scale is attributed to slow thermalization of the electrons in shallow conduction-band-tail states. Radiative tunneling at neutral sites, however, should cause a competing shift to higher energy due to the Coulomb-energy contribution. Such a rise has been reported in a-Si:H:O alloys[27] where the Coulomb energy is larger than in a-Si:H because of the smaller dielectric constant. Recently a similar rise has been observed in sputtered a-Si:H films prepared with very high H concentrations[28] where the dielectric constant is also reduced. Street has suggested[27] that this rise is also present in more typical plasma deposited *a*-Si:H films but that since the shift is small, it is masked by the more extensive thermalization shift occurring on the same time scale. The shift observed to start at much later times has been explained by a correlation between recombination rate and position in the band tail. Since electrons are thought to be in much shallower traps than holes, it is their wave-function extent which is assumed to determine R_0, the scale parameter for radiative tunneling. Deeper electron traps are assumed to be more severely localized and thus to live longer, leading to a progressive shift of the PL to lower energy.

Modeling of the similar PL in chalcogenide glasses has taken a rather different route. Historically the descriptions have focused on the possibility of "negative *U*" centers,[15] and particular types of bonding defects, valence alternation pairs (VAP's), have been suggested as examples of such centers.[17,18] These defects are charged in the ground state and the mean PL position as a function of time has been shown to correspond well to the model of donor-acceptor pair recombination in crystals.[13,21] This approach has not, in general, been thought appropriate for *a*-Si:H. The Stokes shift is more moderate in *a*-Si:H, making "negative *U*" centers less likely, and the fourfold coordination does not support this type of valence alternation defect. In addition, unlike chalcogenide glasses,[29] the PL in *a*-Si:H may be quenched by applied electric fields,[30] implying that the excited electron and hole are not both trapped at charged sites. PL in chalcogenide glasses has also been described as a recombination involving one charged and one neutral site,[27] where there is no Coulomb contribution, and the shift ascribed to thermalization, as in the case of *a*-Si:H. Clearly new experimental information would seem imperative in order to more definitively test these models in the two systems.

Optical excitation using above-band-gap light appears to result in the population of high mobility states which can subsequently sample many sites in the material. This causes difficulty in distinguishing between homogeneous and inhomogeneous contributions and precludes any clear-cut discrimination between the different models. Sub-band-gap excitation, on the other hand, has the potential of exciting only a particular set of band-tail states (or defects), allowing a study of the PL behavior from these states alone. Some preliminary results of ir pumping have indicated the feasibility of this approach. Shah[31] has observed a shift in the cw luminescence at laser frequencies below about 14 000 cm^{-1} (1.74 eV). Chen *et al.*[32] have noted a similar shift in the 1-μs delay spectrum. In this paper we present a comprehensive study of the time evolution of the PL in *a*-Si:H as a function of excitation frequency and reexamine some of the models for the luminescence in light of the new results.

II. EXPERIMENTAL TECHNIQUES

The *a*-Si:H films used in this study were prepared by decomposition of $\mathrm{SiH_4}$ mixed with Ar in a capacitively coupled rf plasma decomposition system. These undoped films were produced under the same conditions as those used for deep-level transient spectroscopy (DLTS) measurements in our laboratory,[33] but were deposited on roughened quartz to avoid interference fringes. Film thickness ranged from 0.8 to 2.0 μm. The optical quantum efficiencies were estimated to fall in the range of 1–20%. Absorption spectra were also measured, and an optical gap E_0 defined from fits of the optical-absorption coefficient α versus photon energy E to $\alpha \sim (E-E_0)^{1/2}/E$. Values measured for E_0 were 1.75 ± 0.02 eV and 1.82 ± 0.03 eV at room temperature and 12 K, respectively. No sample-to-sample variation was noted within this accuracy for the samples used in this study. The detailed results presented correspond to a single sample, but the same qualitative behavior was observed in other samples. For low-temperature measurements the samples were placed in a flowing He gas optical cryostat.

