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Radiative recombination at dangling bonds in *a*-Si:H

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New time-resolved luminescence measurements in annealed *a*-Si:H films confirm that the low-energy luminescence band at 0.7 eV represents radiative recombination at dangling-bond defects. A simple quantitative model is presented based on recombination between an electron trapped in a conduction–band-tail state and a hole trapped at a dangling bond which accounts for the optical and optically detected magnetic resonance results.

In addition to the broad main luminescence band at 1.3–1.4 eV, there have been numerous observations of an additional band in the 0.7–0.9-eV region in doped,[1–3] annealed,[4] and electron- or ion-bombarded (Ref. 5) *a*-Si:H. In annealed and bombarded materials, this band is narrower and has been found to increase with dangling-bond (DB) densities below $\sim 10^{18}$ cm^{-3} and to decrease at higher densities. Some authors[4,5] have suggested that it may arise from radiative recombination at the DB itself, but no specific mechanism was proposed. On the other hand, optically detected magnetic resonance (ODMR) measurements in annealed films[6] have revealed that the DB resonance is active only as a quenching signal in this band. This was taken to imply that the DB acts only as a nonradiative center and that some other defect produced along with the DB must be responsible for the photoluminescence (PL). In this Rapid Communication we present new evidence which confirms the role of DB as a radiative center, and propose a specific quantitative model which reconciles the optical and ODMR results.

For these studies a set of identical 1.4-μm-thick *a*-Si:H films were grown simultaneously on roughened quartz substrates by plasma deposition of silane, under conditions known to produce optimal materials.[7,8] Each of the films was subsequently annealed in vacuum for 20 min at a temperature in the range 300 to 600 °C. Annealing evolves hydrogen and creates dangling-bond defects. Optical measurements including absorption, cw luminescence, time-resolved luminescence, and Raman scattering were performed on these films, and the optical properties correlated with hydrogen content and spin density, N_s. A complete account of these results will be published elsewhere.[8]

We focus here on the luminescence and ESR measurements which provide the basis for modeling the DB as a radiative center. The cw luminescence spectra were excited with the 5145-Å line of an argon-ion laser and detected with cooled Ge and InAs photodiodes using lock-in detection. The spectra were corrected for the system response. Pulsed PL measurements were taken with 15-ns excitation pulses from a doubled Nd:yttrium aluminum garnet (YAG) laser (5320 Å) and broadband Ge photodiode detection using interference filters to isolate the two bands. For both cw and pulsed PL measurements the samples were cooled to 15 K in a temperature-controlled flowing-He-gas optical cryostat. The spin signal was measured at room temperature with a Varian E-4 spectrometer.

The progression of the cw luminescence with annealing temperature is shown in Fig. 1. The main luminescence band, peaking at ~ 1.35 eV in the as grown material, is monotonically quenched with annealing, and shifts to

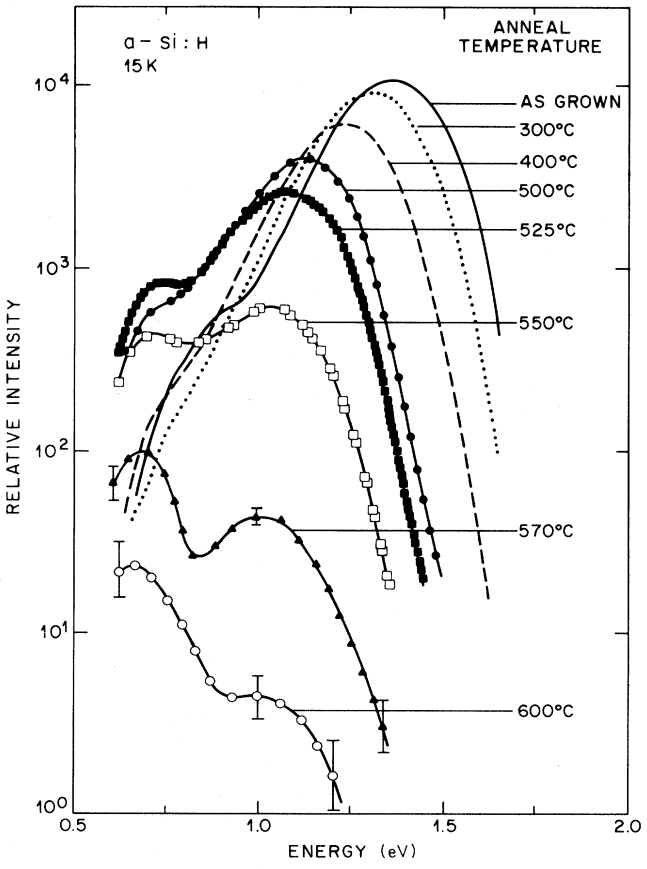

FIG. 1. cw luminescence spectra as a function of annealing temperature.

