

Temperature dependence of photoluminescence in hydrogenated amorphous silicon

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The temperature dependence of the photoluminescence (PL) intensity in hydrogenated amorphous silicon (*a*-Si:H) has been studied. At temperatures below 100 K the nonradiative probability has a power-law behavior with a temperature dependence T^γ , where γ is in the range 4 to 1.5, which is quite different from that above ≈ 100 K. After prolonged illumination at room temperature, a considerable change of the temperature dependence of the photoluminescence in undoped *a*-Si:H has been observed below about 100 K. The PL quenching begins at temperatures below 50 K for samples with a high defect density, while the quenching occurs at temperatures above 50 K for undoped *a*-Si:H with a low defect density. We propose a model assuming shallow radiative hole trap centers to explain our results. The temperature dependence of the photoluminescence below 100 K is probably due to the power-law temperature dependence of the capture cross sections for these radiative hole trap centers.

I. INTRODUCTION

The luminescence of hydrogenated amorphous silicon (*a*-Si:H) has been extensively studied in recent years. The steady-state photoluminescence (PL) in *a*-Si:H consists of two bands; one is the main PL band at around 1.4 eV, another is called defect luminescence and appears at ~ 0.9 eV.¹ The main PL band is known to be due to the radiative recombination of electrons and holes separately trapped in band tail states. Nevertheless, there is little agreement on the details of the recombination processes. It is not yet clear whether its kinetics are geminate or distant pair,^{2,3} nor whether it is significantly Stokes shifted or is due to essentially zero-phonon transition.^{4,5} Also, the charge states of the sites at which electrons and holes are trapped are not yet clear.⁶

The temperature dependence of the PL intensity in *a*-Si:H has been studied in an attempt to obtain information about the electronic structure of glow discharged (GD) and sputtered *a*-Si:H films.⁷⁻⁹ Most models of luminescence kinetics assume that the temperature dependence arises from the competition between radiative recombination of electrons and holes, and a nonradiative recombination. In this case, the photoluminescence intensity as a function of temperature can be expressed in the form

$$I(T) = I_0 \frac{P_r(T)}{P_r(T) + P_{nr}(T)}, \quad (1)$$

where P_r and P_{nr} are the radiative and nonradiative recombination probabilities, respectively. Using Eq. (1), one can obtain P_{nr}/P_r as a function of temperature by plotting $[I_0/I(T)] - 1$. An expression of the form $P_{nr}/P_r \propto \exp(T/T_0)$ is a well-known experimental formula for the temperature dependence of the main PL band above 100 K in *a*-Si:H.¹⁰ Similar behavior has been observed in chalcogenide glasses, and several possible interpretations have been proposed including spatial tunneling,¹¹ a distribution of activation energies,^{9,12} and

phonon-assisted local relaxation at internal surfaces.¹³

In Eq. (1), I_0 , considered to be constant, represents a noncompetitive process such as the direct capture of thermalizing carriers,¹⁴ or temperature-independent competitive tunneling to a random distribution of nonradiative recombination centers.¹⁵ However, it is probable that the luminescence efficiency is temperature dependent even at low temperatures satisfying $P_{nr} \ll P_r$.

In this paper, we present new experimental results on the temperature dependence of the main PL band at low temperatures for undoped and doped *a*-Si:H. The nonradiative mechanism at temperatures below 100 K, which is quite different from that above 100 K, has been observed. Doping and light illumination affect the temperature dependence of PL, especially at low temperatures. A tentative model is proposed to explain the results.

II. EXPERIMENTAL DETAILS

Hydrogenated amorphous silicon (*a*-Si:H) films were deposited on roughened Corning 7059 glass by rf glow-discharge decomposition of silane mixed with hydrogen in a capacitively coupled plasma reactor. Doped samples were prepared by adding phosphine (PH₃) or diborane (B₂H₆) to the gas phase. The thicknesses of all samples were 1 μ m. The samples were placed in a flowing-He-gas cryostat, where the temperature could be varied between 15 and 300 K. The He-Ne laser line at 6328 Å (1.96 eV) was used for excitation. The incident light was chopped at 13.6 Hz in order to use the lock-in amplifier and the PL signal was detected using a PbS cell. A grating monochromator with a resolution of 0.05 eV was used for the measurements of PL spectra and of the temperature dependences of PL at various luminescence energies. The laser line was removed from the PL signal with a 700-nm low-pass filter. Light soaking effects were studied using a He-Ne laser with an intensity of 200 mW/cm² at 300 K.