The samples were excited with 10-ns pulses from a 10-Hz Nd:YAG pumped dye laser using ir Styryl dyes. The average power was typically 5–20 mW, and the beam was expanded to a $\sim$15-mm^2 spot to avoid sample damage. The beam was passed through narrow-band filters to remove broadband dye fluorescence. The PL was dispersed with a double monochromator and detected with an InGaAs:P photocathode photomultiplier which provides sensitivity across the whole PL spectrum and avoids the rapidly changing response of the *S* 1 tubes typically used for these measurements. A boxcar integrator was used to time resolve the signal. The system response to the laser pulse was measured to be 15 ns, which determines our minimum time resolution. The spectra are calibrated for the spectral sensitivity of the system, and are plotted as *intensity per unit energy range,* in order to be relevant to discussions involving densities of states $g(E)$ and Stokes shifts. The peak position of these broad spectra are estimated using the average of the half-intensity points.

III. RESULTS

When pumped in the visible, our samples behave as typically described in the literature. The spectrum shifts to lower energy as a function of delay, both regions of shift being evident. The early time shift in our sample is somewhat smaller than reported by Tsang and Street,[5] and is apparently sample dependent. We note that the "zero delay" spectrum is slightly broader than those at later times. Although an increased width at early times has been reported in g-As_2S_3,[13] it has not been previously noted in a-Si:H. A set of sample spectra taken with excitation frequency $\tilde{\nu}_{ex} = 18\,790$ cm^{-1} (2.34 eV) is shown in Fig. 1(a). When $\tilde{\nu}_{ex}$ is lowered below about 14 000 cm^{-1} (1.74 eV) we see shifts of the time-resolved spectra to lower energy. Sample data for $\tilde{\nu}_{ex} = 13\,330$ cm^{-1} (1.65 eV) are shown in Fig. 1(b). Figure 2 is a plot of the observed peak positions versus $\tilde{\nu}_{ex}$ with delay time as a parameter. The "zero-delay" peak is affected most rapidly and drops essentially linearly with $\tilde{\nu}_{ex}$. The shift of the peak is somewhat smaller than the change in $\tilde{\nu}_{ex}$; the slope of a linear fit is found to be ~ 0.76. At longer delays the shift is less pronounced, becoming substantial only at progressively lower values of $\tilde{\nu}_{ex}$. Thus, as shown more directly in Fig. 3, the early time shift of the spectrum with delay observed with above-band-gap excitation is diminished and finally lost, as $\tilde{\nu}_{ex}$ is progressively lowered.

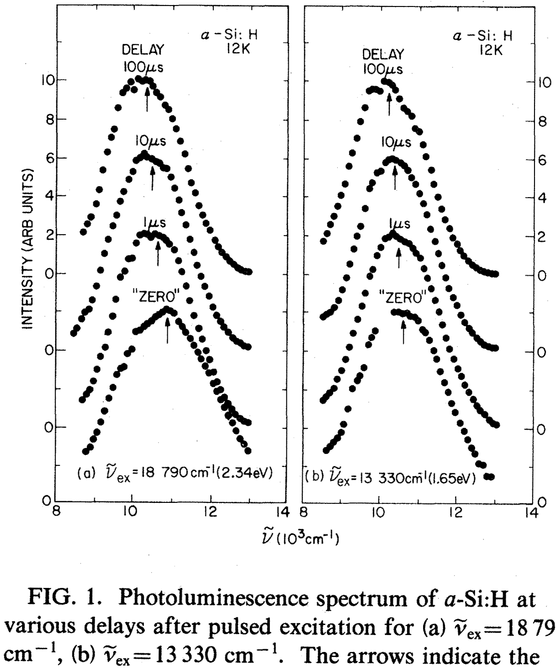

FIG. 1. Photoluminescence spectrum of a-Si:H at various delays after pulsed excitation for (a) $\tilde{\nu}_{ex} = 18\,790$ cm^{-1}, (b) $\tilde{\nu}_{ex} = 13\,330$ cm^{-1}. The arrows indicate the peak positions, defined as the average of the half-intensity points.

