MECHANISM OF PHOTOLUMINESCENCE IN HYDROGENATED AMORPHOUS SILICON DETERMINED BY WIDE-BAND QUADRATURE FREQUENCY-RESOLVED SPECTROSCOPY (QFRS)

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A triple-peak photoluminescence (PL) lifetime distribution is found for a-Si:H at low temperature and low photogeneration rates (geminate condition) by quadrature frequency-resolved spectroscopy (QFRS). Using a newly developed wide-band QFRS technique allowing analysis over almost 11 decades in time (2 ns to 160 s), a third lifetime peak, in addition to the well-known double lifetime peaks, is observed in the range 0.1–160 s, and is attributed to distant-pair recombination based on the temperature and generation rate dependence. These results suggest the coexistence of exciton and distant pair recombination even under the geminate condition. At higher temperatures, the distribution becomes a double-peaked one, with peaks due to geminate (non-excitonic) and non-geminate (distant-pair) recombination. The discrepancy between the present results and previous simulations suggests that Coulomb interaction should be included in simulations for a-Si:H, to more precisely account for the experimental observations. The effect of an external magnetic field on the lifetime distribution also supports the involvement of exciton and distant-pair recombination under the geminate condition at low temperature.

(Received December 9, 2004; accepted January 26, 2005)

Keywords: Exciton, Distant-pair, Lifetime, Coulomb interaction, Spin, Magnetic field

1. Introduction

Photoluminescence (PL) is one of most useful properties for studying the recombination mechanisms of photoexcited carriers in amorphous semiconductors. The distribution of PL lifetimes induced by disorder of the amorphous semiconductor can be measured even at low photogeneration rates (G), by means of quadrature frequency-resolved spectroscopy (QFRS) [1]. Boultrop and Dunstan were the first to identify a double-peak PL lifetime distribution for hydrogenated amorphous silicon (a-Si:H) [2], and the phenomenon was later studied in further detail by Ambros et al. [3]. Stachowitz et al. suggested the involvement of an exciton in the double-peak lifetime distribution, attributing the short-lived (~µsec) component to a singlet exciton and the long-lived (~ msec) component to a triplet exciton [4]. Our group observed a double-peak lifetime distribution for a-Ge:H and chalcogenide glasses (e.g., g-As2S3 and a-Se), with the results supporting the exciton model [5-7]. Using a dual-phase double lock-in (DPDL) QFRS technique to measure the PL lifetime in the nanosecond region, our group has also confirmed the absence of a nanosecond peak in the lifetime distribution of a-Si:H [8], and shown that the singlet exciton lifetime (~µsec), much longer than the radiative dipole-transition time (τ0 ≈ 10−8 s), can be attributed to a discrepancy between the orbital sizes of electrons and holes in the determination of the radiative transition rate [9].

Despite this progress, controversy remains as to whether PL in a-Si:H is due to geminate or non-geminate (distant-pair) recombination. Bort et al. [10] discovered a geminate condition at around

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$G \approx 10^{19}$ cm$^{-3}$ s$^{-1}$, below which the peak lifetime ($\tau$) is independent of $G$ such that the steady-state carrier density $n_s = G \tau$ is proportional to $G$. The intensity of the light-induced electron spin-resonance (LESR), analogous to $n_s$, is also known to be sub-linearly dependent on $G$, with an approximate relation $n_s \approx G^{0.2}$ [11]. The distant-pair recombination model predicts this sub-linear $G$-dependence of the LERS intensity, but cannot explain the $G$-independent lifetime distribution below the geminate condition [12].

By extending the lifetime detection limits of conventional QFRS, our group investigated the lifetime distribution of a-Si:H over almost 11 decades of time (2 ns to 160 s) and discovered a third peak at 0.1–100 s. This third lifetime peak decreased continuously with increasing $G$, even far below the geminate condition, demonstrating a sublinear $G$-dependence of $n_s$ in agreement with the LERS results [13].

The lifetime distributions are further investigated in this study and compared with the simulations by Levin et al. [14]. The distribution is revealed to be triple-peak at low temperatures and double-peak at high temperatures. The effect of a magnetic field on the PL lifetime distribution of a-Si:H at low temperature is also examined. The results support the involvement of exciton and distant-pair recombination in PL generation in a-Si:H at low temperatures, under the geminate condition.

