Photoluminescence Excitation Spectroscopy in *a*-Si:H: Evidence for Phonon-Assisted Absorption

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Photoluminescence in *a*-Si:H has been investigated using optical excitation energies E_x varying from 1.27 to 2.0 eV. At low temperatures ($T < 100$ K) a strong dependence of both the radiative quantum efficiency and the energy distributions of photoexcited carriers on E_x has been observed for $E_x < 1.65$ eV. At higher temperatures ($T > 200$ K), the dependence of the energy distribution of carriers on E_x disappears within a narrow interval of temperature. A model of phonon-assisted absorption is proposed to account for the experimental results.

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Recombination processes in hydrogenated amorphous silicon (*a*-Si:H) have usually been studied using optical excitation where the exciting photons have energies that are on the order of the energy of the mobility gap. It is commonly believed [1-3] that recombination is preceded by rapid thermalization into the manifold of localized band tail states that exist at the edges of the valence and conduction bands in this amorphous semiconductor. A slower thermalization within these localized states results in the fact that the characteristic radiative energies as observed in photoluminescence (PL) are about 0.6 eV less than the characteristic energy of the mobility gap [1-3] (1.7-1.9 eV in *a*-Si:H). Indeed, at a given temperature the shape of the PL spectrum with above gap excitation depends only very weakly on the excitation energy E_x. In addition to the characteristic radiative recombination process just described between electrons in the conduction band tail and holes in the valence band tail (hereafter called band tail PL), a second PL process exists which is commonly attributed to radiative recombination through silicon dangling-bond states near the middle of the energy gap (hereafter called low-energy PL).

The relative independence of the band tail PL spectrum on E_x for energies greater than about 1.8 eV is understandable because the thermalization process results in similar distributions of carriers within the band tails. However, if one were to excite carriers at energies that fall within the recombination band, then different absorption transitions may become important. In fact, one can imagine that some localized states are relatively inaccessible when carriers thermalize from higher energies because recombination from these particular higher energy states is highly probable. On the other hand, these "inaccessible" states can be occupied by direct absorption of carriers into them. Thus at low excitation energies additional PL transitions may occur.

When E_x is decreased below about 1.8 eV in *a*-Si:H, previous measurements have shown that at low temperatures the peak energy of the band tail PL spectrum shifts to lower energy [4-6], but there is no strong dependence of the integrated PL quantum efficiency η on E_x [7]. In this Letter we present the temperature dependence of PL measurements for E_x well below 1.8 eV. Both the temperature dependence of η and the dependence of η on E_x are surprising, as will be described below.

As described elsewhere [8], the high-quality *a*-Si:H samples used in this study were made by the standard glow discharge process, and the PLE experiments were performed using a tunable Ti sapphire laser. All PL and PLE were taken at constant exciting photon flux, and all spectra have been corrected for the response of the measurement system.

Figure 1 shows the PL spectra at 77 K as a function of the E_x from near the optical gap down to 1.32 eV. For higher values of E_x the PL line shapes are essentially the same as that shown in curve *a* and those reported elsewhere [1]. For high values of E_x the decay of the PL at low energies is approximately exponential with a slope on a semilog plot that is similar to those reported earlier [9]. As E_x decreases the low-energy slope of the PL in Fig. 1 decreases. At the lowest values of E_x there is some indication that the low-energy PL which peaks near 0.8-0.9 eV may make a small contribution to the total PL spectrum. One can of course produce a strong, resolved peak in the 0.8-0.9-eV range after strenuous light soaking at 300 K, but even in this case the results to be presented in the present Letter are not altered if this contribution is subtracted from the band tail PL spectrum. Therefore, for simplicity we limit our discussion to samples where the low-energy PL is unimportant.

