

## Photoluminescence mechanism in hydrogenated amorphous silicon studied by frequency-resolved spectroscopy

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In order to reconsider the photoluminescence mechanism in hydrogenated amorphous silicon ( $a$ -Si:H), the lifetime distribution of photoluminescence,  $G(\tau)$ , was evaluated over a wide lifetime range between  $5.3 \times 10^{-7}$  s and  $8.0 \times 10^{-2}$  s using frequency-resolved spectroscopy. The most remarkable finding is that  $G(\tau)$  is dominated by two kinds of lifetime components characterized by specific peak lifetimes at low temperatures. At 12 K, only the lifetime component peaked at about 1 ms is dominant, whereas another component appears distinctively at around 10  $\mu$ s and grows gradually with increasing temperature. Such a discontinuous change of the lifetime from 1 ms to 10  $\mu$ s takes place at temperatures lower than 60 K where the photoluminescence intensity is almost constant. Interestingly, the peak lifetimes for both lifetime components are quite insensitive to the Urbach energy or the emission energy as long as the excitation intensity is held low enough to satisfy the condition for geminate-pair recombination. These characteristic features observed in  $G(\tau)$  do not reconcile with the generally accepted model of tunneling recombination between carriers trapped at the tail states after thermalization. In particular, dominance of the 1-ms lifetime component at 12 K is interpreted following the model as the electron-hole separation enlarges up to a value corresponding to the 1-ms recombination after photogeneration. However, it is hard to understand the absence of the 10- $\mu$ s lifetime component at 12 K, since the 10- $\mu$ s recombination is expected to take place at much shorter electron-hole separation and is actually observed at elevated temperatures. Because of the several arguments against the generally accepted model and of the coexistence of two lifetime components having specific peak lifetimes, it is more appropriate to consider that the photoluminescence in  $a$ -Si:H comes from special localized luminescent centers corresponding to the respective lifetime components. Since the lifetime changes discontinuously from 1 ms to 10  $\mu$ s with increasing temperature while the luminescence intensity remains constant at the low temperatures, some correlation is expected to exist between the two kinds of luminescent centers.

### I. INTRODUCTION

Although photoluminescence (PL) in crystalline silicon is very weak because of its electronic nature of an indirect band gap, hydrogenated amorphous silicon ( $a$ -Si:H) exhibits more efficient PL at low temperatures. High PL efficiency in  $a$ -Si:H is considered to be a result of the breakdown of the  $k$  selection rule due to structural disorder.<sup>1</sup> PL in  $a$ -Si:H has been studied intensively for a long time in order to understand the relaxation process of excited carriers in disordered materials which are considered to interact with localized states in the band gap in a complicated manner. However, a satisfactory understanding of the PL mechanism has not been reached yet. Steady-state PL in  $a$ -Si:H shows several characteristic features, such as a wide spectral width and an energy difference between absorption and emission bands.<sup>1</sup> Early studies were concerned mainly with those properties in a steady state. There are two typical models for explaining PL in  $a$ -Si:H; one is based on the electron-phonon interaction,<sup>2</sup> i.e., the Stokes shift, and the other is based on disorder-related fluctuation of the band gap,<sup>3</sup> instead of taking into account the electron-phonon interaction. But neither of them could explain experimental results quantitatively.<sup>4</sup> As demonstrated by Searle and Jackson<sup>5</sup> through a detailed study of the PL spectrum in connec-

tion with the optical gap and the Urbach energy in  $a$ -Si:H alloys, an unacceptably high phonon energy was required when interpreting according to the electron-phonon interaction model. On the other hand, in the static disorder model, the expected relationship between the spectral width and the Urbach energy, as well as an expected slope in the PL spectrum on the lower energy side, did not agree quantitatively with the experimental results, either.

Besides those studies on characteristic features in the steady-state PL, another approach has been made theoretically and experimentally by focusing on microscopic kinetics of photogenerated carriers at low temperatures. A measurement of transient PL after pulsed excitation has been performed sometimes following this line. It apparently exhibits a very dispersive decay extending from nanoseconds to seconds,<sup>6</sup> as usually observed in other physical quantities in disordered materials, indicating that the recombination lifetime takes on distributed values. Since  $a$ -Si:H contains tail states below the extended states, it has been generally accepted that the photoluminescence is a kind of transport phenomenon related with carriers trapped at the tail states, i.e., tunneling recombination between carriers trapped at the tail states.<sup>1,6</sup> Under weak excitation intensity for satisfying geminate-pair recombination at low temperatures, photo-

generated electrons and holes are expected to thermalize diffusively down in respective tail states until the hopping rate to a neighboring site becomes comparable with the tunneling recombination rate between the paired electron and hole.<sup>1,7,8</sup> Based on such a microscopic picture, Shklovskii, Fritzsche, and Baranovskii analyzed statistically the fate of an isolated electron-hole pair created by band-gap excitation at a low enough temperature where thermal energy has little influence on carrier movement and they got a general function for a distribution of separation between paired electrons and holes. This function exhibits a maximum that is independent of the energy dependence of the density of tail states. Furthermore, a long tail is expected to be sustained at longer lifetimes beyond the maximum. However, such a feature is not observed in the experimentally evaluated lifetime distribution.<sup>4,6</sup> In particular, the theoretically expected long continuing tail at longer lifetimes is absent. The actual mechanism for PL in *a*-Si:H seems to be not as simple as is considered in the generally accepted model of tunneling recombination between tail-state carriers accompanying tail-state thermalization. In order to undertake a more detailed discussion, some spectroscopic study other than the PL spectrum is desirable. Since the lifetime distribution should reflect directly the dynamics of carriers in the recombination process, detailed studies of it under various experimental conditions will give us valuable information for a more detailed discussion. Actually, an increasing number of studies on the lifetime distribution of PL have been performed recently.<sup>6,10-13</sup>

Experimentally, a lifetime distribution can be evaluated from the transient PL after pulsed excitation in the real time domain.<sup>6</sup> However, evaluation of the lifetime distribution over a wide lifetime range with a good accuracy can be done more easily in the frequency domain, i.e., frequency-resolved spectroscopy (FRS). This technique was proposed initially by Depinna and Dunstan.<sup>14</sup> The mathematical background and its sophistication as an exact method for evaluating the lifetime distribution has been given recently by Risten<sup>15</sup> and Stachowitz, Schubert, and Fuhs.<sup>16</sup> The out-of-phase component of the PL signal induced by a sinusoidally modulated excitation, which is usually detected by the phase-sensitive detection technique, can give directly a lifetime distribution when it is plotted against a logarithmic scale of the modulation frequency.<sup>15,16</sup> The Marburg group<sup>12,17-19</sup> has been pursuing the FRS studies of PL and has discussed the effects of nonradiative recombination through defects and temperature. They have observed that the lifetime distribution exhibits a peak at around 1 ms at 10 K in the case of geminate-pair recombination, and the most surprising finding is that there is no change of the peak lifetime in the lifetime distribution at 10 K even if the defect density is increased from  $3 \times 10^{15}$  to  $5 \times 10^{17} \text{ cm}^{-3}$  by electron bombardment, although the PL intensity decreases with increasing defect density.<sup>12,18</sup> According to the reported results,<sup>3,11,18,20</sup> three components characterized by respective peak lifetimes of 1 ms, 10  $\mu\text{s}$ , and 1  $\mu\text{s}$  can be noticed in the lifetime distribution within the measured lifetime range between  $10^{-8}$  and 1 s. The 1-ms and the 1- $\mu\text{s}$  components can be observed at low temperatures,

whereas the remaining component, the 10- $\mu\text{s}$  component, becomes apparent at elevated temperatures. Thus, in contrast with other transport properties usually exhibiting a featureless response or a broad spectrum, the lifetime distribution of PL presents very informative structures. However, it must be noticed that those results were obtained from the measurements for integrated PL.