2. Experimental details

A film of a-Si:H with a defect density of $2 \times 10^{16}$ cm$^{-3}$ was deposited to a thickness of 1.1 µm on a roughened Al substrate. Photoluminescence was excited by irradiation with a 2.33 or 1.81 eV low-noise laser, and the integrated or dispersed PL was detected by an infrared (IR) photomultiplier tube (PMT; R5509-42, Hamamatsu) at photon energies of 0.89 eV or greater. The PL lifetime distributions were measured by QFRS over almost 11 decades in time, from 2 ns to 160 s. The shorter (up to ~ μsec) lifetimes were measured by the DPDL QFRS technique, as illustrated in Fig. 1 [8]. An electro-optic modulator (EOM: 50, Conoptics) was employed to modulate the laser beam at up to 80 MHz, instead of the usual acousto-optic modulator (AOM). As electromagnetic interference between the rf digital lock-in amplifier (SR844, Stanford Research System) and the EOM driver became serious at rf frequencies ($\omega$) above 10 MHz, the laser beam was chopped at 8 Hz ($\omega_m$) and the PL signal was discriminated from the interference by lock-in detection at $\omega_m$. The doubly modulated PL signal is expressed as

$$S(t) = R(\omega) \sin(\omega t - \theta(\omega)) \cdot \sin(\omega_m t)$$  \hspace{1cm} (1)$$

where $R(\omega)$ and $\theta(\omega)$ are the PL amplitude and phase at $\omega$, respectively. The lifetime distribution is principally given by the quadrature part ($R(\omega)\sin\theta(\omega)$) in QFRS. However, as $R(\omega)$ and $\theta(\omega)$ include components of the instrumental response due to the EOM, PMT, and optical and electrical lengths, the quadrature signal was calibrated as mentioned later.

![Fig. 1. Schematic diagram of the DPDL QFRS technique (C, optical chopper; FG, function generator; PA, preamplifier; PMT, photomultiplier tube; PC, personal computer).](image-url)
The rf lock-in amplifier was locked at \( \omega_0 \) and had a low-pass filter (LPF) time constant \( \gg \omega^2 \) and \( \ll \omega_m^{-1} \). The X- and Y-channel outputs were sinusoidal, with frequency \( \omega_m \), as given by

\[
\begin{align*}
X(t) &= \frac{1}{2} R(\omega) \cos \theta(\omega) \sin(\omega_m t) \\
Y(t) &= \frac{1}{2} R(\omega) \sin \theta(\omega) \sin(\omega_m t)
\end{align*}
\]

These signals were again synchronously detected at \( \omega_m \) using two digital lock-in amplifiers (SR830) with LPF time constants of much greater than \( \omega_m^{-1} \). A phase shift \( \psi \) was inserted between the chopped light and the synchronous signal of the chopper driver (Fig. 1). Eliminating \( \psi \) from the X- and Y-channel outputs of the two lock-in amplifiers (\( X_t \), \( X_y \), \( Y_t \) and \( Y_y \)), \( R(\omega) \) and \( \theta(\omega) \) could be obtained as follows.

\[
\begin{align*}
R(\omega) &= 4 \sqrt{X_t^2 + X_y^2 + Y_t^2 + Y_y^2} \\
\theta(\omega) &= \frac{1}{2} \left( \tan^{-1} \frac{X_t + X_y}{X_t - X_y} + \tan^{-1} \frac{Y_t - Y_y}{Y_t + Y_y} \right)
\end{align*}
\]

Measuring the instrumental \( R'(\omega) \) and \( \theta'(\omega) \) of the modulated laser light reflected at an Al plate instead of the sample, the intrinsic QFRS signal of PL was obtained as

\[
R(\omega) \sin(\theta(\omega) - \theta'(\omega)) / R'(\omega)
\]

The DPDL QFRS technique has been shown to resolve PL lifetimes \( \sim \) nsec, through observations of the fluorescence of Rhodamine 6G, which has a PL lifetime of 4 ns [15].

Longer lifetimes up to 160 s were measured using an AOM coupled with the SR830 digital lock-in amplifier in internal mode, with synchronous filtering to avoid phase noise. Fibre optics was employed to avoid magnetic field disturbances at the PMT. PL lifetime distributions were also obtained under external magnetic fields of up to 0.9 T for an a-Si:H film deposited on a Corning 7059 glass substrate, by illuminating the glass side of the sample and detecting the PL from the opposite side.

