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Recombination in *a*-Si:H: Defect luminescence

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A study of defect photoluminescence in *a*-Si:H is presented. In both doped and undoped samples we observe a broad defect-related transition peaking at 0.9 eV with a width of ~0.35 eV. The line shape, temperature dependence, and excitation energy dependence of this luminescence are described. The recombination is interpreted as a transition between an electron in a doubly occupied dangling bond, and a valence-band tail hole. We estimate that the electron trap depth is ~0.5 eV and involves a distortion energy of about 0.1 eV. The relation between the luminescence data and light-induced electron spin resonance is also discussed.

I. INTRODUCTION

There have been several recent investigations of photoluminescence in hydrogenated amorphous silicon (*a*-Si:H). Most studies conclude that photoluminescence in *a*-Si:H is dominated by radiative transitions between valence-band and conduction-band tail states,[1–5] although there are substantial differences in the detailed interpretation of the spectrum. The quantum efficiency of this band-edge luminescence depends on the density of defect states in the gap, which act as nonradiative centers such that luminescence is strongly quenched when the defect density exceeds about 10^{17} cm^{-3}.[6] The mechanism of nonradiative recombination at low temperatures is believed to be tunneling of the band tail electron into a neutral defect state.[4,6,7] In a previous publication[4] we tentatively identify this electron trap as the gap states denoted by E_x that are observed in field-effect measurements.

In addition to the band-edge luminescence, various other luminescence bands which evidently arise from recombination at localized states in the gap have been observed in *a*-Si:H. An example is an oxygen impurity luminescence band centered near 1.1 eV.[6] One property of this emission is that thermal quenching occurs at a lower temperature than the band-edge luminescence. The early studies of *a*-Si:H also identified luminescence at 0.8–0.9 eV and 1.0–1.1 eV in addition to band-edge luminescence at about 1.25 eV.[1] (The variation in the peak position apparently depended on the measurement temperature, and possibly the structure of the sample.) Both additional luminescence bands were found to quench at a higher temperature than the band-edge luminescence, and therefore presumably have a different origin from the oxygen luminescence. Although there have been no further reports of the band at 1.0–1.1 eV, the luminescence at 0.8–0.9 eV has been observed by others,[8,9] and is also the subject of this paper. Luminescence at this energy is found in *n*- and *p*-type *a*-Si:H at doping levels of about 10^{-3}, measured as the gas concentration of dopant in SiH_4.[8,9] Similar luminescence is also found in undoped samples, particularly after electron bombardment[10] and at high temperature.[11] One of the intentions of this paper is to show that the 0.8–0.9 eV luminescence observed in all these types of samples has a common origin, and is related to defect rather than impurity states. We find that this luminescence is observed when the defect density is ~10^{18} cm^{-3}. A substantially smaller defect density results in strong band-edge luminescence which masks any defect band, whereas a larger defect density completely quenches the luminescence. By studying the 0.9-eV luminescence band we obtain detailed information about the nature of defects in *a*-Si:H. Of particular interest are the determination of the electronic energy levels of the defect, the strength of the electron-phonon interaction at the defect, and the mechanisms of radiative and nonradiative recombination.

Various models for defect states in amorphous silicon have been proposed in the past. The earliest model, applied to unhydrogenated *a*-Si, was a dangling bond on a silicon atom, tacitly assumed to have a positive correlation energy.[12] Thus the dangling bond is normally neutral, and contains an unpaired electron, giving the large ESR spin density that is always observed at a *g*-value of 2.0055. The plasma deposition of *a*-Si:H results in a material with a much reduced spin density compared to evaporated material. However, localized states in the gap are still present, and are seen in field effect measurements.[13] Spear suggested that these originate from divacancylike voids characterized by having paired electrons, and therefore no net spin in their neutral state.[14] An alternative model of a spinless neutral defect was proposed recently by Adler.[15] Using a tight-binding approximation he showed that a twofold coordinated silicon defect had a lower energy than a dangling bond. Adler also suggested a second low-energy defect, comprising two adjacent dangling bonds which undergo charge transfer, giving a positive and negative pair. This defect is presumably closely related to the void reconstruction model suggested earlier by Connell and Pawlik.[16]

Models based on defects with a negative correlation energy have also been proposed for *a*-Si:H. Fisch and Licciardello[17] have proposed the three-center bond, whilst another type of negative *U* defect has been suggested by Elliot.[18] However in the latter model, the defects occur as neighboring charged pairs, therefore having different electronic properties from isolated negative *U* defects. The experimental evidence for negative *U* defect states was based largely on the observation of a strong light-induced ESR (LESR) effect in *a*-Si:H.[19] Recently, however, new experimental results show that LESR is closely related to the defect luminescence, and that both experiments strongly support the dangling bond model.[20] These results are summarized briefly in Sec. III. In Sec. II we describe the experimental results, giving the observations of defect luminescence, and the properties of samples in which it is observed. In Sec. III we discuss the electronic states of the defect and describe a detailed model to understand both luminescence and ESR data.

II. EXPERIMENTAL RESULTS

Luminescence measurements were performed using Kr^+ ion laser excitation and a cooled PbS detector. All the spectra are normalized for the response of the detection system. The weak luminescence from the defects required the use of wide slits in the spectrometer. The low resolution resulted in substantial broadening of the band-edge luminescence line, but no significant effect on the defect luminescence. The spectral resolution is indicated in the figures.