Relative values of η for the PL measured at several different energies from 1.2 down to 0.8 eV are shown in

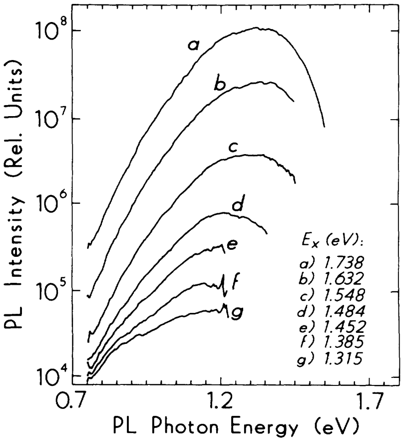

FIG. 1. The PL spectra of *a*-Si:H sample after annealing as a function of excitation photon energies E_x at 77 K.

Fig. 2 for two different measurement temperatures (77 and 220 K). To determine η only the exponential portion of the absorption edge was used, for two reasons. First, the band tail PL is a recombination process between electrons in the conduction band tail and holes in the valence band tail, while excitations that contribute to the below-gap absorption can produce only one type of band tail carrier per photon and are therefore much less effective in exciting the band tail PL. Second, the curves shown in Fig. 2 are essentially independent of the magnitude of the below-gap absorption provided that the low-energy PL does not dominate the total PL. To determine the absorption at different temperatures we used the values of α determined by photothermal deflection spectroscopy (PDS) at 300 K and corrected for the temperature dependence of the optical band gap measured by transmission [10] using previously published results [11,12] for the temperature dependence of the slope of the exponential absorption tail. The general features of Fig. 2 are insensitive to the latter correction. We estimate the relative error of the individual points in Fig. 2 to be less than a factor of 2 in all cases.

For E_x above about 1.5 eV the values of η are independent of E_x for all values of the PL energy and for all measurement temperatures. This behavior, which is fully consistent with previous results using higher values of E_x, is indicative of the production of thermalized distributions of carriers in the two band tails that are independent of the initial excitation process. For E_x below about 1.4 eV, η increases rapidly with decreasing E_x, and this increase at about 1.3 eV is between 10 and 100 for all PL energies at all temperatures studied (up to 250 K). This behavior is at least qualitatively consistent with the suggestion that carriers excited deep in the band tails cannot diffuse as readily to nonradiative centers as those carriers that are excited higher in the tails.

In addition to the rapid rise of η below about 1.4 eV for all measurement temperatures, there are two additional features of the data in Fig. 2 that are striking. First, even at the lowest value of E_x ($\sim$1.27 eV) where the carriers are presumably excited very deep within the band tails, η decreases by an order of magnitude between 77 and 220 K. Second, the ratio of η at constant E_x for different PL energies changes dramatically as E_x decreases at 77 K (open symbols in Fig. 2), but these ratios are constant at 220 K (curves with solid symbols in Fig. 2 are parallel). One of the possible ratios is plotted semilogarithmically in Fig. 3 (PL at 1.1 eV divided by PL at 0.8 eV). The general trends established in Fig. 3 are independent of the particular ratio chosen. The trends shown in Fig. 3 suggest that at low temperatures (below about 100 K) and at low excitation energies ($E_x \leq 1.6$ eV) the relative probability of recombination from carriers deep in the band tails is enhanced. At higher temperatures ($T \geq 200$ K) the carrier distributions in the band tails appear to be independent of E_x down to the lowest excitation energies (1.27 eV). Finally, it should be noted that the transition between these two very different behaviors occurs very abruptly between about 100 and 200 K (see the inset to Fig. 3).

Without invoking a specific model, one can qualitatively understand most of these results by assuming that one obtains thermalization into a well-defined set of band tail states where radiative recombination is probable for all excitation energies at temperatures above about 200 K and that at temperatures below about 100 K such thermalization dominates only at high enough excitation energies ($E_x \geq 1.6$ eV). As long as thermalization dominates, the ratio η_1/η_2 in Fig. 3 is independent of E_x. However, when one excites directly into the recombination band different states deep in the band tails can be accessed, states that are predominantly unaccessible by thermalization processes from much higher energies be-