Recently, I have noticed through measurements of the lifetime distribution for monochromatized PL that the spectrum of lifetime distribution differs greatly depending on the emission energy, especially at low temperatures where geminate-pair recombination prevails.<sup>21</sup> Since PL in *a*-Si:H ranges widely in emission energy, the integrated PL receives contributions from each monochromatic luminescence weighted with a factor which is a product between relative magnitude of the PL intensity and relative sensitivity of the detector at the corresponding emission energy. As a result, measurement for the integrated PL will result in some distorted lifetime distribution.

In order to avoid such an ambiguity, the lifetime distribution in *a*-Si:H is evaluated for monochromatized PL in this paper, and it is evaluated for various combinations of excitation energy and emission energy at different temperatures. Based on the results, the generally accepted model for the radiative recombination in *a*-Si:H will be reconsidered.

## II. EXPERIMENT

The specimens used for the measurement of lifetime distributions were undoped *a*-Si:H prepared by radio-frequency glow discharge of  $\text{SiH}_4$  gas at substrate temperatures between 100 and 300°C. The optical gap of the specimens determined from Tauc's plots ranges between 1.72 and 1.75 eV at room temperature. Detailed measurements were performed mainly for one specimen having good quality, which was made at a substrate temperature of 300°C, and has the optical gap and the spin density of 1.72 eV and  $5 \times 10^{15} \text{ cm}^{-3}$ , respectively. In this paper, results for this specimen will be shown without notice.

A specimen installed within a closed-cycle cryostat was excited with a Kr laser whose output was modulated sinusoidally with an acousto-optic modulator. Luminescence from the specimen was detected with a photomultiplier after passing through a monochromator. Two kinds of photomultipliers were used alternately, depending on the emission energy: S1 type cooled with dry ice and S20 type operated at room temperature. The signal from the photomultiplier was fed into a lock-in amplifier combined through a preamplifier. The lifetime distribution was evaluated using frequency-resolved spectroscopy. Since an electronic circuit consisting of the preamplifier and the lock-in amplifier has its own characteristic frequency response, calibration of the frequency response of the electronic circuit was performed beforehand. Taking into account the calibrated frequency response of the detection system, the true out-of-phase component of the modulated signal of PL was measured with the lock-in amplifier by varying the modulation frequency  $f$  in a range between 2 Hz and 300 kHz. Thus the obtained

spectrum of the out-of-phase signal gives a lifetime distribution  $G(\tau)$  when converting the variable from  $\log_{10} f$  to  $\log_{10} \tau$  according to the relation  $\tau^{-1} = 2\pi f$ .<sup>15,16</sup> The spectrum of  $G(\tau)$  was normalized to the maximum value. It was evaluated for different combinations of excitation energy  $E_x$  and emission energy  $E_{PL}$ . Usually, the intensity of the excitation light was held weak enough to satisfy the condition for geminate-pair recombination at low temperatures.

### III. RESULTS AND DISCUSSION

#### A. Temperature dependence of $G(\tau)$

To start with, we would like to point out general features observed in the temperature evolution of  $G(\tau)$  for *a*-Si:H when it is evaluated for monochromatized PL. Figures 1(a) and 1(b) show  $G(\tau)$  for  $E_{PL}$  of 1.24 and 1.41 eV, respectively, at every 10 K below 100 K against the 1.83-eV excitation with the intensity of 0.11 mW cm<sup>-2</sup>. For ease of comparison, the spectra are shifted vertically with each other and zero level for each  $G(\tau)$  is marked with a short line at the left. The PL spectrum in a steady state for this specimen has a peak at around 1.34 eV at 13 K against the band-gap excitation. Monitoring energies of  $E_{PL}$  were chosen as those at both sides of the 1.34-eV peak. Three distinct components can be recognized in the lifetime distributions, although a temperature range where each lifetime component is active differs depending on the lifetime component. At the lowest temperature of 13 K,  $G(\tau)$  is dominated mainly by a component peaked at about 1 ms, irrespective of  $E_{PL}$ . As observed previously,<sup>11-13,18,20</sup>  $G(\tau)$  at low temperatures exhibits a plateau at short lifetimes around 1  $\mu$ s, indicating that there exists another component having a lifetime shorter than 1  $\mu$ s. However, its contribution to  $G(\tau)$  is not so efficient compared to another lifetime component which will be discussed here. With increasing temperature up to around 50 K, a second component grows up gradually at around 10  $\mu$ s. Furthermore, a third component becomes evident at longer lifetimes of around 10 ms above 60 K, and is going to dominate  $G(\tau)$  at higher temperatures. It is curious at first glance that the lifetime becomes longer again in the course of elevating temperature. It can be seen in Figs. 1(a) and 1(b) that the relative magnitude among those lifetime components changes with temperature in a different manner, depending on  $E_{PL}$ . Therefore, when  $G(\tau)$  is evaluated for integrated PL as carried out previously,<sup>11,12,17-20</sup> the resulting lifetime distribution misses such a difference in  $G(\tau)$  depending on  $E_{PL}$ . The difference in  $G(\tau)$  depending on  $E_{PL}$  will reveal one aspect of the PL mechanism in *a*-Si:H.

At temperatures higher than 100 K, where the PL intensity decreases successively,  $G(\tau)$  comes to be dominated mainly by the lifetime component with the longest characteristic lifetime. Furthermore, its peak position starts to shift towards shorter lifetimes with increasing temperature. The peak shift of the third component is related to thermal quenching of PL and it will be discussed later.