Figure 1 shows the luminescence spectra at three temperatures from an *n*-type sample of *a*-Si:H. The deposition conditions were 10% SiH_4 concentration in argon, 25 W rf power and a substrate temperature of 230 °C (denoted 10% 25 W 230 °C).[21] The dopant was 3×10^{-3} (gas concentration) of PH_3. The spectra clearly show two peaks. The high-energy peak at 1.35 eV is the usual band-edge luminescence, and the second peak near 0.9 eV is the luminescence band which is the subject of this paper. The relative temperature dependence of the two peaks emphasizes their distinct origins. The band-edge luminescence is quenched rapidly above ~80 K, and shifts strongly to lower energy. Both properties agree with previous observations of the band-edge luminescence. In contrast the defect luminescence has a much weaker thermal quenching, and has a small shift of the peak to low energy. Similar observations of band-edge and defect luminescence in *n*-type samples of about the same doping level have been reported by both Rehm *et al.*[8] and Austin *et al.*[9]

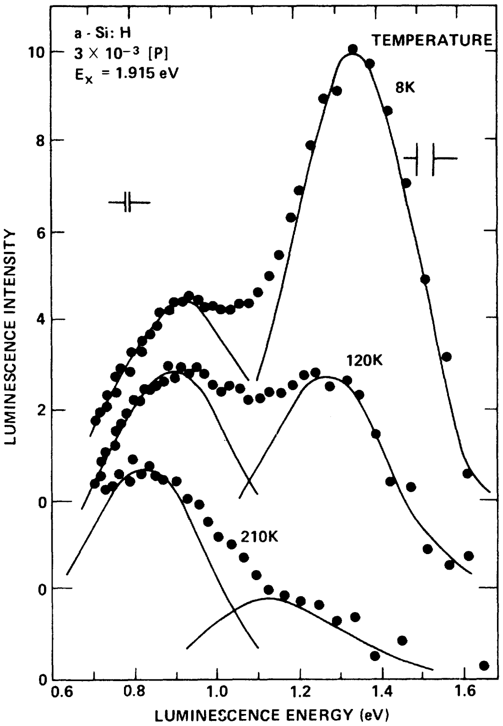

FIG. 1. Luminescence spectra of *n*-type *a*-Si:H at three temperatures, showing band-edge and defect luminescence.

Rehm *et al.*[8] also report a peak at 0.8 eV in *a*-Si:H doped 2×10^{-2} with boron. In Fig. 2 we show

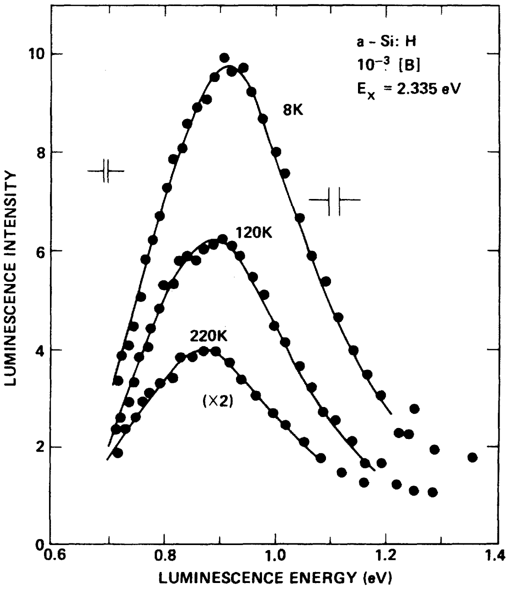

FIG. 2. Defect luminescence spectra from a *p*-type sample of *a*-Si:H.

luminescence spectra at different temperatures from a 5% 25 W 230 °C sample doped 10^{-3} with boron. We observe a single peak at 0.9 eV which is the same energy as the low-energy luminescence band of Fig. 1. However it is important to establish that this luminescence does not originate from band-edge transitions. This possibility exists because the position of the band-edge luminescence can vary a great deal and in some samples, particularly with a low quantum efficiency, it is observed as low as 1.1 eV.[6] Figure 3 shows the temperature dependence of the luminescence intensity of the 0.9 eV band in both the n- and p-type samples. The thermal quenching is very similar in the two samples, and is quite distinct from the much stronger thermal quenching of the band-edge luminescence. This result establishes that the 0.9-eV band in both samples has a common origin. The lower energy (0.8 eV) observed by Rehm *et al.*[8] probably does not represent a significant difference, and is most likely explained by a different sample composition with a smaller band gap.

The weak intensity of the defect luminescence only allows the observation of thermal quenching of about a factor of 30 in Fig. 3. Over this range, the data cannot be described by a single activation energy. Thermal quenching is usually described by a competition between a temperature-independent radiative rate P_r and a thermally activated nonradiative rate $P_{nr}\exp(-E/kT)$. The temperature dependence of the luminescence intensity is then given by

$$I(T)/I(0)=[1+(P_{nr}/P_r)\exp(-E/kT)]^{-1} \quad . \quad (1)$$

If we assume that a process of this type occurs with a temperature-dependent activation energy then, for the data near room temperature in Fig. 3, $P_{nr}/P_r \sim 10^3$. This result is interesting when compared to a similar analysis of the band-edge luminescence which yields $P_{nr}/P_r \sim 10^9$. The large difference indicates that either the radiative or nonradiative mechanism is quite different in the two cases.