III. EXPERIMENTAL RESULTS

Figure 1 shows the plot of $\log[(I_0/I)-1]$ versus T at various luminescence energies of the main PL band for undoped a -Si:H. I_0 was separately determined by the zero-temperature extrapolation of $I(T)$ in the saturation regime. In most of our undoped samples, a saturation of $I(T)$ occurs as T is lowered below 50 K when the excitation light intensity is low. Since $I(T)$ is nearly constant below 50 K, I_0 can be determined accurately. But for samples with high-defect density (a -Si:H doped or with prolonged illumination), the PL intensity is found to be a monotonic decreasing function of temperature even below 50 K.

Figure 1 suggests that the PL intensity as a function of temperature at all emission energies in the main PL band can be described by the same formula. That is, $I_0/I(T)-1$ has the same temperature dependence at all emission energies in the main PL band, and only the prefactor increases with increasing luminescence energy. This means that the quenching of the PL at a higher energy begins at a lower temperature. Thus the PL peak shifts to a lower energy as the temperature is raised. Street has proposed that band-edge localized states have a considerable electron-phonon interaction, leading to a Stokes shift of 0.4–0.5 eV.⁴ In his model, the depth and the width of the PL emission band are due to this Stokes shift, and the zero-phonon energies of the radiative states are distributed over a relatively narrow band of energies at about 1.6 eV. Street quoted some features of the luminescence as evidence for a Stokes shift. One of the

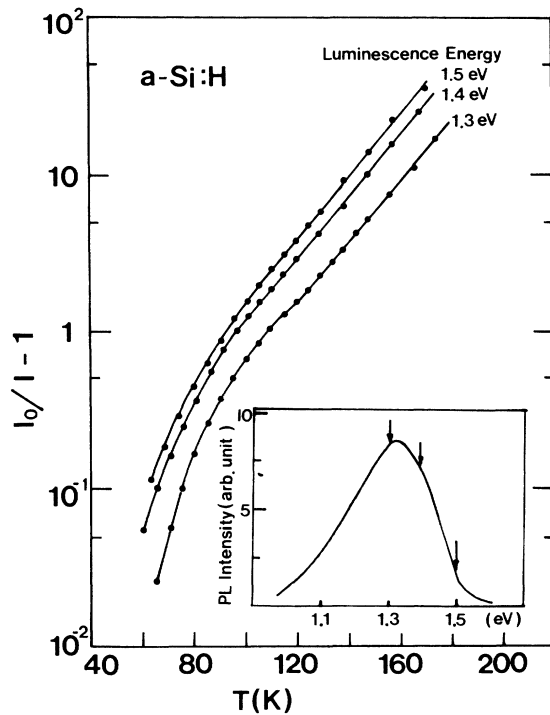


FIG. 1. $I_0/I-1$ vs T at three different luminescence energies in the main PL band of undoped a -Si:H. I_0 was determined separately at each luminescence energy. Inset is the luminescence spectrum and an indication of the three energies used.

features is that essentially the same temperature dependence of the PL intensity is observed at all emission energies, which agrees with our result. However, we do not know why the prefactor increases with increasing the emission energy. Above 100 K, the temperature dependence of PL at each luminescence energy can be described experimentally by an inverse Arrhenius dependence:

$$I_0/I(T)-1 \propto \exp(T/T_0), \quad T > 100 \text{ K}. \quad (2)$$

This equation has already been found to describe the temperature dependence of the total luminescence in a -Si:H with a scale temperature $T_0 \sim 25$ K. In the lower temperature range the temperature dependence of the PL is quite different. Plotting $[I_0/I(T)-1]$ as a function of temperature on a log-log graph shows that $[I_0/I(T)-1]$ increases as a power-law behavior with temperature

$$I_0/I(T)-1 \propto T^\gamma, \quad T < 100 \text{ K}. \quad (3)$$

The observed value of the exponent γ is 3–4 for undoped and phosphorus-doped a -Si:H. Equation (3) is satisfied at all emission energies for all investigated samples. The data of others also show the power-law dependence of the nonradiative process at low temperatures. For example, Fig. 2 shows the result replotted from