Following the above observations, we can summarize

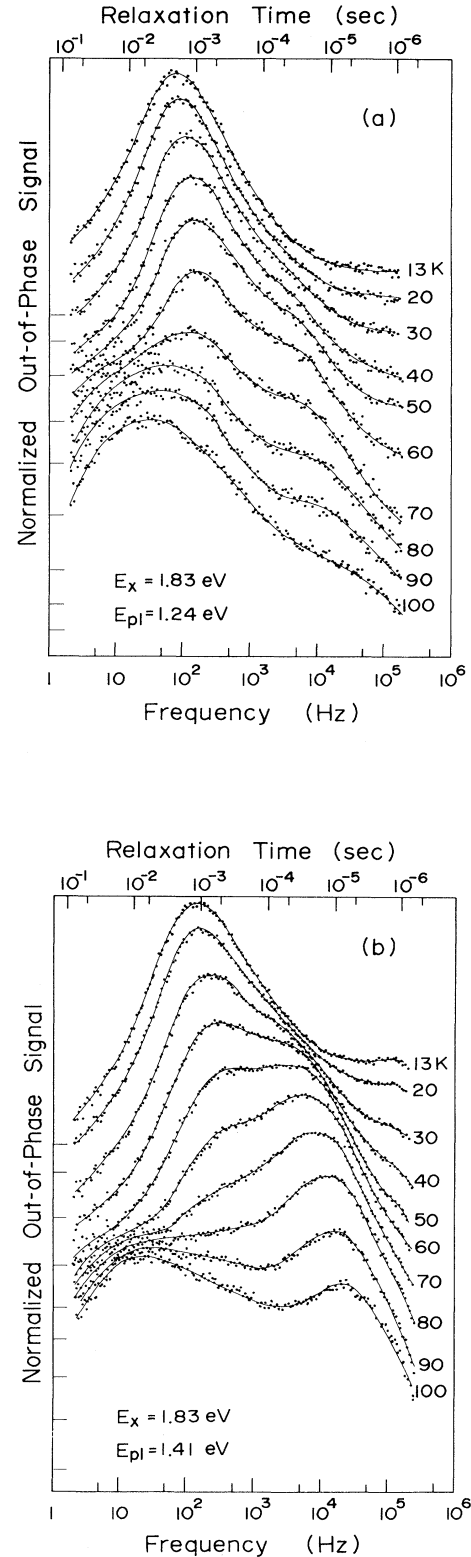


FIG. 1. Temperature evolution of  $G(\tau)$  for the 1.83-eV excitation with the intensity of 0.11 mW cm<sup>-2</sup>. Emission energies are for (a) 1.24 eV and (b) 1.41 eV.  $G(\tau)$  is normalized to the maximum value and zero level for each  $G(\tau)$  is marked with short line at the left.

several remarkable features of  $G(\tau)$  in  $a$ -Si:H: (1)  $G(\tau)$  exhibits a rather complex structure in contrast with other physical quantities related to carrier transport in disordered materials; (2) each lifetime component in  $G(\tau)$  seems to be characterized by its own specific peak lifetime; and (3) although relative magnitude among the three lifetime components differs depending on  $E_{PL}$  at any temperature, it seems that there exists some correlation among the components. Now we will examine each feature more precisely in the following sections.

### B. Effect of excitation intensity on $G(\tau)$

The PL comes from radiative recombination between photogenerated electrons and holes at low temperatures.<sup>1</sup> However, a way of recombination differs depending on the generation rate; it is usually classified into either geminate-pair recombination or distant-pair recombination.<sup>6,17,22</sup> When the excitation intensity is low enough, an electron-hole pair generated by the same photon completes the recombination between them and the recombination lifetime is not influenced by the excitation intensity. Such a situation is called geminate-pair recombination. On the other hand, when the excitation intensity is high enough and the interpair distance becomes comparable to the intrapair distance, recombination between an electron and a hole which are excited by different photons becomes possible. This is called distant-pair recombination. In this case, the recombination lifetime depends on the excitation intensity or the distance between recombining electron and hole when tunneling recombination prevails.<sup>6,22</sup> A critical excitation intensity separating the two regions has been estimated experimentally to be roughly about  $10^{19}$  photons  $\text{cm}^{-2}\text{s}^{-1}$  at around 10 K for a band-gap excitation in  $a$ -SiH.<sup>17,22</sup> Theoretical study for the fate of an electron and hole pair by Shklovskii, Fritsche, and Baranovskii<sup>9</sup> and related arguments<sup>4,23-26</sup> were mainly concerned with the case of geminate-pair recombination.

In order to identify which kind of character each lifetime component in  $G(\tau)$  has, the influence of the excitation intensity on  $G(\tau)$  was examined. A comparison of  $G(\tau)$  between the two excitation intensities of 0.11 and 1.1  $\text{mW cm}^{-2}$  for the 1.83-eV excitation and for  $E_{PL}=1.41$  eV at three different temperatures is summarized in Fig. 2. At the lowest temperature of 13 K, the whole shape of  $G(\tau)$  was unchanged, irrespective of the excitation intensity. At 50 K were the two components with characteristic lifetimes of 1 ms and 10  $\mu\text{s}$  became noticeable, neither component changed its peak position against the change of the excitation intensity. However, the third component, which became evident in addition to the 10- $\mu\text{s}$  component at 100 K, shifted its peak position to a shorter lifetime with increasing excitation intensity, although the 10- $\mu\text{s}$  component held almost the same peak position irrespective of the excitation intensity. Judging from the dependences of the peak lifetime of each component on the excitation intensity, it can be said that the 1-ms and the 10- $\mu\text{s}$  components, which are dominant at low temperatures, have the characteristics of geminate-pair recombination, whereas the third com-

ponent, observed at a longer lifetime region at elevated temperatures, has the characteristics of distant-pair recombination. It is likely that, with increasing temperature, the geminate pairs are dissociated thermally and some part of the dissociated carriers recombine radiatively as distant pairs. Through the measurements of  $G(\tau)$  for various specimens having different defect densities, it was found that such a long lifetime component became weaker with increasing defect density, and it eventually disappeared when the defect density exceeded  $10^{17} \text{ cm}^{-3}$ . Carriers may be captured by the defects during the diffusion at high temperatures before recombining radiatively.

Here it is interesting to examine how temperature dependence of the PL intensity itself changes with increasing excitation intensity. Temperature dependences of the PL intensity in a steady state for  $E_{PL}=1.24$  and 1.41 eV under the two different excitation intensities are compared in Fig. 3, where the PL intensity for each case is adjusted to coincide with each other at 13 K for the sake of comparison. As one can see, the temperature quenching of PL, which becomes efficient above 60 K, reduces somewhat in the case of intense excitation. Since the distant-pair recombination is the dominant lifetime component at higher temperatures, this result indicates that a possibility for the distant-pair recombination after thermal dissociation of the geminate pairs is enhanced with increasing excitation intensity.

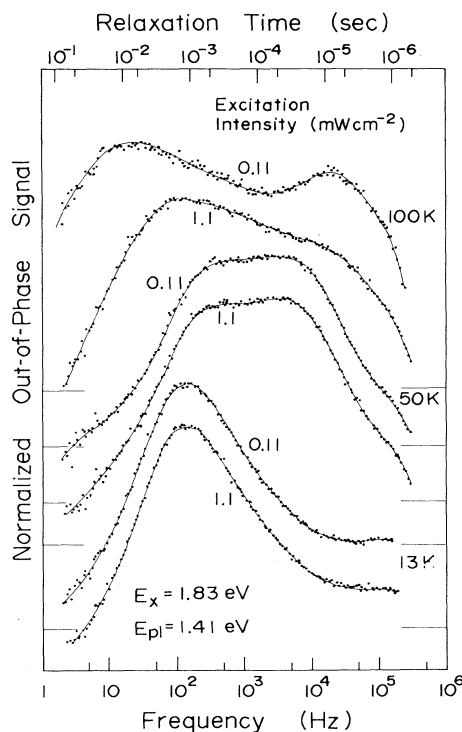


FIG. 2. Comparison of  $G(\tau)$  at two different excitation intensities of 0.11 and 1.1  $\text{mW cm}^{-2}$  for the 1.83-eV excitation at three different temperatures. Emission energy is 1.41 eV.  $G(\tau)$  is normalized to the maximum value and zero level for each  $G(\tau)$  is marked with short line.