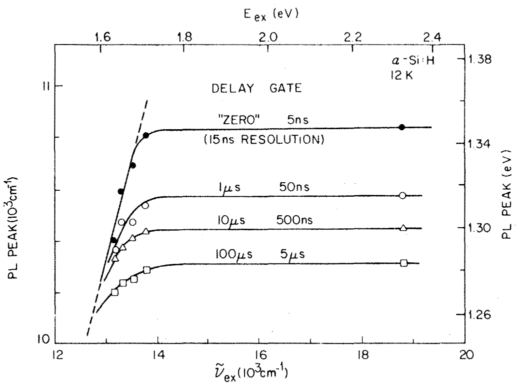

FIG. 2. PL peak position vs excitation frequency with delay as a parameter.

Figure 3 also shows the dependence of the width (FWHM) on $\tilde{\nu}_{ex}$ and on delay. The spectra are uniformly broader at shorter delay, but only the width at the earliest time is affected by $\tilde{\nu}_{ex}$, exhibiting a slight decrease as $\tilde{\nu}_{ex}$ is lowered. In Fig. 4 we compare the time decay of the peak height for various excitation frequencies. Clearly the decay is not affected by the change in $\tilde{\nu}_{ex}$. Even taking into account the slight increase in the width of the zero-delay spectrum, the ratio of the integrated intensity at zero-delay compared to that at 1-μs delay drops by less than 20% across this range of $\tilde{\nu}_{ex}$ in which we observe almost a total loss of the early time spectral shift. Finally we note that the spectral shift occurring at later times appears relatively unaffected by changes in $\tilde{\nu}_{ex}$.

Let us briefly compare these results with those of Higashi and Kastner[14] who have taken some of the analogous measurements on g-As_2S_3. They also see an essentially linear drop of the "zero-delay" (10 ns resolution) peak position with $\tilde{\nu}_{ex}$ below some critical value $\tilde{\nu}_{ex} \sim 18\,500$ cm^{-1} (2.3 eV). Above this frequency, however, the PL abruptly starts to broaden as intensity grows on the low-frequency side of the PL band. Apparently a different mechanism sets in at this energy which

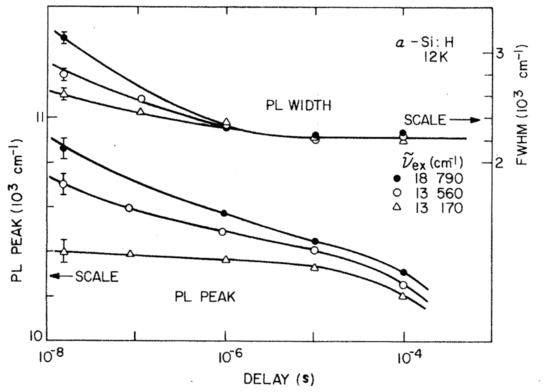

FIG. 3. PL peak position and width (FWHM) vs delay with $\tilde{\nu}_{ex}$ as a parameter.

effectively populates states that luminesce at lower energy. We see no such effect in *a*-Si:H. In contrast, the PL behavior saturates, remaining approximately stable and independent of $\tilde{\nu}_{ex}$ at higher frequencies.

IV. DISCUSSION

The shift of the peak positions with $\tilde{\nu}_{ex}$ becomes significant for $\tilde{\nu}_{ex} \lesssim 14\,000$ cm^{-1} (1.74 eV). This value is slightly lower than our 1.82 ± 0.03-eV (14 600 cm^{-1}) measurement of the optical-absorption gap at 12 K, but one would expect to see substantial shifts occurring immediately below E_0 only for *truly zero-delay* data. As pointed out before, our earliest scan, the so-called zero-delay spectrum, in fact corresponds to a 15-ns time resolution, and there are strong indications that a substantial shift has already taken place on a shorter time scale. As Fig. 2 demonstrates, the shorter the time delay, the higher the excitation frequency at which a significant shift is evident, and we anticipate that experiments run on a much shorter time scale would exhibit shifts starting at somewhat higher $\tilde{\nu}_{ex}$, even closer to our measured E_0. Since the turnover occurs just below E_0, it seems likely that the shift in the peak position occurs as the laser frequency is dropped low enough to directly populate band-tail states (or defects). Higashi and Kastner[14] suggest that the onset of similar behavior (plus the change in PL width) in *g*-As_2S_3 occurs so abruptly as to indicate the presence of a sharp dividing line between extended and localized states—i.e., a true mobility edge. We see no such clear evidence in *a*-Si:H where the effects occur more gradually.