Also shown in Fig. 3 is the temperature dependence of light induced ESR (LESR) in similar n- and p-type samples.[20] For these experiments, the samples were illuminated with light at 1.915 eV at an intensity of about 100 mW/cm^2. As reported previously,[19] the n-type sample has a single resonance at $g=2.0055$, while the p-type samples also has a broader resonance near $g=2.013$. We find that the temperature dependence of LESR in both cases agrees very closely with that of the defect luminescence, strongly indicating that the two measurements have a common origin. LESR in a-Si:H is discussed in more detail elsewhere.[20]

Figure 4 summarizes the temperature dependence of the peak position and the linewidth of the 0.9 eV luminescence in both n- and p-type samples. The larger uncertainties in the n-type sample result from the necessity of deconvolution. The two sets of data agree on the linewidth, and on the peak position except for some difference at the highest temperatures. The data also agree reasonably well with those of Austin *et al.*[9] (see Fig. 4). The linewidth of 0.35–0.4 eV is larger than the width of the band-edge luminescence (0.25–0.3 eV). However, the width shows no discernible temperature dependence, in contrast to the rapid increase above 150 K found in the band-edge luminescence.[4] We also find that the peak posi-

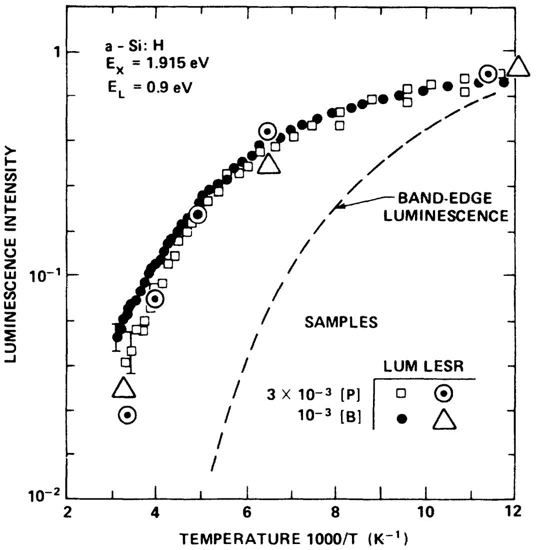

FIG. 3. Temperature dependence of the defect luminescence intensity compared to the LESR spin density, and to the band-edge luminescence intensity.

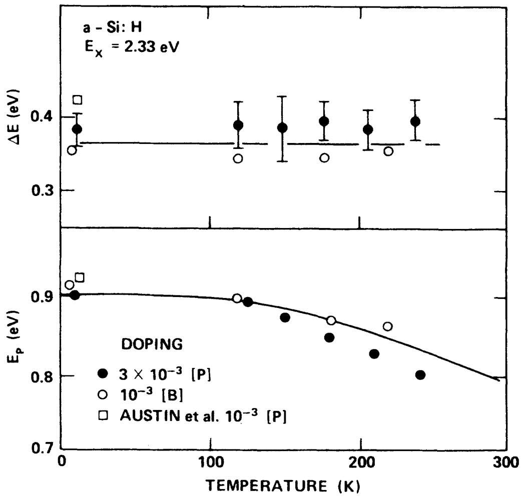

FIG. 4. Peak position and linewidth of defect luminescence between 10 and 250 K. Data from Ref. 9 are shown for comparison. The solid line in the lower figure represents the temperature shift of the band gap from Ref. 4.

tion roughly follows the shift of the band gap instead of the much larger shift seen in band-edge luminescence.

The luminescence intensity of the 0.9 eV peak is too weak to measure a complete excitation spectrum. However, Fig. 5 shows luminescence spectra of the *n*-type sample at three different excitation energies. It is seen that at the lowest energy the intensity of the band-edge luminescence is decreased by at least an order of magnitude relative to the 0.9 eV peak. The 0.9 eV peak is also weakly enhanced at high energy. However, this result is possibly due to the high excitation density decreasing the intensity of the band-edge luminescence. Also shown in Fig. 5 is the absorption edge of an undoped sample and an *n*-type sample.[22] These are room-temperature data shifted by 0.07 eV to higher energy to compensate for the temperature dependence of the band gap.[4] In the *n*-type sample the edge changes slope at 1.7 eV, evidently due to an extrinsic absorption band which is not present in low defect density undoped samples. The lowest excitation energy in the spectra of Fig. 5 is within this absorption tail. We therefore conclude that at least part of the extrinsic tail arises from absorption at the defect that gives 0.9 eV luminescence. On the other hand it is clear from Fig. 5 that the extrinsic absorption does not excite the band-edge luminescence, which is only generated by absorption above the onset of band-to-band transitions. This result provides further strong evidence that the 1.4 eV peak indeed originates from states at the band edges, rather than from extrinsic localized states in the gap.