lower-energy tracking the observed shift of the absorption edge.[8] An additional narrower band at ~ 0.7 eV is seen first to grow in absolute intensity with low-temperature annealing, and then to quench at higher temperatures. The peak position of this band remains approximately constant.

The decay of the spectrally integrated intensity of both PL bands[8] reveals that quenching occurs in two steps on very different time scales. The first loss occurs in a time scale faster than our 15-ns resolution. Subnanosecond experiments[9] have indicated that the early time-quenching process is extremely rapid, < 100 ps, and most likely due to the initial trapping of some of the mobile carriers in deep defect states by a process of multiphonon emission. The quenching at later times, ≥ 1 μs, which dominates the loss in cw quantum efficiency at large N_s, has generally been associated with nonradiative tunneling from band-tail states to DB states.[3] We monitor the effects of the fast quenching process by measuring the spectrally integrated luminescence intensity at a delay of 100 ns after pulsed excitation. The intensities of the two bands at 100 ns, along with the cw intensities, are shown in Fig. 2. The 100-ns results follow a pattern similar to those noted for the cw data; the main band signal falls monotonically, while that of the 0.7-eV band first rises and then falls. When the ratio of the intensity in the 0.7-eV band to that in the main band is plotted versus spin density, N_s, we find a simple linear relationship which holds over three decades, as shown in Fig. 3. This relationship holds both for the cw data which is absolute, and for the 100-ns data which is normalized to the same magnitude. This implies that the ratio remains constant over all time scales, and consequently that the later quenching mechanism affects the two bands in the same manner.

The model we propose to explain all these observations requires the consideration of only two types of states: tail states of the conduction and valence bands, and dangling-bond defects, T_3^-, T_3^0, and T_3^+. We assume that in these undoped materials at low temperatures the singly occupied state, T_3^0, is the predominant charge state prior to photoexcitation. We propose that the 0.7-eV band is the result of radiative recombination of a photoexcited pair with the electron (e) trapped in a conduction-band-tail state, and the hole (h) trapped at a DB, i.e., a T_3^+ state.

First we consider the early time mechanisms that initially populate the radiative and nonradiative states. The mobile photoexcited pairs can become trapped in four possible configurations. The e and h can both be trapped in band-tail states, both at DB states, the e at a DB and the h in a band-tail state, and vice versa. An electron trapped in a band-tail state may subsequently recombine with a hole also in a band-tail state leading to the luminescence in the main