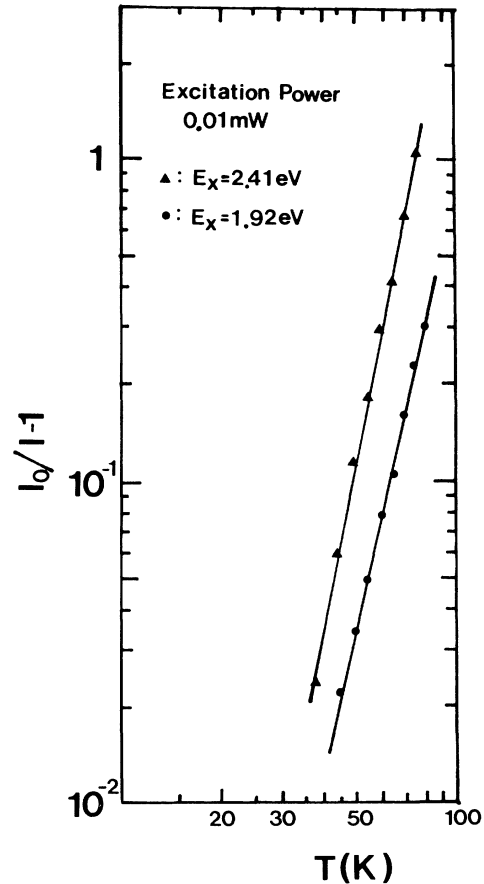


FIG. 2. $I_0/I-1$ vs T for undoped a -Si:H. The data are replotted from Street's paper (Ref. 16) using the maximum values as I_0 .

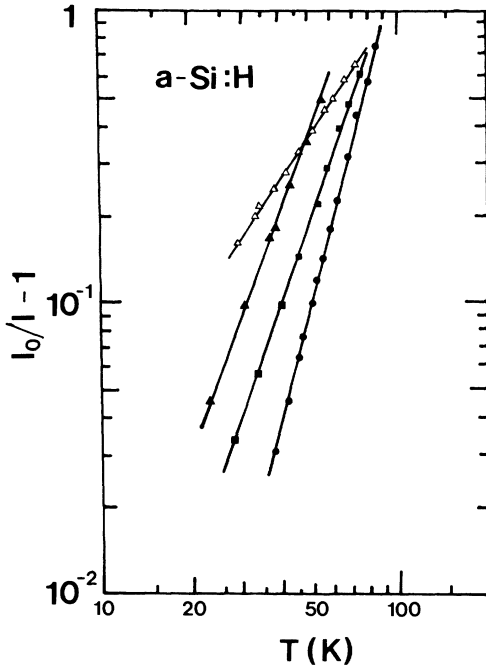


FIG. 3. $I_0/I - 1$ vs T for various a -Si:H samples. ●, undoped; ■, 0.5 ppm, n type; ▲, 50 ppm, n type; △, 2500 ppm, p type.

Street's data.¹⁶ We can see an excellent satisfaction of Eq. (3).

The temperature dependences of total luminescence of various samples at low temperatures are shown in Fig. 3. Most doped samples have smaller values of γ compared with undoped samples. For heavily boron-doped samples, the PL intensity is weakly temperature dependent.