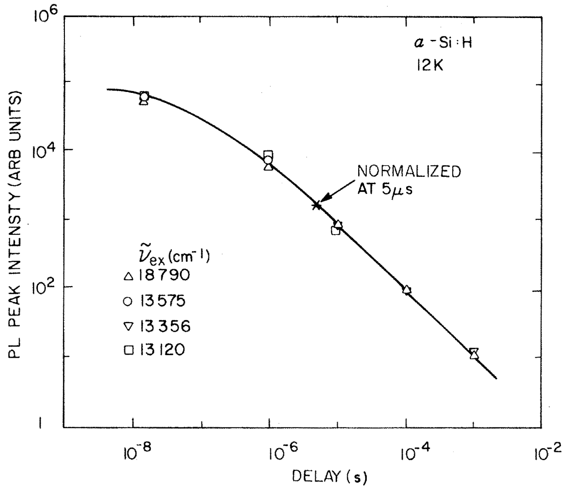

FIG. 4. Time decay of the PL peak intensity at various excitation frequencies. The curves are normalized at 5 μs.

Our results taken as a whole also provide new insight into the dynamics of the spectral shift. Our data clearly show that as $\tilde{\nu}_{ex}$ is lowered, the early time shift is diminished and finally lost, while over the same range in $\tilde{\nu}_{ex}$ the time decay remains essentially unchanged. If the early time shift were due to any type of correlation between recombination energy and lifetime, by exciting only those states of lower recombination energy, one should see a concomitant loss of all the fast components in the decay. Thus, this observed decoupling of the luminescence energy and lifetime directly rules out any model of the early time spectral shift based on such a correlation. In particular it precludes a description of the early time shift based on the Coulomb term associated with charged defect recombination. One word of caution, however. In *a*-Si:H the predominance of the fast decay rates has been correlated with the overall quantum efficiency of the sample,[5] indicating that the early time fast-decay modes may contain nonradiative contributions. Thus, for a completely definitive statement, one would want to examine a very high quantum efficiency sample where any changes in the distribution of radiative rates could be observed without interference from nonradiative channels. No corresponding data on changes in the time decay with $\tilde{\nu}_{ex}$ in the chalcogenide glasses have been published to date.

Our results are consistent with the idea that the early time shift reflects slow thermalization in the conduction-band tail. A schematic representation of the electronic energy levels used in this description of the evolution of the PL peak position E_{PL} as a function of excitation energy E_{ex} is shown in Fig. 5. Within this framework, the insensitivity of the decay statistics on $\tilde{\nu}_{\mathrm{ex}}$ indicates the absence of any strong correlation between position in the band tail and the recombination rate. Since the radiative tunneling rate depends on the wave-function extent R_0 this implies that the degree of localization is not strongly correlated with electronic binding energy. As mentioned earlier this behavior is contrary to theories of localization which predict a wave-function extent that falls exponentially with energy below the mobility edge.[22] These theories are derived from a consideration of relatively weak potentials (e.g., Coulomb potentials) that pull the band tail only slightly beyond the band edge. It may be, however, that the band-tail states in *a*-Si:H are due to strong local potentials which draw the localized wave function from points *throughout* the band structure, in analogy to the case of deep levels in crystalline semiconductors.[34] In such a case, fine gradations in the energy-level position relative to the conduction-band edge, such as associated with the early time shift, would not necessarily be correlated with the degree of localization of the state.