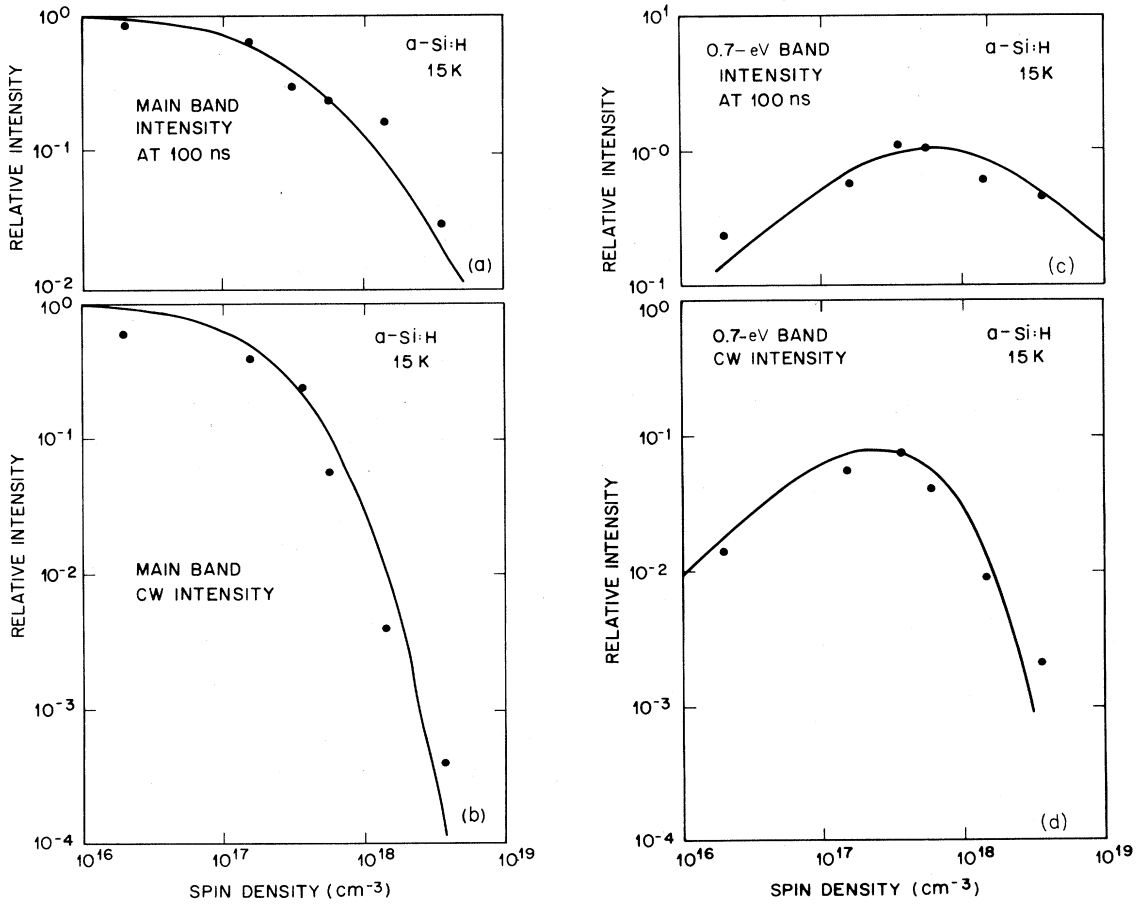

FIG. 2. PL intensity of the main luminescence band vs spin density (a) at 100-ns delay after pulsed excitation, and (b) cw. Equivalent data for the 0.7-eV band attributed to radiative recombination at dangling bonds are shown in parts (c) and (d). The 100-ns data are spectrally integrated; the cw data represent the signal at the spectral peak. The solid lines represent fits to the model described in the text.

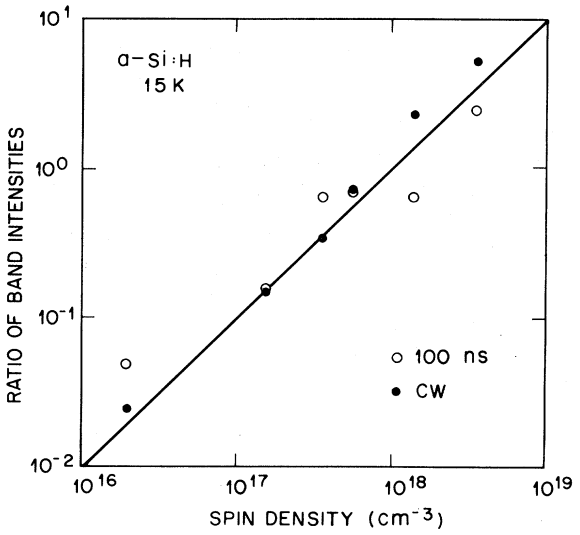

FIG. 3. Ratio of the intensity in the 0.7-eV band to that in the main PL band. The open circles represent the ratio of the spectrally integrated intensities 100 ns after pulsed excitation, closed circles the ratio of the cw intensities at the spectral peaks.

band, or with a hole at a DB resulting in luminescence in the 0.7-eV DB band. If the electron is initially captured at a DB, then no subsequent emission can occur within the detection range of these experiments because the energy separation from the valence-band tail is too small, especially in low hydrogen content materials such as the annealed films studied here.[10,11]