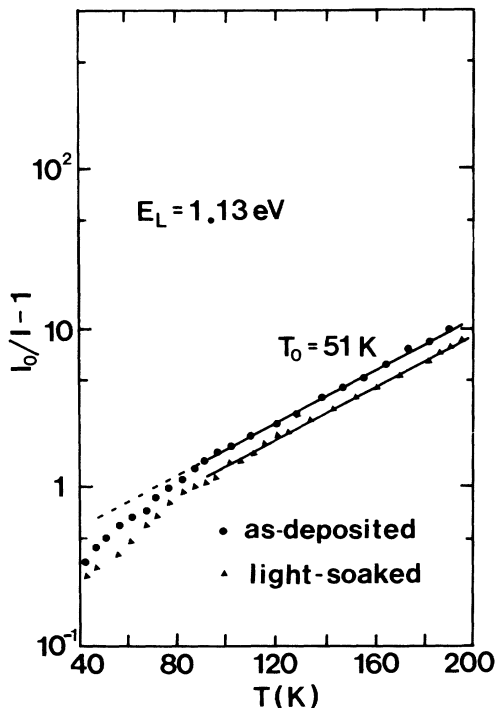


FIG. 4. $I_0/I - 1$ vs T at the PL peak energy of p -type a -Si:H deposited with a gas mixture $[B_2H_6]/[SiH_4] = 2.5 \times 10^{-3}$.

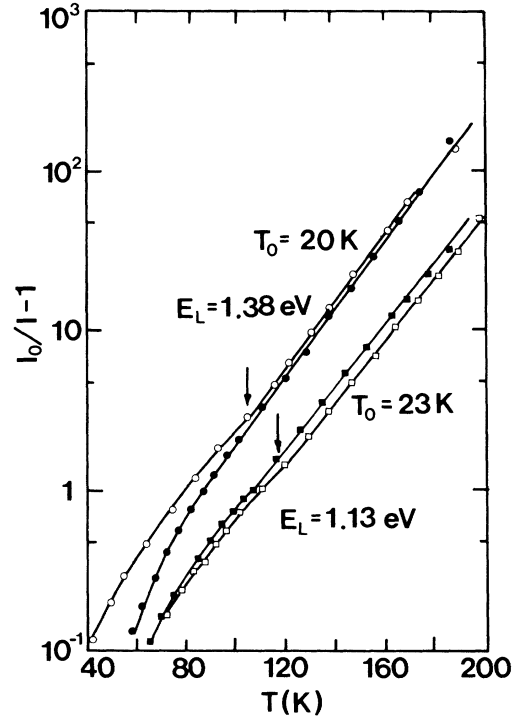


FIG. 5. $I_0/I - 1$ vs T at two different luminescence energies of undoped a -Si:H. Closed symbols represent as-deposited state and open symbols light-soaked states. The vertical arrows indicate the temperature at which the change of the PL quenching mechanism occurs.

The temperature dependence of the PL at peak energy for a heavily boron-doped a -Si:H ($[B_2H_6]/[SiH_4] = 2.5 \times 10^{-3}$) is shown in Fig. 4. One of the distinctive features is a small value of $\gamma \sim 1.5$. However, there is no evidence that the value of γ correlates directly with the dangling bond density, whereas the prefactor in Eq. (3) correlates strongly with the defect density. The prefactor increases with doping concentration and also increases after prolonged illumination for undoped a -Si:H.

The effect of prolonged illumination on the temperature dependence of PL in undoped a -Si:H clearly shows that the quenching mechanism of PL at low temperatures below 100 K is quite different from that at higher temperatures. The change of the temperature dependence of the PL intensity after prolonged illumination of undoped a -Si:H is shown in Fig. 5. The considerable change of the temperature dependence of the PL intensity occurs at low temperatures below about 100 K, while the value of T_0 does not change in the temperature range where an inverse Arrhenius dependence is satisfied. T_0 is remarkably constant for samples exhibiting a wide range of gap-state densities. The value of T_0 is rather related to the distribution of localized tail states.⁹ In doped a -Si:H films, a change of the temperature dependence of PL intensity after illumination has not been observed even at low temperatures.

IV. DISCUSSION

The interpretation of the thermal quenching of PL in a -Si:H has been based on the activated release of carriers

from an exponential-type set of band tail states.¹⁷ Collins and Paul interpreted the temperature dependence of the intensity of the PL peak near 1.4 eV in *a*-Si:H in terms of a distribution of activation energies for nonradiative recombination.⁹ In this case, it is assumed that nonradiative recombination occurs when an electron is emitted from the radiative center to the conduction-band edge, and that the width of the distribution of activation energies is related to the distribution of localized tail states. This model has great difficulty in explaining the temperature dependence of PL at various emission energies in the main PL band. It should be able to explain why the temperature dependence of PL at all emission energies in the main PL band can be described by the same formula (see Fig. 1). Moreover, the power-law dependence at low temperatures and the thermal quenching beginning at a lower temperature for a sample with a higher defect density cannot be explained by this model. To explain the results we assume the following.