### 3. Results and discussion

The results of the present ultra wide-band QFRS measurements, extending far below the geminate recombination condition (\( G < 10^{19} \text{ cm}^{-3} \text{ s}^{-1} \)), are shown in Fig. 2, for photoexcitation energies (\( E_X \)) of 2.33 eV (above-bandgap excitation) and 1.81 eV (bandgap excitation). Darkened areas in the figure indicate lifetime ranges extended by the present work. The PL lifetime distributions are triple-peak at \( T \leq 20 \text{ K} \), but become double-peak (\( \tau_g \) and \( \tau_{ng} \)) at approximately 100 K, regardless of \( E_X \). This can be explained by the coexistence of exciton (i.e., geminate pair) and non-geminate (i.e., distant-pair) recombination at low temperatures, and geminate (non-excitonic) and non-geminate recombination at higher temperatures [13]. The exciton model attributes the short-lifetime peak \( \tau_s \) to a singlet exciton and the long-lifetime peak \( \tau_l \) to a triplet exciton at lower temperatures [4-7]. It has been reported for a-Si:H that self-trapped holes become unstable with increasing temperature, accompanied by a disappearance of the triplet self-trapped exciton at around 85 K [16]. This corresponds to the disappearance of the \( \tau_l \) peak at around 80 K in Fig. 2. The smaller binding energy of the singlet exciton, related to the exchange energy, is responsible for the disappearance of the \( \tau_s \) peak at \( T \geq 30 \text{ K} \). At approximately 40 K, \( \tau_g \) develops as a shoulder between \( \tau_s \) and \( \tau_{ng} \), growing to a new peak at higher temperature [13].

The third peak \( \tau_{ng} \) occurring at 1 s at 3.7 K, may have been overlooked in the past, due to the limitations of QFRS at very low frequencies. This third peak is attributable to non-geminate or distant-pair recombination [13]. It is selectively enhanced with increasing temperature, leading to the establishment of a double-peak distribution with maxima at \( \tau_g \) and \( \tau_{ng} \) at around 100 K under both excitation conditions.
Fig. 2. QFRS spectra of a-Si:H photoexcited at (a) $E_X = 2.33$ eV with $G \approx 1.0 \times 10^{17} \text{cm}^{-3}\text{s}^{-1}$ and (b) $E_X = 1.81$ eV with $G \approx 5.0 \times 10^{15} \text{cm}^{-3}\text{s}^{-1}$. Darkened regions are lifetime ranges extended by the present work.

Fig. 3 shows plots of the peak lifetime $\tau_{np}$ against $G$ at 3.7 K, for comparison with previously reported values of $\tau_S$ and $\tau_T$ [9]. The continuous reduction of $\tau_{np}$ with increasing $G$ suggests the occurrence of non-geminate recombination, even far below the geminate condition ($G < 10^{19} \text{cm}^{-3}\text{s}^{-1}$). The $\tau_{np}$ fit to the curve was calculated from the balance equation determining the steady-state carrier density $n_e$ [17,18] assuming a radiative dipole transition time $\tau_0$ of $10^{-8}$ s, an effective electron localization radius $a$ of 10 Å, and ignoring the radii of holes. As $G$ increases from $10^{15}$ to $10^{17} \text{cm}^{-3}\text{s}^{-1}$, at which the a-Si:H film starts photodegrading, $\tau_{np}$ continuously decreases even below the geminate condition where $\tau_S$ and $\tau_T$ remain constant.

Fig. 3. Peak lifetimes $\tau_S$, $\tau_T$ and $\tau_{np}$ as functions of $G$ at 3.7 K with $E_X$ of (○) 2.33 and (●) 1.81 eV.