Branching ratios for these four possible configurations may be expressed quite simply. We define

$$\alpha^e \equiv \frac{\nu_s^e}{\nu_{\rm BT}^e N_{\rm BT}^e} \quad , \quad \alpha^h \equiv \frac{\nu_s^h}{\nu_{\rm BT}^h N_{\rm BT}^h} \quad ,$$

where ν_s refers to the capture rate at a dangling bond, $\nu_{\rm BT}$ to some average capture rate at a band-tail state, $N_{\rm BT}$ to the number of band-tail states, and the superscripts to electrons and holes. We make the assumption that $N_{\rm BT}$ does not change grossly over this range of annealing temperatures and spin densities, and that the excitation density is held low enough not to saturate either the band-tail or DB states. Then the fraction of photoexcited pairs trapped in states leading to luminescence in the main and DB bands are given by

$$f(\text{main band}) \sim \frac{1}{(1+\alpha^e N_s)(1+\alpha^h N_s)} \quad ;$$

$$f(0.7\text{-eV band}) \sim \frac{\alpha^h N_s}{(1+\alpha^e N_s)(1+\alpha^h N_s)} \quad .$$

Thus the ratio of the two populations is simply proportional to N_s. Ignoring small factors due to differences in spectral line shapes, the fit shown in Fig. 3 yields $\alpha^h \sim 10^{-18}$ cm^3. In addition, the branching fraction predicts a rise and subsequent fall of the 100-ns DB band intensity with N_S. The peak intensity occurs at $N_s = (\alpha^e \alpha^h)^{-1/2}$, and the fit to the data shown in Fig. 2(c) provides a value for $\alpha^e \sim 3\times 10^{-18}$ cm^3. A test of this picture of the early time mechanism lies in the use of only these two parameters to self-consistently fit the quenching curves of both bands as well as the absolute ratio of the two curves. The three fits, which are shown as solid lines in Figs. 2(a), 2(c), and 3, clearly meet this test.

We turn now to the long-time quenching processes of these two bands. Both radiative mechanisms depend on the presence of an e trapped in a conduction-band-tail state, and the dominant quenching path is most likely the tunneling or diffusing of this e to a nearby DB state. Since the distribution of rates for the two radiative recombinations are found to be comparable,[8] this quenching process will affect the cw quantum efficiency of the two bands in a similar manner. The hole may also diffuse or tunnel, but it is thought to be more localized and less mobile than the electron, resulting in a lower rate. Using the model of Street, Knights, and Biegelsen[12] in which pairs excited within a critical distance, R_c, of a DB recombine by such a nonradiative tunneling mechanism, we convolute this additional loss factor $\exp(-\frac{4}{3}\pi R_c^3 N_s)$ with the earlier branching ratio to fit the cw data. Excellent fits to the intensity in both bands are shown in Figs. 2(b) and 2(d), with the single additional parameter, $R_c = 70$ Å.

The spectral data also tend to reinforce this picture. Photoemission data have shown that the valence band moves closer to the DB levels as hydrogen is evolved, while the spacing of the conduction band and DB levels remains about constant.[11] Thus we would expect luminescence between conduction and valence-band-tail states to track the shrinking absorption gap, while luminescence between conduction-band-tail states and the DB level remains stationary, as observed. The narrowness of the 0.7-eV band in comparison to the main PL band, coupled with the observation of PL in the same spectral region in microcrystalline materials,[13] lead one to speculate that the majority of the DB sites may lie on internal surfaces as suggested by Phillips,[14] and that $2R_c$ may represent the average spacing between these surfaces. The band at 0.8–0.9 eV observed in doped samples[1-3] is not generally narrower than the main band, and there have been reports of associated enhancing ODMR signals[15] at the DB resonance. Consequently it is possible that this band (or bands) may not have the same origin.

We note that this model is completely consistent with the previously reported ODMR data in annealed films[6] which was interpreted to preclude the DB as the source of this PL band. Since the radiative transition does not involve a singly occupied DB state, but rather an e in a conduction-band-tail state and an unoccupied DB state which has no spin, the recombination is spin independent and no enhancing signal should be observed at the T_3^0 resonance. Only the quenching signal due to the spin-dependent long-time-scale tunneling of the e to a nearby DB would be observed in ODMR, consistent with the literature.[6] Since our model identifies fast trapping rather than fast recombination as the initial loss mechanism, it is also consistent with photoinduced absorption results[16] which rule out any fast recombination processes. A comparison with transport measurements finds the relative sizes of α^e and α^h to be consistent with time-of-flight measurements,[17,18] but the absolute magnitudes determined here are considerably larger. Such differences between optical and transport results are common in these materials, but as yet unexplained.

In conclusion, we have presented new time-resolved luminescence data in annealed a-Si:H films that confirm the assignment of the low-energy luminescence band to radia-

tive recombination at dangling-bond defects. A simple quantitative model based on this assignment is able to fit all the luminescence and ODMR results.

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