(a) There are some radiative centers capturing a certain proportion of holes. The zero-phonon energies of the radiative states are distributed over a relatively narrow range of energy.

(b) The radiative centers possess a Coulomb attractive charge (negative charge) and have a very large hole capture cross sections at temperatures below 50 K ($\sim 10^{-13}$ cm²). The capture cross sections for the radiative centers decreases rapidly with increasing temperature as $T^{-\gamma}$ with γ as large as 4.

In this model, the quantum efficiency of PL is governed by the proportion of holes captured initially by the radiative centers and by the process of the release of holes from these centers. The rate of the loss of holes from the radiative centers rises in accordance with the law $\exp(T/T_0)$. The PL intensity at low temperatures where the rate can be neglected is mainly governed by the proportion of holes captured by the radiative centers, which is determined by the temperature-dependent capture cross section for the radiative hole centers.

PL 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.² But the results of time-resolved PL detection demand that either the electron or the hole be trapped at a charged center.⁶ Although the results do not discriminate between which of the two centers is charged, one might speculate that the hole, more quickly and more deeply trapped, is captured by a charged center. On the other hand, it is reported that recombination occurs at neutral sites in the materials such as *a*-Si:H:O alloys and sputtered *a*-Si:H films with high hydrogen concentration.^{18,19}

Cross sections so large, from 10^{-15} to 10^{-12} cm², have been observed for centers known or presumed to possess a Coulomb attractive charge.^{20,21} The works on Au in Si and Sb in Ge indicate that the capture cross sections for Coulomb attractive centers increase rapidly with decreasing temperature as $T^{-\gamma}$ with γ as large as 4. For neutral centers, we expect a much less temperature-dependent cross section. So far, one is tempted to conjecture that the cascade mechanism is likely to explain this behavior.^{22,23} This cascade hypothesis asserts that carriers are

captured into some highly excited states, and that they then continue to lose energy primarily by a cascade of one-phonon transitions between the bound states. Since the energy levels are separated by less than the phonon energy, we are normally considering shallow centers. It might apply to amorphous materials where hole capture into the charged shallow center exhibits a capture coefficient which decreases with increasing temperature according to a power-law behavior. However, the classical theoretical model applies to the situation in which the carrier mean free path for scattering is considerably longer than the capture radius of the trap.²² For *a*-Si:H in which electrons and holes have a low mobility, we cannot interpret a mechanism for capturing into such levels and thus we will not discuss the detailed mechanism which gives the temperature dependence of the capture coefficient.

Our model is shown schematically in Fig. 6. Photogenerated holes thermalize very rapidly to the band edge. A certain proportion of the holes are captured into shallow radiative centers, while direct nonradiative transitions take place for holes having been diffused near to nonradiative centers. The holes captured by the radiative centers recombine radiatively with the electrons trapped at the conduction-band tail states, or nonradiatively by competitive release from these centers. In the model described by Fig. 6, the rate equations for the densities of free holes in valence-band edge, p , and of the holes trapped at the radiative centers, N_{PL} , can be written as follows:

$$dp/dt = G - p\beta_L(N_L - N_{PL}) - pP_{dnr}, \quad (4)$$

$$dN_{PL}/dt = p\beta_L(N_L - N_{PL}) - N_{PL}P_r - N_{PL}P_{nr}, \quad (5)$$

$$I(T) \propto N_{PL}P_r, \quad (6)$$

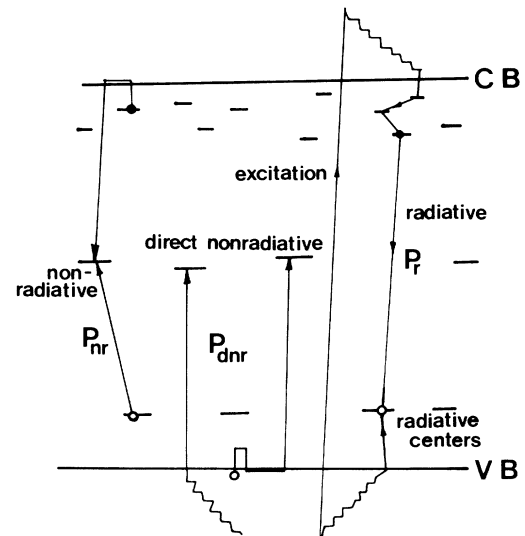


FIG. 6. One-dimensional representation of the model used to describe the recombination processes. P_{dnr} , the direct nonradiative transition rate of free holes; P_{nr} , the rate of the release of holes from the radiative centers; P_r , the radiative transition rate of the electrons trapped at conduction-band tail states and the holes at the radiative centers.