We propose, then, that as $\tilde{\nu}_{\mathrm{ex}}$ is progressively lowered, deeper band-tail states are excited, reducing the extent of thermalization that can occur on a 1-μs time scale and thus the corresponding early time shift. By $\tilde{\nu}_{\mathrm{ex}} = 13\,170$ cm^{-1} the peak position shifts by only 75 cm^{-1} out to 1 μs. In the absence of a sizable shift due to thermalization, any Coulomb effects should be exposed, and it becomes possible to critically examine the assumption of neutral recombination centers.[5] Recombination at neutral sites introduces a Coulomb term equal and opposite to that for charged defects, which shifts the spectrum to higher energy with delay. Within the model of recombination by radioactive tunneling, the range of lifetimes reflects the distribution of electron-hole separations, which in turn can be used to calculate the magnitude of the corresponding Coulomb energies. We take the maximum radiative rate ν_0 to be 10^8 Hz, and assume a dielectric constant of 11.5. Then using 12 Å for the electron Bohr radius R_0, as suggested by the results of Tsang and Street,[5] we calculate an expected Coulomb shift of 500 cm^{-1} (61 meV) between 10^{-7} and 10^{-5} sec. Changing ν_0 merely shifts the time scale on which this predicted rise of the peak energy would occur. Even taking an overestimate of 20 Å for R_0, a rise of 300 cm^{-1} (36.4 meV) is expected. Since the entire early time shift is less than 100 cm^{-1} at $\tilde{\nu}_{\mathrm{ex}} = 13\,170$ cm^{-1}, it can no longer be thought to hide a Coulomb effect of this magnitude. On the other hand, the lack of any substantive change in the decay statistics with $\tilde{\nu}_{\mathrm{ex}}$ indicates that even the lowest $\tilde{\nu}_{\mathrm{ex}}$ must create essentially the same distribution of electron-hole separations. Consequently, the absence of a Coulomb shift precludes radiative tunneling at sites that are both neutral (or both charged) requiring instead that one site be neutral and the other charged. This result is rather surprising. As discussed earlier, a rise in the PL peak position is observed in *a*-Si:H:O alloys and high H concentration sputtered *a*-Si:H films, which has been taken to indicate that recombination occurs at neutral sites in these materials. The assumption has been that the same mechanism is operant in typical plasma-deposited films but just more difficult to identify because of the smaller Coulomb energies. Our results indicate that this is not the case, at least when samples are excited by sub-band-gap light. If one concludes on the basis of the decay statistics that the decay mechanism is radiative tunneling without major excitonic influences, then our results demand that either the electron or the hole is trapped at a charged center. Our results do not discriminate between which of the two centers is

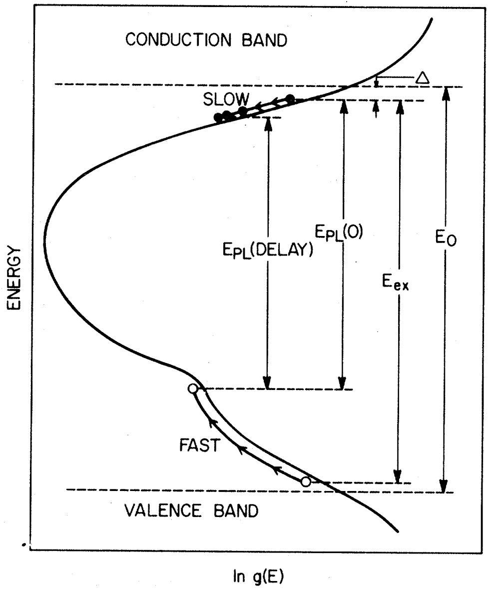

FIG. 5. Schematic diagram of the electronic energy levels proposed to describe the PL evolution.

charged. On the one hand, one might speculate that the hole which is more quickly and more deeply trapped is captured by a charged defect. Coulomb effects are relatively small in comparison to other disorder effects in these materials, however, and may not greatly affect trap cross sections or depths. In fact it could be precisely because the hole is trapped (or self-trapped) so rapidly that it might not diffuse far enough to locate charged sites.

From Fig. 2 it is seen that as $\tilde{\nu}_{ex}$ is lowered, the peak positions at all time decays appear to asymptotically approach a single line. States that lie deeper in the band tail have much reduced tunneling rates due to the exponentially decreasing density of states. Thus, as $\tilde{\nu}_{ex}$ is scanned further down the band tail any subsequent cascading of the population to lower energy will take place on a progressively longer time scale. The asymptotic line therefore represents the peak position of the luminescence from the states originally populated by the laser pulse before any thermalization occurs. The slope of the line in Fig. 2 is 0.76, implying that as $\tilde{\nu}_{ex}$ is scanned down the band-tail states the peak luminescence from these states falls by only 0.76 of the change in $\tilde{\nu}_{ex}$. Since holes are thought to be rapidly trapped into much deeper states, Shah has suggested[35] that the energy separation of the hole from the valence band in the original excitation process will no longer be represented in the PL position. The shift will be determined solely by the equivalent electron energy separation, designated as Δ in Fig. 5. With equally steep conduction- and valence-band tails, one would expect $\Delta \sim 0.5\ (E_0 - E_{ex})$. The conduction-band tail is known to fall more rapidly,[21] however, resulting in a slope between 0.5 and 1.0 as observed. There could also be a progressively larger Stokes shift associated with deeper conduction-band-tail states. Although this effect may contribute to the shift it is unlikely to play an important role, as there is no indication of an increased PL width at longer delays or lower $\tilde{\nu}_{ex}$.