### C. Lifetime distribution at 12 K

Now we focus on  $G(\tau)$  at the lowest temperature where thermal energy has little influence on carrier transport. Figure 4 summarizes  $G(\tau)$  at 12 K for several  $E_{PL}$  and for the excitation of 1.83-eV light with the intensity of  $0.11 \text{ mW cm}^{-2}$ , which satisfies the condition for geminate-pair recombination. All the distributions exhibit a single-peak structure accompanying a long continuing tail down to  $1 \mu\text{s}$ . Such a feature was commonly observed in the reported lifetime distributions at around 10 K evaluated for integrated PL.<sup>6,11–13,18,20</sup> The most remarkable feature in Fig. 4 is that the peak positions in all distributions take almost the same lifetime of about 1 ms irrespective of  $E_{PL}$ . The peak lifetime is plotted as a function of  $E_{PL}$  in Fig. 5, in which results for other excitation energies of 1.65 and 1.55 eV are also included. The peak lifetime is nearly constant at lower  $E_{PL}$  and decreases slightly at higher  $E_{PL}$  beyond 1.4 eV. However, the change of the peak lifetime remains within a factor of 3 over the measured emission energies between 1.15 and 1.55 eV. Furthermore, the peak lifetime for any  $E_{PL}$  does not depend on  $E_x$ .

If PL at low temperatures is dominated by the tunneling recombination between carriers trapped at tail states

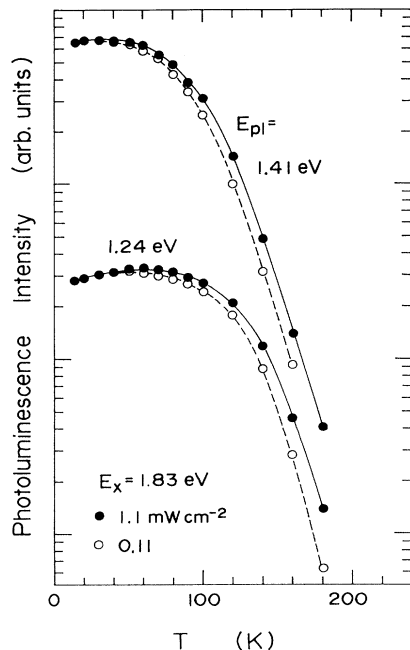


FIG. 3. Temperature dependences of the photoluminescence intensity for the emission energies of 1.24 and 1.41 eV against the 1.83-eV excitation. Comparison is made for each emission energy at two different excitation intensities; open circles are for  $0.11 \text{ mW cm}^{-2}$  and closed circles for  $1.1 \text{ mW cm}^{-2}$ . Photoluminescence intensities for respective emission energies are adjusted to coincide with each other at the lowest temperature for the sake of comparison.

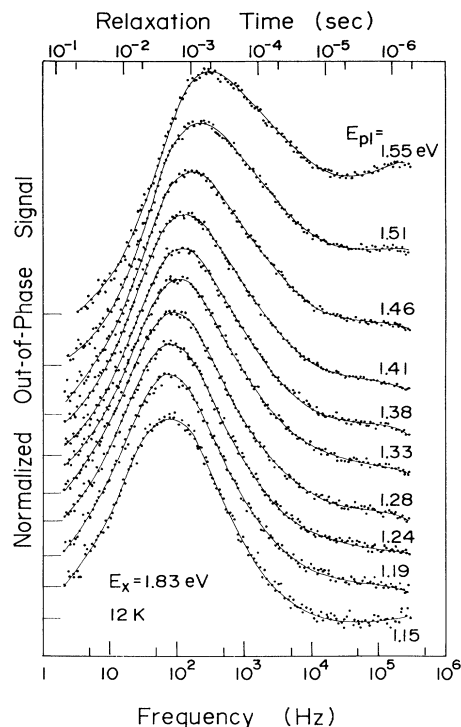


FIG. 4.  $G(\tau)$  for several emission energies at 12 K. Excitation energy is 1.83 eV with the intensity of  $0.11 \text{ mW cm}^{-2}$ .  $G(\tau)$  is normalized to the maximum value and zero level for each  $G(\tau)$  is marked with short line at the left. At 12 K,  $G(\tau)$  is dominated only by the lifetime component peaked at around 1 ms.

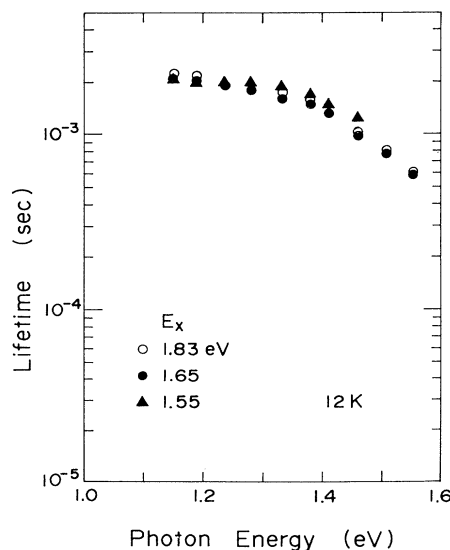


FIG. 5. Peak lifetime observed in  $G(\tau)$  at 12 K (Fig. 4) as a function of emission energy. Results for other excitation energies of 1.65 and 1.55 eV are also included.

after thermalizing in their respective tail states as usually understood,<sup>1</sup> the peak lifetime should depend exponentially on the separation between the recombining electron-hole pair.<sup>6</sup> When a carrier thermalizes down deeper in the tail states by hopping, available states for subsequent hops become fewer since tail-state density decreases with energy from the extended states. As a result, the hopping distance increases successively with proceeding thermalization and the separation between paired electron and hole also increases gradually.<sup>9</sup> Of course, it may happen that the population of carriers among the tail states is brought about directly by rapid capture of generated carriers without thermalization. Even in this case, the deeper the carriers are trapped, the longer the separation between recombining the electron-hole pair because of the monotonic decrease of the density of tail states with energy. Anyway, when such situations actually take place, the radiative lifetime depends very sensitively on the final energy location in the tail states that a carrier can reach just before the recombination. It is expected that the lower the emission energy, the longer the radiative lifetime becomes, so that the peak lifetime is expected to change by several orders of magnitude even if the final energy location of the thermalized carrier ranges over only a few tenths of electron volts. But this expectation conflicts obviously with the experimental result in Fig. 5. The peak lifetime exhibits a very slight change against a change of  $E_{PL}$  of over 0.4 eV. This is the first clue which makes me unsure about the generally accepted model of tunneling recombination between carriers trapped at tail states.

Here, it must be stressed again that the arguments in this paper are limited to a case satisfying the condition of geminate-pair recombination at low temperatures. When the excitation intensity exceeds some critical value, for example, about  $10 \text{ mW cm}^{-2}$  for the 1.83-eV excitation, the invariance of the peak lifetime in  $G(\tau)$  irrespective of  $E_{PL}$  breaks down even at low temperatures and the peak lifetime starts to shift towards a shorter lifetime with increasing excitation intensity, indicating that the distant-pair recombination becomes efficient even at 12 K.