Similar plots for the double-peak lifetime distribution at 100 K are shown in Fig. 4. As $G$ increases, the lifetime $\tau_{np}$ continuously decreases and finally merges with $\tau_S$, which remains constant against $G$. The curve of $\tau_{np}$ as a function of $G$, obtained from the balance equation assuming $a = 42$ Å, fits the plots well, although the validity of the equation at high temperature is unclear, as both down-hops and up-hops of photoexcited carriers will occur in the tails and non-radiative recombination can no longer be ignored. The $\tau_S$ peak is situated between $\tau_S$ and $\tau_T$ (Fig. 2) and remains constant with increasing $G$ up to $\approx 10^{19} \text{cm}^{-3}\text{s}^{-1}$ (Fig. 4). Therefore, the peak at $\tau_S$ is thought...
to originate from geminate recombination at high temperature, where thermal disturbance prevents an electron-hole pair from forming an exciton, even though the pair is geminate. The value of $\tau_g$ between $10^{-5}$ and $10^{-4}$ s is in agreement with that given by $\tau_g(v_0T_0)^{3/4} = 1.6 \times 10^{-5}$ s based on electron-hole separation that maximises the geminate recombination function assuming a phonon frequency $v_0$ of $10^{12}$ s$^{-1}$ order, although the temperature is not low ($T = 100$ K) [17].

![Graph](image)

**Fig. 4.** Peak lifetimes $\tau_g$ and $\tau_{ng}$ as functions of $G$ at 100 K with $E_X = (\circ) 2.33$ eV and (●) 1.81 eV.

The occurrence of geminate recombination at temperatures as high as 100 K, and the stronger non-geminate component $\tau_{ng}$ at $E_X = 2.33$ eV compared to $E_X = 1.81$ eV, can be explained using a classical Onsager model. It is assumed that an electron is excited to an energy $E_X - E_g$ above the mobility gap $E_g$ and a hole is fixed at the location where the electron-hole pair was generated. Emitting phonons of energy $h\nu_0$, the electron will diffuse a distance $r_d$ given by [19]

$$r_d = \left[ \frac{D(E_E - E_g + \frac{e^2}{4\pi \varepsilon r_d})^{3/2}}{h \nu_0^2} \right]$$  \hspace{1cm} (5)

before it is thermalised. Here, $D$ is the electron diffusion constant given by $\mu kT/e$ in terms of the electron mobility $\mu$, and $\varepsilon$ is the dielectric constant of a-Si:H. After thermalisation, the electron-hole Coulomb energy becomes $e^2/4\pi \varepsilon r_d$. If this is lower than the thermal energy $kT$, the electron will escape from the hole and recombine with another one (non-geminate or distant-pair recombination). If $e^2/4\pi \varepsilon r_d > kT$, the electron cannot escape from the hole created by the photon, resulting in geminate recombination. The electron-escape probability can be expressed as

$$p = \exp \left( -\frac{e^2}{4\pi \varepsilon r_d kT} \right)$$  \hspace{1cm} (6)

The relative quantum efficiency (QE) $\eta$ is obtained by dividing the area of the $\tau_{ng}$ component by the total area of the $\tau_S$, $\tau_T$, and $\tau_{ng}$ components at low temperature, and by the total area of the $\tau_S$ and $\tau_{ng}$ components at high temperature, as in Fig. 2. The values obtained are plotted as a function of $T$ in Fig. 5. The electron-escape probability $p$ is estimated using $\mu = 10$ cm$^2$/V s and $E_g$ as obtained from Tauc plots for various temperatures. The quantum efficiency of distant-pair recombination and the electron-escape probability increase with $T$, and both $\eta$ and $p$ are larger at higher $E_X$. Thus, although nonradiative recombination at high temperature is ignored, the $T$ and $E_X$ dependences of the $\tau_{ng}$ component can be explained by the distant-pair model. The discrepancy between $p$ and the measured $\eta$ at low $T$ is due largely to a disregard for hopping diffusion in the band tails in Eq. (5).

Fig. 5 also shows that the QE of geminate or excitonic recombination is about 60%, compared with the value of 20% predicted by simulation for low temperature and a photogeneration
rate of $G \approx 10^{17}$ cm$^{-3}$ s$^{-1}$ [14], and that geminate recombination takes place even at temperatures greater than 100 K (Fig. 2). The discrepancy between the present experimental results and the theoretical calculations is probably due to the omission of Coulomb interaction between electrons and holes in the simulations [14]. As Coulomb attraction is essential for the formation of the exciton, spin effects as well as Coulomb interaction should be included in order to obtain a more complete theoretical description of the PL lifetime distributions for a-Si:H.