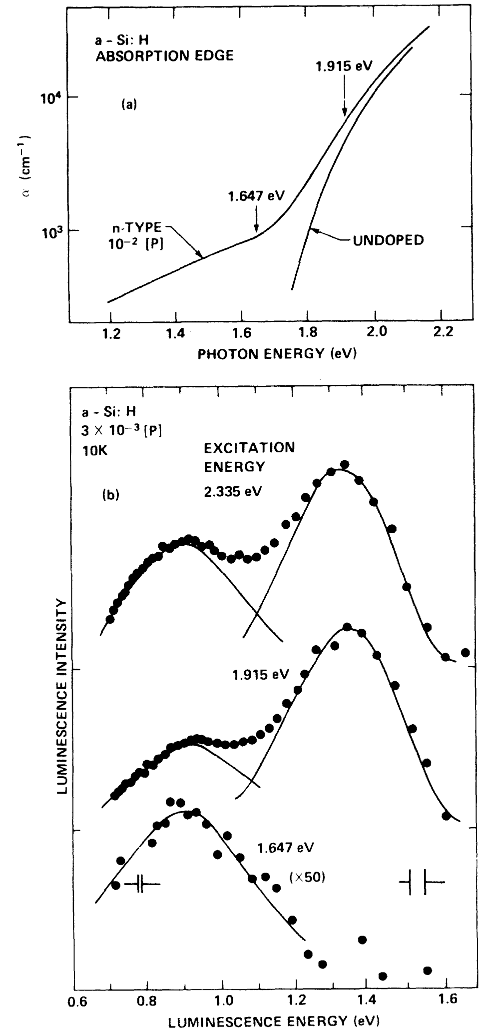

FIG. 5. (a) Absorption of undoped and *n*-type *a*-Si:H, showing the extrinsic absorption tail in the doped material. The data are from Ref. 22 and shifted 0.07 eV to low energy to account for the temperature dependence of the gap. (b) Luminescence spectra of *n*-type *a*-Si:H taken at different excitation energies. Note that excitation in the extrinsic absorption tail excites only the defect luminescence.

Since the same 0.9 eV luminescence band is observed in both *n*- and *p*-type *a*-Si:H, the recombination is clearly not specific to any one dopant and therefore can be attributed to defects. Thus similar luminescence might be anticipated in undoped samples of sufficient defect density. One problem is that such samples, for example deposited at low temperature, generally show band-edge luminescence shifted down to ~1.1 eV and broadened,[6] thereby masking any peak at 0.9 eV. However, Engemann and Fischer[1] and Engemann,[11] have shown that the luminescence is present by measuring spectra at elevated temperatures.

Electron or ion bombardment introduces a large defect density as observed by ESR, and quenches the luminescence, while annealing removes the defects.[23] In a separate study it is shown that the 0.9 eV defect luminescence is observed in electron bombarded samples.[10] A typical spectrum is shown in Fig. 6. The

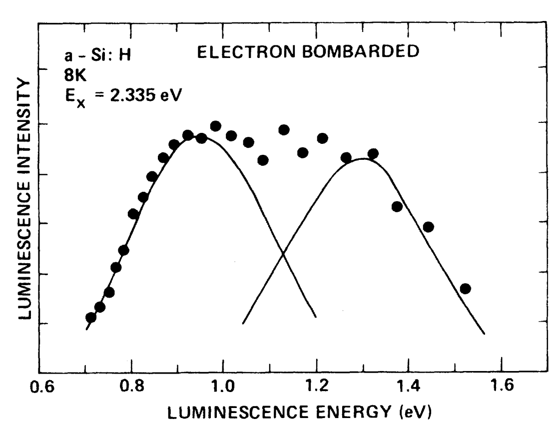

FIG. 6. Luminescence spectrum of an electron bombarded, undoped *a*-Si:H sample, showing 0.9 eV defect band (from Ref. 10).

0.9 eV luminescence is observed in samples with spin density between $\sim 3\times 10^{17}$ and 3×10^{18} cm^{-3}. Within this range, the ESR spectrum has a g value of 2.0055 and a width of 7.0–7.5 G, which is identical to that found in unbombarded *a*-Si:H, and other forms of amorphous Si. The defect luminescence intensity increased monotonically with spin density up to about 10^{18} cm^{-3} while higher spin densities quench all the luminescence. The other studies of undoped *a*-Si:H also find that the defect luminescence is strongest in samples where the band-edge luminescence is weak indicating a fairly large spin density. Another common feature of all these observations is the weakness of the defect luminescence. The luminescence is never more than 1% of the maximum intensity of band-edge luminescence, and is more typically 0.1%. Evidently there is an efficient nonradiative recombination path.

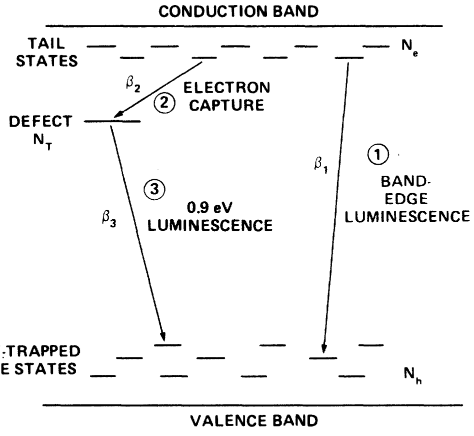

FIG. 7. Schematic recombination diagram for defect and band-edge luminescence.