#### D. Lifetime distribution at 50 K

The lifetime distribution for  $a\text{-Si:H}$  starts to change with increasing temperature just above 12 K. Surprisingly, this change takes place even at low temperatures where PL intensity holds a nearly constant value. Figure 6 shows PL spectra in a steady state at temperatures of 13, 50, and 100 K under three different excitation energies. Only a limited range of spectra at around the maximum are shown there, and a set of spectra for each excitation energy is shifted vertically with each other. This figure indicates that the whole PL spectrum or an intensity of monochromatized PL is almost invariant at temperatures between 13 and 50 K for all excitations of 1.55-, 1.65-, and 1.83-eV light with the intensities of 102, 3.6, and  $0.11 \text{ mW cm}^{-2}$ , respectively.

In contrast with the results at 12 K,  $G(\tau)$  at 50 K differs greatly depending on  $E_{PL}$ . The results for the 1.83-eV excitation are summarized in Fig. 7. It is in-

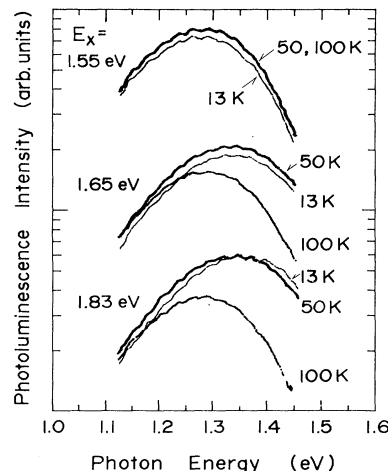


FIG. 6. Photoluminescence spectra in a steady state for three different excitation energies at three different temperatures. Each set of spectra for respective excitation energies is displaced vertically from each other.

teresting that  $G(\tau)$  is dominated commonly by the 1-ms and the 10- $\mu\text{s}$  components irrespective of  $E_{PL}$ . However, a relative magnitude between them changes with  $E_{PL}$ . Dependences of the peak lifetimes of the 1-ms and the 10- $\mu\text{s}$  components on  $E_{PL}$  at 50 K are summarized in Fig. 8 as in Fig. 5 at 12 K. The peak lifetimes of both com-

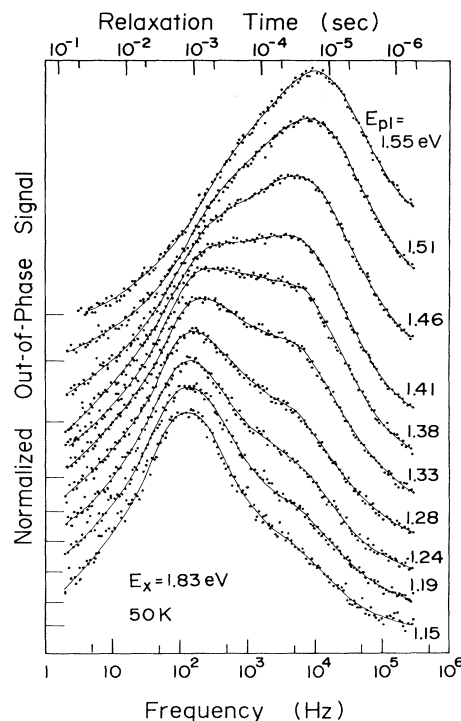


FIG. 7.  $G(\tau)$  for several emission energies at 50 K. Excitation energy is 1.83 eV with the intensity of  $0.11 \text{ mW cm}^{-2}$ .  $G(\tau)$  is normalized to the maximum value and zero level for each  $G(\tau)$  is marked with short line at the left. At 50 K,  $G(\tau)$  becomes a double-peak structure with peaks at around 1 ms and 10  $\mu\text{s}$ .

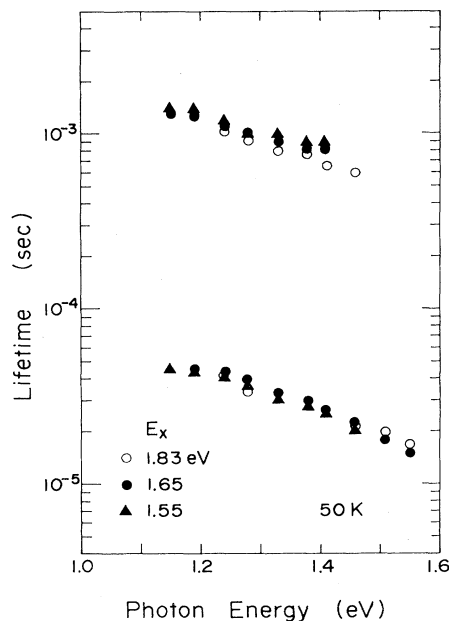


FIG. 8. Peak lifetimes observed in  $G(\tau)$  at 50 K (Fig. 7) as a function of emission energy. Results for other excitation energies of 1.65 and 1.55 eV are also included.

ponents decline monotonically with increasing  $E_{PL}$ . A similar dependence of PL lifetime on the emission energy has been observed at room temperature in porous silicon.<sup>27-29</sup> in which it has been interpreted tentatively as a result of thermally activated hopping of carriers among localized radiative states.<sup>29</sup> However, the results in Figs. 5 and 8 for  $a$ -Si:H are phenomena observed at low temperatures, so it is not sure at present whether the de-

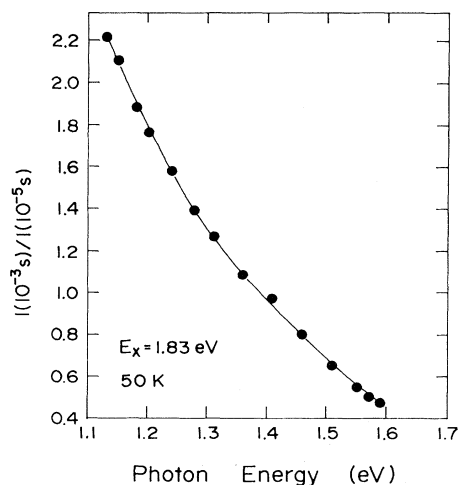


FIG. 9. Relative magnitude between intensities of  $G(\tau)$  at 1 ms and 10  $\mu$ s at 50 K as a function of emission energy.  $G(\tau)$  were evaluated for the 1.83-eV excitation.

crease of the lifetime with  $E_{PL}$  has the same origin as in the porous silicon.