Assuming that this asymptotic line continues unchanged beyond the range of our data, an extrapolation in either direction constitutes a prediction of the peak position for a given $\tilde{\nu}_{ex}$ prior to any tunneling to lower states. It is interesting to extend this to $h\tilde{\nu}_{ex} = E_0$, which results in a predicted luminescence peak at 11 530 cm^{-1} (1.43 eV), implying an electron thermalization process covering a total range of ~ 0.13 eV, in good agreement with other estimates of the width of the conduction-band tail.[24–26] Note that in contrast to other authors we define this range to start at the band edge rather than at the peak position of an arbitrarily chosen zero-delay spectrum. Thus, we include states at the top of the band tail that tend to be overlooked because the excited electrons cascade through them faster than the experimental time resolution. On the other hand, we have omitted the later time shift which continues beyond the scope of our measurements with no well-defined energy scale. This extrapolation also provides the first estimate from optical measurements of the magnitude of the Stokes shift plus hole-trap depth, since the remaining 0.39 eV to the optical gap must be divided between these fast relaxation processes. If most of this energy is due to the electronic binding energy of the trap, then the hole state lies in the first shoulder in $g(E)$ observed in similar samples by DLTS,[33] a feature whose strength is sample dependent. If a substantial component is Stokes shift, of which only the part associated with the excited state is measured in transport experiments, then the hole state lies within the valence-band tail. Drift mobility measurements[36] have also suggested a hole activation energy in the range 0.26–0.35 eV, but these are high-temperature results (≥ 200 K), and may not be applicable here. Note that the precise relationship between the optical edge and the mobility edge remains a controversial question which adds to the uncertainty of these estimates. Finally we note that by the time $\tilde{\nu}_{ex}$ is lowered far enough to eliminate the early time shift, the peak position is clearly lower than the position reached after about 5 μs following above-band-gap excitation, i.e., at the end of the early time shift. Thus the simplest picture, that lower $\tilde{\nu}_{ex}$ merely excites the same set of states that would have been populated through thermalization, is not adequate to describe all the details of the observed behavior. In g-As_2S_3 the complete matrix of the PL dependence on delay time and on $\tilde{\nu}_{ex}$ effects has not been examined, so a full comparison cannot be made. The zero-delay spectra are available[13] and resemble the equivalent a-Si:H data, but the fall with $\tilde{\nu}_{ex}$ has a slope closer to 1.0.

We also observe the shift occurring at later times, $t > 10\ \mu$s. This shift continues beyond the 10-ms range of our longest delay. In our samples this stage of shift is not always as well separated from the early time shift as in the case of the data published by Tsang and Street.[5] Nevertheless, our ir results leave no doubt that two separate processes are involved, since the later time shift appears unaffected by those changes in $\tilde{\nu}_{ex}$ which cause a complete loss of the early time shift. Although we observed little or no correlation between recombination rate and position in the band tail in the narrow range of the early time shift, we cannot rule out such a correlation on a larger energy scale. Thus, it is not unreasonable that the later time shift may be evidence of increased localization deeper in the band tail as suggested.[5,27] Experiments at even lower $\tilde{\nu}_{ex}$ should be able to answer this question.