III. DISCUSSION

A. Origin of 0.9 eV peak

The observation of identical luminescence at 0.9 eV in both *n*- and *p*-type samples demonstrates that impurity states of phosphorous or boron are not specifically involved. The conclusion is confirmed by the observation of the luminescence band in some undoped *a*-Si:H samples. Instead the 0.9 eV luminescence is generally associated with the ESR line at $g=2.0055$ and a spin density of about 10^{18} cm^{-3}. Many studies have shown that this ESR signal is from a primary defect evident in all forms of amorphous silicon.[12,24] This defect is also known to be important in recombination, acting as a nonradiative center for band-edge luminescence.[6] It is argued that the rate limiting process for band-edge nonradiative recombination is the tunneling of an electron to the singly occupied defect which acts as an electron trap. The natural explanation of the 0.9 eV luminescence is therefore the subsequent recombination of the trapped electron with a hole in the valence band.[10] A schematic diagram is shown in Fig. 7. We expect that the recombination mechanism is radiative tunneling, as it is for band-edge luminescence, although lifetime measurements have not been performed to test this assertion. (In view of the low quantum efficiency it is doubtful whether lifetime measurements would give much information about the radiative rate.)

The recombination model of Fig. 7 is strongly supported by recent combined measurements of luminescence and LESR.[20] The 30 K LESR spectra are shown in Fig. 8. In all cases the equilibrium ESR signal is negligible. The defect resonance at $g=2.0055$ is observed in both *n*- and *p*-type material while the *p*-type material also shows a broad line at $g=2.013$, known to be associated with hole states.[24] The LESR spectrum of the undoped sample contains the same broad line and also a narrow resonance with a distinctly different shape from the defect line (which is attributed to conduction-band tail electrons). From the temperature dependence (Fig. 3 and Ref. 20) it was established that LESR observed the same excited states as the luminescence in the three types of sample. These measurements therefore show that the 0.9 eV luminescence indeed involves the $g=2.0055$ defect and also the same hole states that are involved in band-edge luminescence, as indicated in Fig. 7.

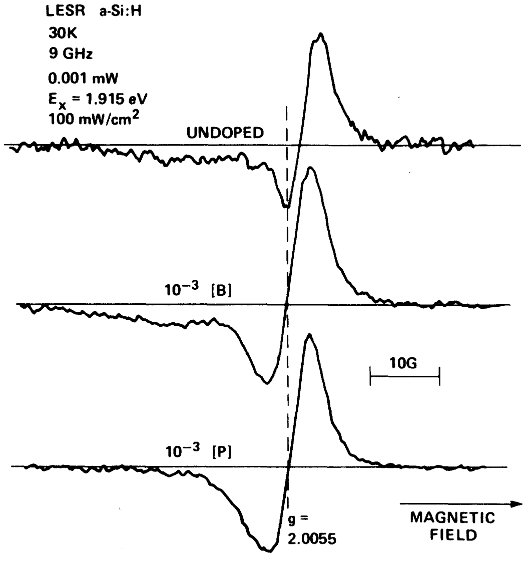

FIG. 8. Light induced ESR spectra of doped and undoped *a*-Si:H (from Ref. 20).

B. Defect energy-level analysis

Based on the line shape and position of the luminescence we can estimate the energy levels involved in the recombination. This procedure is rather approximate because it is not yet possible to separate unambiguously the contribution to the linewidth of the electron-phonon interaction and the distribution of zero-phonon energies. However, if we assume that the linewidth ΔE originates entirely from the electron-phonon coupling then

$$\Delta E = 1.667\sigma = 1.667(2W_p\hbar\omega_0)^{1/2} \quad . \tag{2}$$

ΔE is the full width at half height of the spectrum as given in Fig. 4, σ is the Gaussian linewidth parameter $\exp[-(E/\sigma)^2]$, W_p is the distortion energy, and $\hbar\omega_0$ is the appropriate phonon energy. Setting $\hbar\omega_0 = 0.06$ eV, which is the largest phonon energy of the silicon lattice, gives $W_p \sim 0.4$ eV. The zero-phonon energy E_0 of the transition is given by $E_L + W_p$, where E_L is the energy of the luminescence peak. Hence, E_0 is about 1.3 eV. Previously we have estimated the zero-phonon energy of the band-edge luminescence to be $\sim$1.7 eV,[3] indicating that the electron trap depth is about 0.4 eV below the band tail.

The analysis is modified if part of the line broadening of the luminescence is due to a distribution of zero-phonon energies. Assuming a Gaussian distribution of width, σ_D gives

$$\sigma^2 = \sigma_{\text{ep}}^2 + \sigma_D^2 \quad , \tag{3}$$

where σ_{ep} is the contribution from the electron-phonon coupling. According to our model, the 0.9 eV recombination involves similar self-trapped hole states that cause most of the line broadening of the band-edge luminescence. Thus we expect a minimum value of σ_{ep} of $\sim$0.16 eV and therefore from Eq. (3), a maximum value of σ_D of $\sim$0.16 eV. This assumption leads to a mean zero-phonon energy of 1.1 eV, and therefore an electron trap depth of 0.6 eV. However, in practice we expect that any trap of this depth would have some electron-phonon coupling associated with it.