where G and N_L are the generation rate and the density of the radiative hole centers, respectively, and P_{dnr} , P_{nr} , and P_r are the direct nonradiative transition rate of free holes, the rate of release of holes from the radiative centers, and the radiative transition rate, respectively, and β_L designates the capture rate constant of holes for the radiative centers. The last term on the right-hand side of Eq. (5) can be neglected at low temperatures below about 100 K since P_{nr} is considered to be much lower than P_{dnr} or P_r , while the PL efficiency at higher tempera-

tures is mainly determined by this last term:

$$I_0/I(T) - 1 = P_{\text{nr}}/P_r \propto \exp(T/T_0), \quad T > 100 \text{ K}. \quad (7)$$

In a steady state $dp/dt = dN_{\text{PL}}/dt = 0$. Thus one obtains the steady-state population of the holes trapped at radiative centers, N_{PL} from Eqs. (4) and (5). Neglecting the rate of the release of holes from the radiative centers at $T < 100$ K, the PL efficiency is given from Eq. (6) by

$$I(T) \propto \frac{(\beta_L N_L P_r + P_{\text{dnr}} P_r + \beta_L G) - [(\beta_L N_L P_r + P_{\text{dnr}} P_r + \beta_L G)^2 - 4\beta_L^2 N_L P_r G]^{1/2}}{2\beta_L}. \quad (8)$$

Since the condition that $N_L \gg N_{\text{PL}}$ is satisfied for not too large a generation rate, the PL efficiency is given by the simple form

$$I(T) \propto G/[1 + P_{\text{dnr}}/\beta_L(T)N_L]. \quad (9)$$

If we assume that P_r and P_{dnr} are temperature independent, the temperature dependence of the capture coefficient $\beta_L(T)$ can be estimated from the temperature dependence of PL (Fig. 7). We can, therefore, suggest that the capture coefficient for the radiative centers gives the power-law dependence.

Figure 8 shows the change of the PL efficiency as a

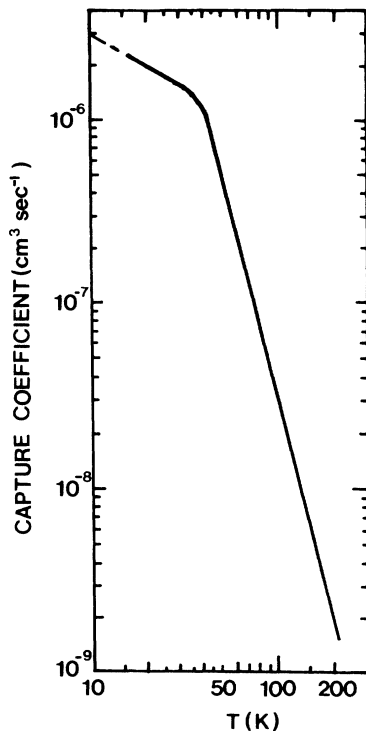


FIG. 7. The capture coefficient for the radiative hole trap centers estimated from the temperature dependence of PL for undoped $a\text{-Si:H}$ at the following tentative values: $N_L = 10^{17} \text{ cm}^{-3}$, $P_{\text{dnr}} = 5 \times 10^9 \text{ sec}^{-1}$, $P_r = 10^5 \text{ sec}^{-1}$, and $G = 10^{21} \text{ cm}^{-3} \text{ sec}^{-1}$.

function of T with increasing P_{dnr} when all other parameters are fixed at the values used in Fig. 7. The data for undoped $a\text{-Si:H}$ fit well with the calculated curve with the value of $P_{\text{dnr}}/N_L\beta_L = 0.05$ at $T = 40$ K. The dashed lines are the curves including the additional nonradiative recombination term, $P_{\text{nr}}N_{\text{PL}}$ in Eq. (5). Our model clearly explains the change of the temperature dependence of PL at low temperatures with increasing defect density as shown in Fig. 8.