Focusing again on Fig. 7, the relative magnitude of the 1-ms component with respect to the 10- $\mu$ s component decreases with increasing emission energy. A ratio between the relative magnitudes of  $G(\tau)$  for the two lifetime components at 50 K is plotted as a function of  $E_{PL}$  in Fig. 9 when the excitation energy is 1.83 eV. By comparing

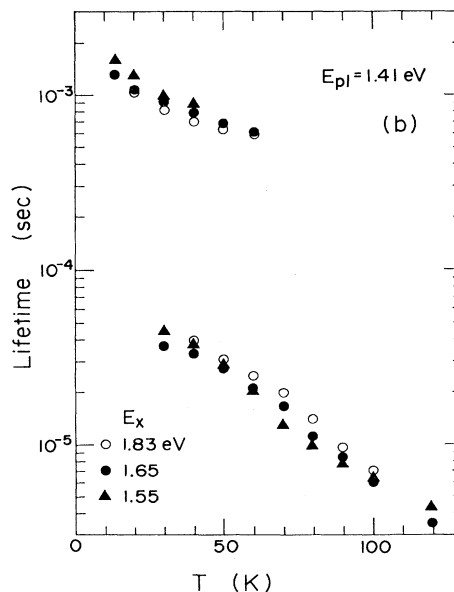
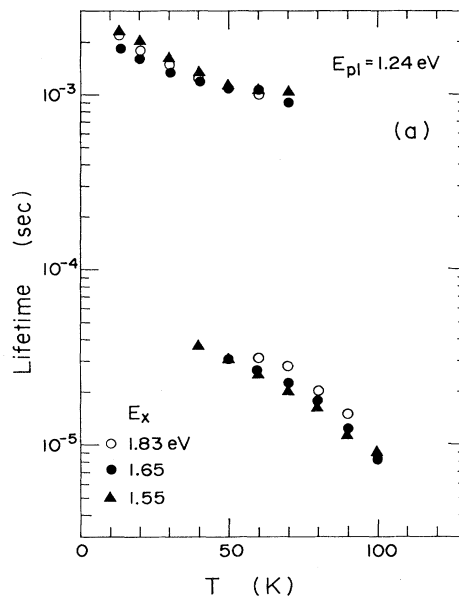


FIG. 10. Temperature dependence of peak lifetimes observed in  $G(\tau)$  for the 1.83-eV excitation (Fig. 1). Emission energies are for (a) 1.24 eV and (b) 1.41 eV. Results for other excitation energies of 1.65 and 1.55 eV are also included. It is obvious from the figures that the lifetime change from 1 ms to 10  $\mu$ s takes place discontinuously with increasing temperature.

$G(\tau)$  at 12 K (Fig. 4) and those at 50 K (Fig. 7), one can understand that some drastic change takes place in  $G(\tau)$  at the low temperatures between 12 and 50 K, although the intensity of monochromatized PL holds a nearly constant value. This feature could be observed more enhancedly for a subband-gap excitation.

By a close look at Fig. 1, it can be noticed that growth of the 10- $\mu$ s component with increasing temperature takes place in a specific manner. The 10- $\mu$ s component does not shift its peak position by separating from the 1-ms component, but it appears distinctively at around 10  $\mu$ s and its magnitude increases with increasing temperature. This feature can be seen more clearly in Figs. 10(a) and 10(b), in which temperature dependences of the peak lifetimes of the 1-ms and 10- $\mu$ s components for  $E_{PL}=1.24$  and 1.41 eV, respectively, against different excitation energies, are summarized. It is obvious that continuity between the 1-ms and 10- $\mu$ s components is completely lacking. Because of the nearly constant intensity of monochromatized PL at low temperatures, it can be said that a part of the 1-ms component will be converted discontinuously into the 10- $\mu$ s component with increasing temperature.

Such characteristics of the lifetime conversion from 1 ms to 10  $\mu$ s with increasing temperature could commonly be seen for as-deposited specimens, irrespective of their native defect density. The lifetime conversion was still observed even in a specimen with the high defect density of  $6 \times 10^{17} \text{ cm}^{-3}$ , although another lifetime component characterized with a lifetime shorter than 1  $\mu$ s was enlarged greatly.

#### E. Influence of defects on $G(\tau)$

At the end of the preceding section, we pointed out that the lifetime conversion between 1 ms and 10  $\mu$ s is not affected by the defect density. However, when the defect density becomes high, the possibility for nonradiative recombination is expected to be enhanced.<sup>30,31</sup> Here, in order to examine more precisely the influence of defect or the nonradiative recombination on the peak positions of respective lifetime components,  $G(\tau)$  for specimens prepared at different substrate temperatures were evaluated for  $E_{PL}=1.41$  eV against the 1.83-eV excitation. Those specimens have different native defect densities ranging from  $10^{15}$  to  $10^{18} \text{ cm}^{-3}$ . As observed in the good quality specimen (Fig. 1), all the specimens exhibited a single-peak structure in  $G(\tau)$  at 13 K, whereas  $G(\tau)$  changed into a double-peak structure at 50 K irrespective of its defect density. The peak lifetimes for the two lifetime components are summarized as a function of defect density  $N_S$  in Figs. 11(a) and 11(b) at 13 K and 11(b) at 50 K. Concerning the 1-ms component which dominates the lifetime distribution at around 10 K, Bort, Carius, and Fuhs,<sup>12</sup> Schubert *et al.*,<sup>18</sup> and Muschik, Fischer, and Schwarz<sup>13</sup> have already reported that the peak lifetime in  $G(\tau)$  evaluated for integrated PL is almost invariant irrespective of the defect density, which has been varied by electron bombardment and subsequent annealings. As in those previous works for integrated PL, the 1-ms component at 13 K does not change its peak lifetime, ir-

respective of the defect density [Fig. 11(a)] and, furthermore, the peak lifetime of the 10- $\mu$ s component as well as that of the 1-ms component were also nearly invariant at 50 K [Fig. 11(b)], too.

The Urbach tail in those specimens broadens from 50 to 80 meV by changing substrate temperature from 100 to 300°C.<sup>32</sup> So it can be said alternatively that the peak lifetimes of both lifetime components do not depend on the Urbach energy. But, following the generally accepted model, it is expected that the larger the Urbach energy, the shorter the separation between paired electron and hole when comparing at a given emission energy among systems having different Urbach energies. Thus the invariance of the peak lifetimes irrespective of the Urbach energy is the second clue casting doubt about the generally accepted model.

Since the PL intensity decreases with increasing defect density, as is well known, a question arises concerning at which stage preceding the radiative recombination the defect quenching or the nonradiative recombination takes

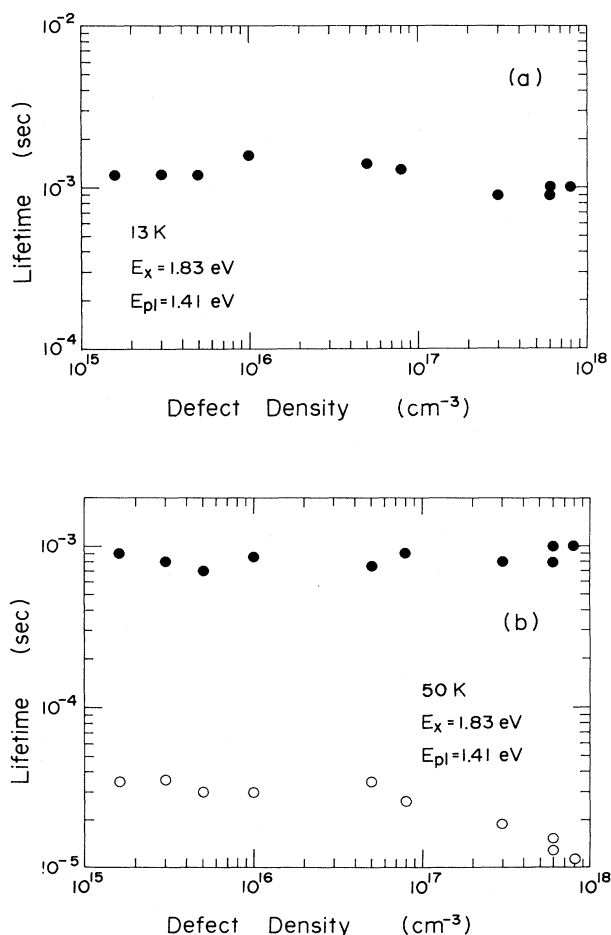


FIG. 11. Peak lifetimes for the 1-ms and 10- $\mu$ s components as a function of defect density at (a) 13 K and (b) 50 K. Excitation and emission energies are 1.83 and 1.41 eV, respectively.