Field effect data provide some specific information about trapping levels to compare with the luminescence data. Spear and co-workers observe an electron trap denoted E_x with a binding energy of 0.4 eV below the mobility edge and with a disorder broadening that is approximately given by $\sigma_D \sim 0.08$ eV.[13] The electron trap originates from a defect level, and apparently correlates with the spin density, in that both increase as the deposition substrate temperature decreases. We therefore tentatively associate the E_x level with the electron trap in the recombination. The trap depth is in reasonable agreement with our estimates above from the luminescence, and from the fairly small disorder broadening of the level given by the field effect data we roughly estimate a distortion energy in the range 0.05–0.15 eV. Field effect[13] and photoemission data[25] also identify localized states above the valence band. However, the density of states is much larger than the defect density as measured by ESR,[4,6] and elsewhere we have suggested that these states are self-trapped holes[4] (see Sec. III C).

The weak intensity of the defect luminescence indicates an effective nonradiative recombination mechanism. At present we have no clear indication of this mechanism, and several alternatives are feasible. Auger recombination is possible because of the extra electron in the neutral defect. Alternatively there may be multiphonon transitions—possibly involving the high-energy Si-H phonon. We expect that the quenching of the luminescence at high doping levels is explained by a high density of states allowing rapid thermalization of carriers to the Fermi energy by tunneling. An alternative model involving internal electric fields[26] is apparently not consistent with the luminescence decay, as discussed in Refs. 7 and 9.

The origin of the temperature quenching is also not yet clear. Thermal excitation of one or other carriers to the band edges does not seem a likely mechanism since the observed activation energy of $\sim$100 meV is too low, and the temperature dependence is independent of the sign of the majority carrier. Thermally activated hopping between defects is a possible mechanism. An alternative is activation over the crossing point of the configurational coordinate diagram for the recombination. This process should require an energy of $E_L^2/4W_p$,[27] which is $\sim$0.5 eV. However, it is found in other systems that below room temperature the observed activation energy is much lower than the calculated value.

C. Model for recombination in *a*-Si:H

Figure 9 summarizes our recombination model based on the above discussion, and on data for band-edge luminescence published elsewhere.[4] The energies are uncertain to about 0.1 eV owing to the broadness of the spectral features. The effect of the electron-phonon coupling is shown in Fig. 9 for the electron trap, and for the band tail holes as the separation between the dotted and full curves. The main features of the model follow, and the remainder of the discussion is based on this model:

(i) The dominant native defect is a dangling band which is singly occupied when neutral, giving ESR at $g = 2.0055$. The neutral defect traps an electron with a binding energy of 0.4–0.6 eV. The binding energy for a hole is not known. We do not completely exclude other defects, but only assert that this defect dominates.

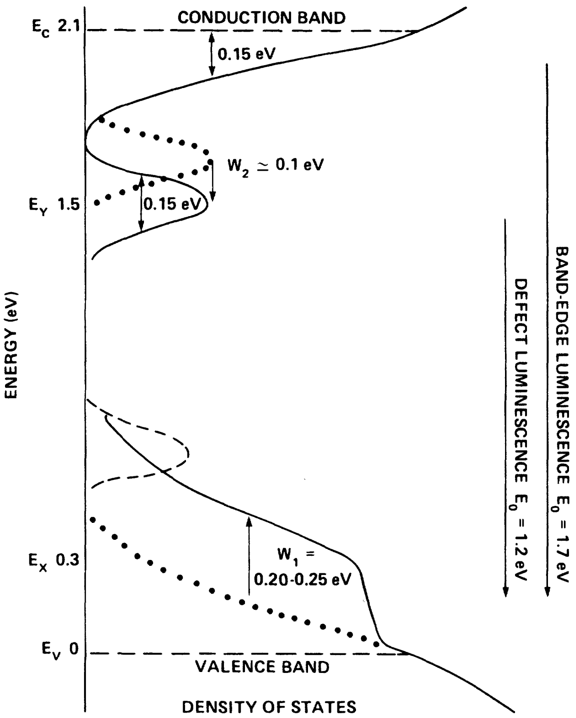

FIG. 9. Schematic energy-level diagram proposed for *a*-Si:H as described in the text. The separation between the full curves and the dotted curves represents the effect of lattice distortion. The energies of the two luminescence transitions refer to zero-phonon values.

(ii) Band tail holes are self-trapped in *a*-Si:H. Self-trapping is assumed to occur only at sites for which a rigid-lattice model would give localized tail states. These sites are characterized by a large disorder potential that arises through local strain introduced by the topological constraints of the lattice. From luminescence experiments we find the self-trapping energy W_h to be 0.2–0.25 eV and anticipate a density of states of 10^{19}–10^{20} cm^{-3}. We have suggested that self-trapped holes form the band E_Y found in field effect measurements. We also suggest that self-trapped holes are the origin of the 20 G ESR line at $g = 2.013$, observed in *p*-type samples both in the dark and with illumination.[20]

(iii) Band tail electrons do not have a strong electron-phonon coupling. Instead they occupy shallow tail states (binding energy ≤ 0.15 eV), and have an average Bohr radius of 10–12 Å.