Included in Fig. 3 are measurements of the PL width as a function of delay time and $\tilde{\nu}_{ex}$. A careful interpretation must take into account that the zero-delay spectrum is not equivalent to the later measurements. First of all, the time scale in this case is the same as the laser pulse length so that a delta-function excitation picture is inappropriate, and an analysis of the buildup of state populations would be required for a complete analysis. Secondly, the zero-delay spectrum is not measured at the same 5% ratio of boxcar gate width to delay time. Our zero-delay scan actually records a superposition of all the spectra from the *true zero delay* out to the 15-ns system resolution. Consequently, the recorded spectrum may be artificially broadened. Higashi and Kastner have pointed out that to the extent the decay follows a power law, the luminescence observed during any time gate is dominated by centers whose lifetimes fall in the center of the gate.[13] We have found this to hold true in *a*-Si:H at longer delays, where we find the spectra approximately independent of gate width, and it is likely to be true at early times as long as there is no drastic increase in the distribution of lifetimes at very short delays. A *real* decrease in the width of the early time spectrum as $\tilde{\nu}_{ex}$ is lowered into the band tail may be anticipated according to the following argument. The conduction-band states excited by above-band-gap light may be trapped into a range of initial band-tail states, creating a distribution of electronic energies and contributing an additional inhomogeneous width to the spectrum. Pumping directly into the band-tail states eliminates this extra width in a manner analogous to fluorescence line narrowing techniques. Unfortunately, a resolution of the source of this narrowing must await experiments on a faster time scale. The increased width at zero delay remaining even at the lowest $\tilde{\nu}_{ex}$ where the early time shift has disappeared suffers no such experimental ambiguity and must be taken as real. It is not clear, however, if one assumes that this is also due to an inhomogeneous contribution, why the population packet should become more restricted in energy with time. Higashi and Kastner discuss a similar increase in width seen at early times in chalcogenide glasses[13] in terms of the charged defect-pair model. Their spectra, however, would appear to suffer the same ambiguities discussed above. In contrast to our data on *a*-Si:H they do not observe a narrowing of the zero-delay spectrum once $\tilde{\nu}_{ex}$ is below the band gap.[14]

V. SUMMARY

We have presented a comprehensive study of the time evolution of photoluminescence in plasma deposited *a*-Si:H as a function of excitation frequency, extending $\tilde{\nu}_{ex}$ to ir frequencies well below the band gap. The results provide new insight into the nature of the luminescing centers and the dynamics of the spectral shift with delay. As $\tilde{\nu}_{ex}$ is lowered below the optical gap, the luminescence spectrum also shifts to lower energy, and the early time shift is lost. The lack of a corresponding change in the decay rate precludes a description of the early time shift based on an energy-lifetime correlation such as the charged defect model proposed by Kastner *et al.* to describe similar PL behavior in chalcogenide glasses.[13]

We assume instead that the early time shift reflects electron thermalization within the conduction-band tail. This requires there to be no strong correlation between the degree of localization and the binding energy of the state, a condition implying that the band-tail states may be due to strong local potentials. The ability to reduce the thermalization shift by exciting deeper in the band tails allows an analysis of the charge states of the recombination sites. Of the three possibilities only recombination involving one charged and one neutral center is consistent with the lack of an observable Coulomb shift at early times.

Since the tunneling rate immediately after excitation becomes progressively slower as lower $\tilde{\nu}_{ex}$ excites states deeper in the band tail, it is possible to examine the peak position as a function of $\tilde{\nu}_{ex}$ prior to thermalization. The slope of the change in the peak position with $\tilde{\nu}_{ex}$ is ~0.76. If the holes are rapidly trapped into deeper states only the energy gap between the excited electron states and the conduction band will be represented in the PL position, leading to an expected slope between $\frac{1}{2}$ and 1. An extrapolation of this line predicts a ~ 0.39 eV energy for the fast relaxation processes—the trapping of the hole and the Stokes shift. The later time shift was found to be relatively independent of $\tilde{\nu}_{\mathrm{ex}}$, verifying that a different mechanism is responsible. Although our data on the width are difficult to interpret, it is clear that the spectrum narrows to some extent during the first μs. Wherever possible our data and interpretations have been compared with results on the PL behavior observed in chalcogenide glasses.

ACKNOWLEDGMENT

We are grateful to J. P. Harbison for preparing the *a*-Si:H films used in this work. We also thank R. W. Collins and W. Paul for communication of their results prior to publication.