place. It is usually considered that, when the nonradiative recombination competes directly with the radiative recombination, the observed lifetime is expected to shift to a shorter lifetime with increasing defect density.<sup>31</sup> This expectation conflicts with the experimental observations shown in Fig. 11.<sup>12,18</sup> Recently, Schubert *et al.*<sup>18,19</sup> have argued that such a theoretical expectation assuming lifetimes for radiative and nonradiative recombination as constant values is incorrect, and they have tried to explain the invariance of the peak position irrespective of the defect density by taking into account a distribution for nonradiative recombination times as well as that for radiative lifetimes under a circumstance where direct competition between radiative and nonradiative recombination takes place. Here, the direct competition between recombination channels means that an electron-hole pair has a chance to select one of accessible recombination channels. Their simulation of  $G(\tau)$  for a series of different defect densities has agreed apparently well with the experimental ones. However, their assumed distribution for the nonradiative recombination times spreads very widely in lifetime: its full width at half maximum extends approximately over 6 decades.<sup>18</sup> So the assumed distribution for the nonradiative recombination times is nearly a uniform one as compared to that for radiative lifetimes, leading to apparently a uniform suppression of  $G(\tau)$  for a case of purely radiative recombination when the defect density becomes high. It is said that apparent invariance of the peak lifetime in  $G(\tau)$  irrespective of the defect density as simulated by Schubert *et al.*<sup>19</sup> is a result of assuming a broad distribution for the nonradiative recombination times. It is not natural to assume such a very broad distribution for lifetimes in the nonradiative recombination process. Alternatively, it is better to consider that the nonradiative recombination, i.e., the capture of carriers at defects, will happen at a much earlier stage after carrier generation and will compete with capture at some radiative centers.

#### F. Discontinuous change of radiative lifetime with temperature

As we have argued in the previous sections, the invariance of the peak lifetimes of the 1-ms and 10- $\mu$ s components against a change of the emission energy and the Urbach energy casts doubt on the validity of the generally accepted model of recombination between carriers trapped at the tail states. Further contradiction with the model comes from the coexistence of the two lifetime components at low temperatures and the mode of change of  $G(\tau)$  with temperature. Although the coexistence of the 1-ms and the 10- $\mu$ s components in  $G(\tau)$  indicates that there exist two kinds of recombination channels, the most controversial point is what kind of relationship exists between them.

At first glance, growth of the 10- $\mu$ s component with increasing temperature seems as if the recombination path changes from a channel characterized with a lifetime of 1 ms to a channel with 10  $\mu$ s. In general, when direct competition between two recombination channels having respective lifetimes of  $\tau_a$  and  $\tau_b$  happens, only a single

component having a peak at  $\tau_{0b}$  ( $\tau_{0b}^{-1} = \tau_a^{-1} + \tau_b^{-1}$ ) will be observed in the resulting  $G(\tau)$ . A typical example for such a case is a transition between triplet-singlet excitonic states, which has been observed in several materials such as *a*-As<sub>2</sub>Se<sub>3</sub> as well as *c*-As<sub>2</sub>Se<sub>3</sub> (Refs. 33 and 34) and porous silicon.<sup>35–37</sup>  $G(\tau)$  was dominated by a long lifetime component peaked at around 1 ms in *c*-As<sub>2</sub>Se<sub>3</sub> and 1–10 ms in porous silicon as in *a*-Si:H at low enough temperature. The peak lifetimes in  $G(\tau)$  for these materials shortened continuously with increasing temperature, and it was interpreted as a gradual change of recombination channel for excited carriers caused by thermal activation from the triplet state having a long lifetime to the singlet state having a short lifetime.<sup>34–37</sup> At temperatures where a continuous change of the lifetime took place, the recombination rate was limited by a thermal activation rate between the two states, and an energy difference between the singlet and triplet states could be evaluated as an activation energy in the Arrhenius plot of the peak lifetimes.

Direct competition between two recombination channels is observable even in *a*-Si:H as a thermal quenching of PL, in which radiative recombination competes with thermal freeing of trapped carriers. As explained in Sec. III A,  $G(\tau)$  came to be dominated by the lifetime component of the distant-pair recombination characterized by lifetimes of around 10 ms at elevated temperatures. This component started to shift its peak position towards a shorter lifetime above 100 K, where the thermal quenching of PL became efficient. In the course of the thermal quenching of PL,  $G(\tau)$  holds a single-peak structure and its peak position shifted continuously towards a shorter lifetime with increasing temperature.

In contrast to a case of direct competition between the two recombination channels, the two lifetime components coexist in *a*-Si:H at low temperature and a relative magnitude between them varies with temperature, while holding individual peak lifetimes almost invariant. Interestingly, the lifetime changes discontinuously from 1 ms to 10  $\mu$ s with increasing temperature as demonstrated in Fig. 10. Following the above arguments, it can be said that the 1-ms and 10- $\mu$ s components are not competing with each other: they are independent recombination channels having individual characteristic lifetimes.

Recently, Schubert *et al.*<sup>18</sup> have interpreted tentatively within a framework of the usual model of tunneling recombination between tail-state carriers that the growth of the 10- $\mu$ s component with temperature is a result of an accelerating recombination process caused by increasing mobility of tail-state carriers. But this kind of interpretation cannot explain why the lifetime changes discontinuously from 1 ms to 10  $\mu$ s with increasing temperature when the tail states are distributed continuously in energy.

The next argument concerns the mode of the change of lifetime from 1 ms to 10  $\mu$ s with increasing temperature: this observation presents the most serious argument against the generally accepted model. When a photogenerated electron-hole pair recombines by tunneling as expected in the model,<sup>1,6</sup> the calculated separations be-

tween the paired electron and hole just before the recombination are 58 and 35 Å, corresponding to the radiative lifetimes of 1 ms and 10  $\mu$ s, respectively, assuming the localization radius to be 10 Å. Following the model, the lifetime change from 1 ms to 10  $\mu$ s with temperature may be interpreted as follows: the paired electron and hole are once separated from each other as far as about 58 Å at the lowest temperature, whereas the mutual separation within the pair decreases again to a shorter value of 35 Å at elevated temperatures. However, the mutual distance between the paired electron and hole generated by the same photon is expected to enlarge successively after photogeneration according to the model. So if there is a possibility for the pair to recombine radiatively at the shorter separation of 35 Å, it is hard to understand why the electron-hole pair does not recombine at that short separation at the lowest temperature before separating up to 58 Å through thermalization.