(iv) Band-edge luminescence is the radiative recombination of band tail electrons and self-trapped band tail holes. At low temperature the recombination is geminate except at moderately high excitation intensities. Nonradiative recombination is by tunneling of the electron into a defect state.

(v) Defect luminescence is the recombination of an electron trapped at a defect, and a self-trapped hole.

D. Recombination kinetics and light induced ESR

One surprising feature of the defect luminescence is that the transition is identical in both *n*-type and *p*-type material, as shown by Figs. 1–4. Another result that also requires further explanation is that the LESR spectra are different in the two doped samples. Although both have the $g = 2.0055$ defect resonance, the *p*-type sample contains the hole resonance, while the *n*-type sample does not. (It is not possible to determine unambiguously whether the *n*-type sample also contains the narrow conduction-band tail resonance.) We believe that both these results can be explained by the different recombination kinetics that must apply in samples of different doping. At present, because of the weak defect luminescence intensity, we have no decay data to provide information about the recombination, so the following discussion is somewhat speculative. Nevertheless, it is included to show that a reasonable model can indeed explain the data. In undoped *a*-Si:H with low defect density the recombination is known to be geminate provided that the electron-hole pair density does not exceed about 10^{18} cm^{-3}.[4] (Geminate refers to a recombination event in which the electron and hole can be identified as the same particles that were created in the corresponding photogeneration process.) In undoped samples which show defect luminescence we anticipate that geminate recombination will occur for virtually all experimental conditions, because the dominance of nonradiative transitions ensures fast recombination,[4,7] and consequently, a low density of excited electron-hole pairs. The recombination process is therefore expected to be one of band-to-band excitation of an electron-hole pair followed by tunneling of the electron into the defect and then more or less immediate recombination with the hole, with the last step giving 0.9 eV luminescence. The resulting LESR effect will depend on the relative rates of the two transitions. If the second process, recombination with a hole, is sufficiently fast, then the defect occupancy is hardly changed, and there will be no LESR. We assume this situation to occur since no defect LESR is observed in undoped samples.[20] (Only LESR from band tail states is found.) Other evidence also indicates a fast recombination rate for this transition. First, the weak 0.9 eV luminescence intensity suggests that rapid nonradiative transitions dominate. Second, in studies of band-edge luminescence it is found that the rate limiting step in the nonradiative transition is tunneling of the electrons into the neutral defect.[4,7] There is no indication that this process saturates a high intensity, even in samples where the defect density is quite low.[3] Thus, we must conclude that the defects remain predominantly neutral even during photoexcitation, and therefore that the recombination of the trapped electron with holes is sufficiently fast.

The recombination kinetics of doped samples is expected to be quite different. At doping levels of about 10^{-3} when the 0.9 eV band is observed, the excess carrier concentration is greater than 10^{18} cm^{-3} (assuming at least 10% of the dopant atoms are electrically active).[28] Recombination is therefore unlikely to be geminate.[4] Furthermore, in the absence of illumination the defects will be charged, since the Fermi energy is close to one or other band edge. Consider first n-type samples. Holes are the minority carrier and therefore limit the recombination. Photoexcited holes can readily recombine with the large density of trapped electrons, thereby giving the defect luminescence and at the same time both quenching the band-edge luminescence, because there are no available holes, and emptying the electron traps, giving LESR at $g=2.0055$. These traps subsequently capture electrons from the valence band. We can give a simplified analysis of the recombination assuming, for convenience, that the equilibrium Fermi energy lies between the defects and the band tails. This approximately corresponds to samples of 10^{-3} doping.[29] If the photogeneration rate is G, the steady-state recombination is given by

$$G=\beta_2 N_e N_t^0=\beta_3 N_h N_t^- \tag{4}$$

and

$$N_t^0=N_e-N_h \ . \tag{5}$$

N_e and N_h are the band tail electron and hole density, and N_t^0 and N_t^- are the densities of neutral (singly occupied) and negative (doubly occupied) defects. β_2 and β_3 are the mean recombination rates for process 2 and 3 of Fig. 7. We ignore process 1 because we are concerned with samples where the band-edge luminescence is very weak. From Eq. (4)

$$N_e/N_h=\beta_3 N_t^-/\beta_2 N_t^0 \ . \tag{6}$$

In the absence of optical excitation $N_t^0=0$, and therefore during excitation, except at high intensity, we expect that $N_t^0 \ll N_t^-$. Since we also argue above that $\beta_3>\beta_2$, it follows from Eqs. (5) and (6) that

$$N_e \gg N_h \tag{7}$$

and

$$N_t^0 \simeq N_e \ . \tag{8}$$

Thus optical excitation generates neutral defects and band tail electrons, but only a very small density of band tail holes. This result therefore explains the absence of the broad resonance in LESR of n-type material (Fig. 8), and the low density of holes explains the quenching of band-edge luminescence. Finally, the opposite behavior of photoconductivity, which increases rapidly in n-type materials,[30] can also be understood. Photoconductivity is insensitive to the valence-band hole density because transport is by electrons, and is larger than in undoped material because at low light intensities, the available electron trap density N_t^0 is a small fraction of the total defect density. This model predicts bimolecular recombination as observed.[30]