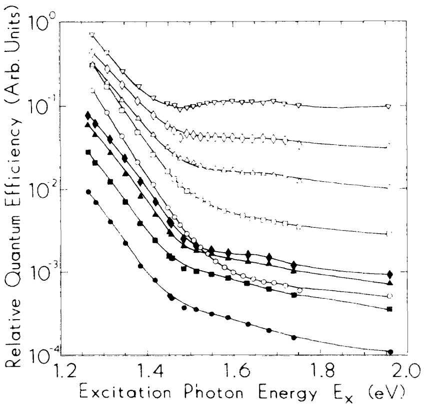

FIG. 2. The relative quantum efficiency as a function of E_x at temperature 77 K (open symbols) and 220 K (solid symbols) for PL measured at 0.8 eV (○), 0.9 eV (□), 1.0 eV (△), 1.1 eV (◇), and 1.2 eV (▽).

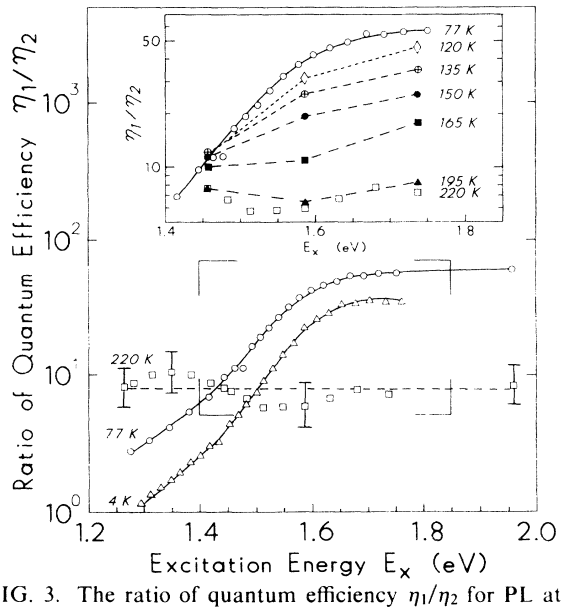

FIG. 3. The ratio of quantum efficiency η_1/η_2 for PL at 1.1 and 0.8 eV as a function of excitation at 4, 77, and 220 K. The inset shows more detail from 77 to 220 K.

cause the higher energy states that feed them have high recombination probabilities. At temperatures above 200 K there appears to be a redistribution of the carriers (partial thermalization) even at the lowest excitation energies.

Since thermalization arguments alone do not satisfactorily account for the data, we suggest that these results, in particular the fact that at the lowest excitation energies there is an order-of-magnitude drop in η between 100 and 200 K and the fact that the excitation spectra change so drastically at excitation energies below 1.6 eV over this same temperature range, can be best explained by a change in the absorption process. At low temperatures, the absorption of light with photon energy E_x is governed by those spatially close pairs of localized states with energies $\varepsilon_1 - \varepsilon_2 = E_x$ (ε_1 is the energy of the states in the conduction band tail, and ε_2, of a state in the valence band tail). At finite temperature T, there is a probability that the photon E_x is absorbed by a spatially close pair of states with $\varepsilon_1 - \varepsilon_2 > E_x$. In this case the absorption process involves the absorption of several phonons. We assume that the probability of such a process obeys the Urbach rule [13], so that it is proportional to $\exp[-\gamma(\varepsilon_1 - \varepsilon_2 - E_x)/kT]$ where γ is a numerical factor.

Let us compare the contributions to the absorption coefficient from the direct and phonon-assisted processes. To simplify the analysis we first neglect the conduction band tail states. In this case the probability of direct absorption is proportional to the density of states in the valence band tail, $\alpha_d \propto g_v(E_g - E_x)$, where E_g is the band-gap energy. For the phonon-assisted processes we denote the total energy of phonons as ε, then the absorption coefficient takes the form $\alpha_{\mathrm{ph}}(\varepsilon) \propto g_v(E_g - E_x - \varepsilon) \times \exp(-\gamma\varepsilon/kT)$. It is seen that compared to α_d, α_{ph} contains a small exponential factor. On the other hand, the corresponding density of states in α_{ph} is higher than in α_d. For an exponential form for the density of states, $g_v(E) \propto \exp(-E/E_v)$, where E_v is the characteristic scale of the valence band tail, the equations for α_d and α_{ph} can be rewritten as

$$\alpha_d \propto \exp\left(-\frac{E_g - E_x}{E_v}\right),$$
$$\alpha_{\mathrm{ph}}(\varepsilon) \propto \exp\left\{-\left[\left(\frac{E_g - E_x - \varepsilon}{E_v}\right) + \frac{\gamma\varepsilon}{kT}\right]\right\}. \tag{1}$$