---

[1] D. Engemann and R. Fischer, in *Structure and Excitation of Amorphous Solids, Williamsburg, Virginia, 1976,* edited by G. Lugovsky and F. L. Galeener (American Institute of Physics, New York, 1976), p. 37.

[2] T. S. Nashashibi, I. G. Austin, and T. M. Searle, Philos. Mag. 35, 831 (1977).

[3] J. I. Pankove and D. E. Carlson, in *Proceedings of the 7th International Conference on Amorphous and Liquid Semiconductors, Edinburgh, 1977,* edited by W. E. Spear (Institute of Physics, London, 1977), p. 402.

[4] R. A. Street, J. C. Knights, and D. K. Biegelson, Phys. Rev. B 18, 1880 (1978).

[5] C. Tsang and R. A. Street, Phys. Rev. B 19, 3027 (1979).

[6] Jagdeep Shah, B. G. Bagley, and F. B. Alexander, Jr., Solid State Commun. 36, 199 (1980).

[7] D. A. Anderson, G. Moddel, R. W. Collins, and W. Paul, Solid State Commun. 31, 677 (1979).

[8] S. Kurita, W. Czajo, and S. Kinmond, Solid State Commun. 32, 879 (1979).

[9] M. A. Bosch and J. Shah, Phys. Rev. Lett. 42, 118 (1979).

[10] G. S. Higashi and Marc Kastner, J. Non-Cryst. Solids, 35/36, 921 (1980).

[11] J. Shah, Phys. Rev. B 21, 4751 (1980).

[12] R. A. Street, Solid State Commun. 34, 157 (1980).

[13] G. S. Higashi and Marc Kastner, Phys. Rev. B 24, 2295 (1981).

[14] G. S. Higashi and Marc Kastner, Phys. Rev. Lett. 47, 124 (1981).

[15] P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

[16] D. Emin, J. Non-Cryst. Solids 35/36, 969 (1980).

[17] Marc Kastner and H. Fritzsche, Philos. Mag. B 37, 199 (1978).

[18] David Adler, Phys. Rev. Lett. 41, 1755 (1978).

[19] J. C. Phillips, Phys. Rev. Lett. 42, 1151 (1979).

[20] P. J. Dean, Prog. Solid State Chem. 8, 1 (1973).

[21] D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. A 140, 202 (1965).

[22] P. W. Anderson, Phys. Rev. 109, 1492 (1958).

[23] A. M. Johnson, D. H. Auston, P. R. Smith, J. C. Bean, J. P. Harbison, and A. C. Adams, Phys. Rev. B 23, 6816 (1981).

[24] P. G. LeComber, A. Madan, and W. E. Spear, J. Non-Cryst. Solids 11, 219 (1972).

[25] T. Tiedje, A. Rose, and J. M. Cebulka, in *Tetrahedrally Bonded Amorphous Semiconductors, Carefree, Arizona,* edited by R. A. Street, V. K. Biegelsen, and J. C. Knights (American Institute of Physics, New York, 1981).

[26] R. S. Crandall, Phys. Rev. Lett. 44, 749 (1980).

[27] R. A. Street, Solid State Commun. 34, 157 (1980).

[28] R. W. Collins and William Paul, Phys. Rev. B 25, 2611 (1982).

[29] Marc Kastner and S. J. Hudgens, Philos. Mag. B 37, 665 (1978).

[30] D. Engemann, Ph.D. thesis, Marburg University, 1976 (unpublished).

[31] J. Shah, American Physical Society, Meeting, Phoenix, Arizona, March, 1981 (unpublished).

[32] Wei-Chung Chen, B. J. Feldman, J. Bajaj, Fei-Ming Tong, and G. K. Wong, Solid State Commun. 38, 357 (1981).

[33] J. D. Cohen, D. V. Lang, and J. P. Harbison, Phys. Rev. Lett. 45, 197 (1980); D. V. Lang, J. D. Cohen, and J. P. Harbison, Phys. Rev. B 25, 5321 (1982).

[34] D. V. Lang, R. A. Logan, and M. Jaros, Phys. Rev. B 19, 1015 (1979).

[35] Jagdeep Shah (private communication).

[36] R. A. Moore, Appl. Phys. Lett. 31, 762 (1977).