In p-type material, electrons are the minority carriers. When the doping is sufficient to empty all the defect states, then the photoexcited electrons must first tunnel into the positive, rather than the neutral defect. If the band tail holes can readily be captured by the resulting neutral defect, then the recombination will not give the 0.9 eV luminescence band according to the model of Fig. 7. Instead, to account for the experimental data, we must assume that hole capture is in fact very slow. We suggest that this is a reasonable assumption in view of our model that band tail hole states are self-trapped, and therefore have a small Bohr radius for tunneling. The result of this assumption is that the capture of electrons by positive defects rapidly saturates, the defects become singly occupied, and recombination can then proceed by the capture of an electron by tunneling, followed by radiative capture of a hole, as in Fig. 7. A simple analysis of the recombination, similar to that for the n-type material yields

$$N_h \gg N_e \tag{9}$$

and

$$N_h \simeq N_t^0 \ . \tag{10}$$

Thus, both the hole resonance and the defect resonance are predicted to occur in LESR in p-type material, in agreement with the observations (Fig. 8).

Summarizing this discussion, we are suggesting that in both doped and undoped material, the defects are predominantly neutral during illumination. The 0.9 eV luminescence then arises from the tunneling of a conduction-band tail electron into a neutral defect, and its radiative recombination with a band tail self-trapped hole. The luminescence mechanism is independent of the doping, in agreement with observations.

IV. ALTERNATIVE DEFECT MODELS

In this section we briefly discuss the possible applicability of defects other than dangling bonds to the luminescence data. The first point to note is that our conclusion that dangling bonds dominate,[20] does not completely exclude defects of another type. Indeed, in some bombarded and annealed a-Si:H samples, there is specific evidence of spinless defects.[10,31] Furthermore, the correlation of luminescence intensity with spin density in as-deposited samples shows substantial scatter in the data, which may be explained by a small variable density of spinless centers. ESR measurements have also demonstrated that in the various forms of a-Si, the spin density is not a unique measure of the electronic states. For example, Voget-Grote *et al.*[32] report that in samples with the same spin density of 3×10^{19} cm^{-3}, the hopping conductivity at 200 K can vary by 8 orders of magnitude, indicating large changes in the density of states at the Fermi energy. Of all the samples measured, unbombarded *a*-Si:H had the lowest conductivity. One interpretation of the variation is that the additional states are the paired electrons associated with reconstructed atoms on void surfaces. Whatever the origin, these results again indicate that the plasma deposited material has the smallest density of spinless defects.

It is of interest to determine to what extent defects other than dangling bonds can account for luminescence and other data. One class of defects are those with a negative correlation energy (U). Models developed for chalcogenide glasses have shown that such defects have the characteristic properties of diamagnetism, a pinned Fermi energy, trap-limited transport of only one carrier, and a large electron-phonon interaction.[33] The three-center bond described by Fisch and Licciardello[17] should have all these properties, whereas in fact none can be confirmed. It is well known that the Fermi energy in *a*-Si:H (Ref. 1) is unpinned[14,29] and that transport of both carriers is observed.[14,34] Furthermore a spin density of 10^{16} cm^{-3} or greater is usually present.[6] Finally the evidence from luminescence is that electrons localized in either band tail states or at defects do not have a large electron-phonon coupling,[4] as Fisch and Licciardello postulate.

An entirely separate question, worthy of brief consideration, is whether the band tail hole states could have a negative U. This possibility exists because holes are apparently self-trapped with a substantial distortion energy. However, we have no estimate of the Coulomb repulsion energy. Such a model would not pin the Fermi energy in undoped material because in equilibrium all the hole states are empty. However, E_F would be pinned in *p*-type material, and indeed it has not proved possible to move the Fermi energy close to the valence-band edge.[28] Thus, although the luminescence data do not provide any specific evidence for negative U hole states, it is not in conflict with the results.

The second class of spinless defects are those with a positive U. Possible examples are the divacancy, or the twofold coordinated Si atom postulated by Adler.[15] In the absence of *a priori* knowledge of the energy levels of the various defects, the only feature that readily distinguishes these defects from dangling bonds are the spin properties. We have already shown that the observed correlation between luminescence intensity and spin density cannot easily be explained by defects other than dangling bonds.[20] Furthermore, the doping dependence of ESR also does not support a model of spinless defects. This model predicts that the spin density increases with doping because additional electrons or holes on the defect will be unpaired. For the same reason the undoped material should give the largest light induced ESR signal because this allows the maximum density of singly occupied defects to be created. In fact, both predictions are directly opposite to the observed results.[19,20]

V. SUMMARY

0.9 eV luminescence has been studied in both *n*- and *p*-type *a*-Si:H samples. We interpret the emission as the radiative recombination of an electron trapped in a doubly occupied dangling bond with a self-trapped valence-band tail hole. Based on the linewidth and the peak energy of the luminescence, we estimate that the electron trap depth is 0.5 ±0.1 eV below the conduction band, and that the defect has a relatively small distribution in energy of 0.1 ±0.05 eV. These values are consistent with the trap being the level E_x observed in field effect measurements.

The luminescence data are related to light induced ESR measurements, in that the same excited states are observed in both experiments. We discuss a model for the recombination kinetics in doped and undoped material, and show that a detailed explanation of both sets of experimental data results.

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