It is seen from Eq. (1) that for temperatures lower than $kT_c = \gamma E_v$, direct absorption predominates; however, for $T > T_c$, phonon-assisted absorption becomes more favorable. Note that the crossover temperature T_c does not depend on ε. Physically this mechanism implies that for $T > T_c$ the holes are excited close to the valence band edge.

If the conduction band tail states are taken into account, then the phonon-assisted absorption coefficient takes the more complicated form

$$\alpha_{\mathrm{ph}} \propto \int_{-\infty}^{\infty} dE_1 g_c(E_1) \int_{-\infty}^{\infty} dE_2 g_v(E_2) e^{-\gamma(E_1 - E_2 + E_g - E_x)/kT} \theta(E_1 - E_2 + E_g - E_x), \tag{2}$$

where $g_c(E)$ is the density of states in the conduction band tail and $\theta(E)$ is the unit step function. To obtain quantitative results, we choose the following form for the functions g_c, g_v:

$$g_c(E) = N_c \begin{cases} 1, & E > 0, \\ \exp(E/E_c), & E < 0, \end{cases} \quad g_v(E) = N_v \begin{cases} \exp(-E/E_v), & E > 0, \\ 1, & E < 0. \end{cases} \tag{3}$$

Using Eq. (7) the calculation of the integral (2) yields

$$\alpha_{\mathrm{ph}} \propto N_c N_v \left[\frac{E_c^2 \exp\left(\frac{E_x - E_g}{E_c}\right)}{\left(\frac{\gamma}{kT} - \frac{1}{E_c}\right)(E_c - E_v)} + \frac{E_v^2 \exp\left(\frac{E_x - E_g}{E_v}\right)}{\left(\frac{\gamma}{kT} - \frac{1}{E_v}\right)(E_v - E_c)} + \left(\frac{kT}{\gamma}\right)^2 \frac{\exp\left(\gamma\frac{E_x - E_g}{kT}\right)}{E_c E_v \left(\frac{\gamma}{kT} - \frac{1}{E_c}\right)\left(\frac{\gamma}{kT} - \frac{1}{E_v}\right)} \right]. \tag{4}$$

An important quantity for analysis of the effect of phonon-assisted absorption on the PL is the effective excitation energy $E_{\mathrm{eff}} = E_{\mathrm{ex}} + \langle E_{\mathrm{ph}} \rangle$, where $\langle E_{\mathrm{ph}} \rangle$ is the average energy gained from the lattice by an excited electron-hole pair. It follows from Eq. (1) that the expression for $\langle E_{\mathrm{ph}} \rangle$ can be written as $\langle E_{\mathrm{ph}} \rangle = -\partial \ln \alpha_{\mathrm{ph}} / \partial(\gamma/kT)$. The dependences of $E_{\mathrm{eff}}(E_x)$ on E_x calculated for several values of temperature using the parameters $E_v = 50$ meV, $E_c = 20$ meV, and $\gamma = 0.35$ are shown in Fig. 4. For $T < 100$ K we essentially have $E_{\mathrm{eff}} = E_x$, so that the effect of phonons is weak. Within the interval $150 < T < 250$ K the slope of the curves decreases rapidly with T which means that for fixed E_x the effective excitation energy rises sharply within this temperature interval. The smaller the value of E_x the larger the phonon-induced addition to the energy of an excited pair.