We conjecture that the value of γ depends on the nature of the radiative centers. Doping and light illumination might change the property of the radiative centers in $a\text{-Si:H}$. The radiative centers in heavily boron-doped $a\text{-Si:H}$ may be neutral as those in $a\text{-Si:H:O}$ alloys and sputtered $a\text{-Si:H}$ films with high H concentrations.

The mechanism proposed in our model is essentially

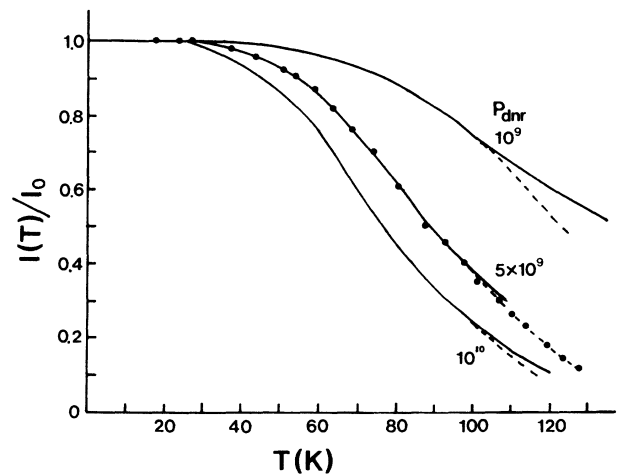


FIG. 8. The change of $I(T)/I_0$ vs temperature curves with the direct nonradiative recombination rate P_{dnr} when the value of γ is fixed. The solid lines are the curves calculated from Eq. (8) using the same values as those in Fig. 7 except P_{dnr} . The curve when $P_{\text{dnr}} = 5 \times 10^9$ is the fit to the data of undoped $a\text{-Si:H}$. The dashed lines are the curves including additional nonradiative recombination term, $P_{\text{nr}}N_{\text{PL}}$ in Eq. (5). Note that the temperature at which the quenching begins decreases with increasing the direct nonradiative recombination rate, i.e., the defect density.

monomolecular: The rate of the loss of holes is independent of the density of nonequilibrium electrons. The monomolecular nature of the radiative recombination processes in *a*-Si:H is supported by the experimental observation that the kinetics of the decay of the PL from the steady state is independent of the rate of excitation.²⁴ Tsang and Street have proposed a model that the PL efficiency at low temperatures is determined by competitive tunneling of electrons to a random distribution of nonradiative recombination centers.¹⁵ Such a process can affect the PL efficiency. However, we believe that at least the temperature dependence of the PL is determined by the change of the steady-state population of the holes trapped at radiative centers with temperature.

V. CONCLUSION

Our experimental results can be summarized as follows: The temperature dependence of the PL intensity at all emission energies in the main PL band can be described by the same formula. Nonradiative probability increases with increasing temperature following power-law dependence at temperatures below 100 K. In this temperature range the change of the temperature dependence of PL after prolonged light illumination at room temperature has been observed for undoped *a*-Si:H. Thus the quenching mechanism at temperatures below 100 K

is considered to be different from that above 100 K because the $\exp(T/T_0)$ dependence of the PL changes a little after light exposure. The temperature where the PL quenching begins decreases with increasing defect density. We have developed a model to explain the temperature dependences of the PL in *a*-Si:H films.

(1) There are radiative centers which capture a certain proportion of photogenerated holes. The PL efficiency is governed by the proportion of holes captured by the radiative centers at low temperatures where the rate of loss of holes from these centers can be neglected.

(2) The radiative centers possess a negative charge, for which the capture coefficient decreases with increasing temperature as $T^{-\gamma}$.

Doping and light illumination can change the temperature dependence of the capture coefficient for the radiative centers in *a*-Si:H. We conjecture that the temperature dependence of the capture coefficient depends on the properties of the radiative centers. The effects of the defect densities on the temperature dependence of the PL intensity at low temperatures can be explained by our model.

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