Thus the characteristic feature of the discontinuous change of the radiative lifetime seems to be unique to *a*-Si:H and should have some specific origin. As concluded above, the recombination channels characterized by lifetimes of 1 ms and 10  $\mu$ s should operate independently. However, there exists some correlation between them since  $G(\tau)$  or the relative magnitude between the two lifetime components changes at temperatures where the PL intensity holds a nearly constant value.

#### G. Localized luminescence centers

For satisfying those apparently conflicting requirements as well as for overcoming the several arguments against the generally accepted model, a convincing model for explaining the PL in *a*-Si:H must be sought, other than tunneling recombination between carriers trapped at the tail states. Through the measurements of  $G(\tau)$  in this work, it becomes clear that there exist two distinct lifetime components characterized by specific peak lifetimes which are almost invariant, irrespective of the quality of specimens or the experimental conditions. Based on this fact, it is adequate to assume that PL in *a*-Si:H comes from special localized luminescent centers associated with respective lifetime components rather than to regard PL simply as recombination between carriers trapped over whole tail states. Then the characteristic features in  $G(\tau)$  can be understood as follows. The change of the relative magnitude between the two lifetime components with increasing temperature is not due to a change in the recombination channel for excited carriers, but it will be due to a change of relative numbers between the two kinds of luminescent centers with temperature while holding the total numbers of the luminescent sites to be constant, indicating that the nature of the luminescent centers is unstable. It is considered at present that the difference in the lifetime between two luminescent centers reflects the difference in the electron nature which will be induced by some change in structural environment around the luminescent centers. So the change of the lifetime from 1 ms to 10  $\mu$ s with increasing temperature may accompany some structural relaxation around the luminescent centers. The fact that  $G(\tau)$  exhibits a dras-

tic change at temperatures lower than around 50 K will mean that such a structural relaxation takes place even at these low temperatures. Since a part of the 1-ms component is readily converted into the 10- $\mu$ s component with a slight increase of temperature just above 12 K, the 1-ms component seems to be stable only at the lowest temperature in *a*-Si:H. If such a picture is correct, the localized luminescent centers should have their structural counterparts. We are now planning to examine this point with some measurement capable of detecting a change in local structures under the condition for the FRS measurement.

There remains a question concerning the energy difference between the absorption and emission bands. When considering the possibility of structural relaxation of the localized luminescent centers, the concept of self-trapping<sup>38</sup> is preferable for explaining this energy difference. However, the coexistence of the two kinds of lifetime components requires the presence of two types of self-trapping states. This point should be examined further.

When there exist two kinds of luminescent centers characterized by specific lifetimes as noticed above, the PL spectrum in a steady state should consist of spectra corresponding to respective lifetime components. We would like to demonstrate finally that the PL spectrum can be deconvoluted into those for individual lifetime components. As an example, this is done for the spectrum at 50 K against the 1.83-eV excitation by separating the PL intensity at any emission energy into those of respective lifetime components by utilizing the ratio between the two lifetime components given in Fig. 9. The resulting spectra are shown in Fig. 12 where the raw spectrum in a steady state is shown by dots and the

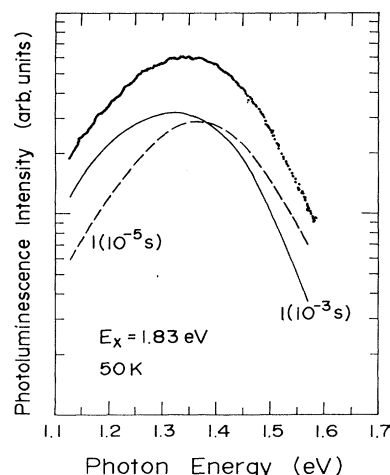


FIG. 12. Deconvolution of photoluminescence spectrum, which is measured in a steady state against the 1.83-eV excitation with the intensity of 0.11 mW cm<sup>-2</sup> at 50 K and is shown by dots, into spectra corresponding to the 1-ms and 10- $\mu$ s lifetime components. They are represented by solid and dashed lines, respectively.

deconvoluted spectra for the 1-ms and the 10- $\mu$ s components are represented by solid and dashed lines, respectively. Roughly speaking, the spectrum for the 10- $\mu$ s component is located at a higher energy with respect to that of the 1-ms component by about 50 meV. This figure says that the difference of  $G(\tau)$  depending on the emission energy is a result of the energetical shift between the deconvoluted spectra corresponding to the two lifetime components. Although the physical meaning for the energetical shift between the spectra is not clear at present, this result demonstrates an advantage of the measurement of the lifetime distribution for monochromatized PL.

#### IV. CONCLUSION

Photoluminescence in *a*-Si:H has been understood for a long time as a result of tunneling recombination between carriers trapped at the tail states after thermalization. However, improved discussions have been proposed recently based on theoretical and experimental studies on microscopic carrier dynamics in the recombination process and have revealed some disagreements with the previously accepted model. In order to reconsider the recombination mechanism in *a*-Si:H more precisely, the lifetime distribution,  $G(\tau)$  was evaluated over a wide lifetime range from  $5.3 \times 10^{-7}$  to  $8.0 \times 10^{-2}$  s using frequency-resolved spectroscopy. In the measurement, the excitation intensity was held low enough to satisfy the condition for geminate-pair recombination at low temperatures and  $G(\tau)$  was evaluated for monochromatized photoluminescence.

The most remarkable feature is that  $G(\tau)$  is dominated by two lifetime components peaked at around 1 ms and 10  $\mu$ s. Those two lifetime components have the characteristics of geminate-pair recombination since their peak

lifetimes are insensitive to a change of the excitation intensity. From a detailed study about these lifetime components under various experimental conditions and for various specimens having different qualities, several contradictions with the generally accepted model emerged. They are the following: (1) the peak lifetime of the 1-ms component is almost invariant at 12 K irrespective of the emission energy. (2) The peak lifetimes for both the 1-ms and 10- $\mu$ s components are also insensitive to a change in the Urbach energy or the defect density. Those results do not reconcile with the generally accepted model, since the lifetime due to tunneling recombination will change significantly even for a slight change of the separation within the recombining electron-hole pair, which is expected to enlarge successively during thermalization in the model. (3) The most serious argument against the generally accepted model is the coexistence of the two lifetime components and the mode of change of the relative magnitude between them with temperature. When there is a possibility for the pair to recombine at a shorter separation corresponding to the lifetime of 10  $\mu$ s, it is difficult to understand following the model why  $G(\tau)$  at 12 K is dominated only by the longer lifetime component peaked at 1 ms.

Based on those arguments against the generally accepted model, we would like to conclude that the photoluminescence in *a*-Si:H comes from localized luminescent centers characterized by specific lifetimes. Since the discontinuous change of the lifetime from 1 ms to 10  $\mu$ s takes place at low temperatures where the photoluminescence intensity itself is almost constant, there must be some correlation between the two luminescent centers. It seems as if a part of the 1-ms component is converted gradually into the 10- $\mu$ s component with increasing temperature. It is speculated at present that the electronic nature of the luminescent center will change with increasing temperature accompanying some structural relaxation around it.

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