The value of $\gamma = 0.35$ was chosen because it provides the best fit to T_c as defined above. Although it is difficult to determine whether this value of γ is reasonable for *a*-Si:H, there is ample precedent for values of this magnitude in other semiconducting systems [13]. In particular, in trigonal Se, $\gamma \approx 0.4$ at 100 K. (In crystals γ is often temperature dependent, a fact we have ignored for simplicity in the present calculation.) The competition between the density of states and the Urbach exponents in Eq. (4)

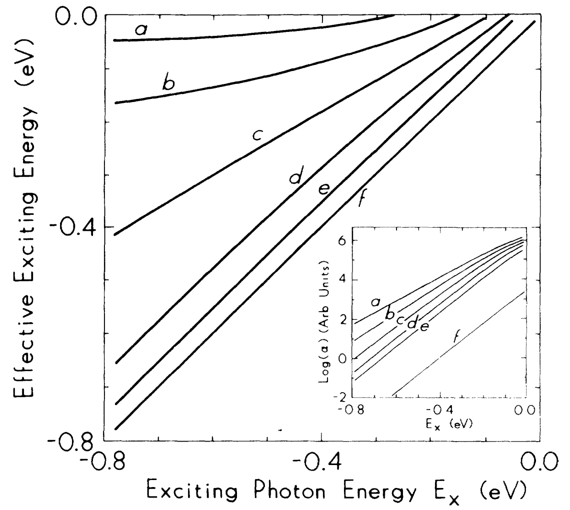

FIG. 4. Calculated E_{eff} as a function of E_x using parameters $E_c = 20$ meV, $E_v = 50$ meV, $\gamma = 0.35$. At temperatures of, curve *a*, 300 K; curve *b*, 250 K; curve *c*, 200 K; curve *d*, 150 K; curve *e*, 100 K; and curve *f*, 1 K. Inset: The calculated α. All values of E_{eff} and E_x are with respect to the energy gap.

results in a rapid crossover between the two regimes of absorption. This crossover occurs within a narrow interval of T. The decrease of quantum efficiency from 77 to 200 K for small excitation energies can be accounted for by the fact that at $T \sim 200$ K the carriers are effectively created in the shallow states and can reach at least some of the nonradiative centers.

If we assume $E_g = 1.9$ eV, then the excitation energy $E_x = 1.35$ eV corresponds to $E_{\text{eff}} = 1.65$ eV. For such an initial energy the carriers first thermalize and then recombine. As a result, the distribution of carriers in the tail does not depend on E_x, which explains why the curve for 220 K in Fig. 3 is flat. Note that for $T = 77$ K (when direct absorption predominates) the ratio of quantum efficiencies for different PL energies also does not depend on E_x for $E_x > 1.6$ eV (cf. 77 K curve in Fig. 3).

Phonon-assisted absorption should also be manifested in the dependence of photoconductivity on E_x. Indeed, if with small E_x the carriers are effectively excited close to the mobility edge, then they can be activated into the extended states and contribute to the photocurrent. The temperature dependence of the quantum efficiency of photocurrent in a reverse-biased *p-i-n* *a*-Si:H solar cell [14] is consistent with the present model. For $E_x = 1.35$ eV a rapid increase in η with T was observed [14] for $T > 180$ K.

Note that despite a dramatic change in the absorption mechanism within a narrow temperature interval, the energy dependence of the absorption coefficient, $\alpha_{\text{ph}}(E_x)$, does not change strongly with temperature. The numerical results for $\log\alpha_{\text{ph}}(E_x)$ calculated at different temperatures from Eq. (4) are shown in the inset to Fig. 4. It is seen that within the interval $0 < T < 300$ K the slope of the curves changes by $\sim 30\%$. The experimental values for this change have been reported to be between 10% and 25% over this temperature range [11,12,15]. Differences between the experimental results and the model predictions may be accounted for by the simplicity of the model used or by competing absorption processes at the lowest excitation energies, such as those through the midgap silicon "dangling-bond" states.

In conclusion, we have measured the PL in *a*-Si:H using E_x from 1.27 to 2.0 eV. The energy distribution probability of photoexcited carriers in the deep tail states was found to have a strong dependence on E_x at low temperatures. This dependence quickly disappears in a very narrow temperature interval of $150 < T < 200$ K. A phonon-assisted absorption model has been proposed to account for the experimental results.

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