The steady-state carrier density $n_s = n_{gg} G \tau_{gg}$ calculated using $n_{gg}$ is proportional to $G^{0.17}$ and agrees with the LESR results reported previously [13]. The variation of $n_s$ with temperature also agrees quite well with the temperature dependence of the LESR data [13]. These results support the notion that the $\tau_{gg}$ component originates from distant-pair recombination.

Fig. 6 shows the PL spectra of the QFRS signals obtained for a-Si:H at 3.7 K, at frequencies of 72.3 kHz, 49.7 Hz and 0.280 Hz, corresponding to $\tau_S \approx 2.2$ ms, $\tau_T \approx 3.2$ ms and $\tau_{gg} \approx 0.57$ s, respectively. The PL peak associated with the short-lived component $\tau_S$ occurs at a photon energy about 40 meV higher than that for the long-lived component $\tau_T$. This difference is attributable to the exchange energy as reported previously [9]. The PL spectrum of $\tau_{gg}$ peaks at a slightly lower photon energy than that of $\tau_T$. Therefore the electron–hole state is deep in the tail before recombining with a lifetime $\tau_{gg}$. On the other hand, LESR only measures some fraction of the light-induced carriers in the tails (i.e., deeply trapped carriers [20]). Thus the PL spectrum of the $\tau_{gg}$ component obtained here can be correlated with the LESR signal, revealing that the $\tau_{gg}$ component appears to obey the distant-pair recombination model.

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**Fig. 5.** Plots of $\eta$ and $p$ as functions of $T$ at $E_X$ of (●, solid) 2.33 eV with $G \approx 1.0 \times 10^{17}$ cm$^{-3}$ s$^{-1}$ and $E_X$ of (○, dotted) 1.81 eV with $G \approx 5.0 \times 10^{15}$ cm$^{-3}$ s$^{-1}$.

**Fig. 6.** QFRS PL spectra for the $\tau_S$ (72.3 kHz), $\tau_T$ (49.7 Hz) and $\tau_{gg}$ (0.280 Hz) lifetime peaks with $G \approx 2.8 \times 10^{17}$ cm$^{-3}$ s$^{-1}$. All the peaks of spectra are normalised to unity.
The dependence of the PL lifetime distribution of a-Si:H at 3.7 K on the intensity of an external magnetic field is shown in Fig. 7. Application of a 0.9 T magnetic field weakens the QFRS signal of the $\tau_{ng}$ component, and enhances that of the $\tau_f$ component, but has little influence on the $\tau_s$ component (Fig. 7(a)). This tendency is clarified in Fig. 7(b), which shows plots of the QFRS signals of the three components measured at 2 $\mu$s, 3 ms and 80 ms as functions of the magnetic field intensity.

![Figure 7](image)

**Fig. 7.** (a) Lifetime distributions at 3.7 K and $G = 7.7 \times 10^{10} \text{cm}^{-3}\text{s}^{-1}$, with (c) and without (●) the application of a 0.9 T magnetic field. (b) QFRS signals of the $\tau_0$, $\tau_f$ and $\tau_{ng}$ components as functions of the magnetic field intensity.

Based on transient PL, Robins and Kastner observed an enhancement of the triplet exciton recombination and a decrease in distant-pair recombination for both amorphous and crystalline $\text{As}_2\text{Se}_3$ under a magnetic field, and suggested an explanation for the results [21]. They observed no singlet exciton state in this material, which our group has also confirmed by DPDQ QFRS [6]. In our analyses, the application of a 0.9 T external magnetic field to a-$\text{As}_2\text{Se}_3$ was also shown to strengthen the $\tau_f$ component and weaken the $\tau_{ng}$ component.

Following [21], the results shown in Fig. 7 are explained in terms of an excitonic model for the $\tau_0$ and $\tau_f$ components. As a singlet exciton has a total spin of zero ($S = 0$), the $\tau_0$ component assigned to the singlet exciton is unaffected by the application of a magnetic field. The three-fold degeneracy of the triplet exciton ($S = 1$) is removed by the anisotropic spin-spin interaction and spin-orbit interaction, causing a zero-field splitting in the absence of an external magnetic field. Each of the three eigenstates couples differently with the excited singlet states, allowing relaxation to the singlet ground state with lifetimes specific to each state. Furthermore, the Zeeman interaction with the magnetic field mixes the zero-field eigenstates and further separates their energies, thereby changing the lifetime of the triplet exciton. Thus, the enhancement of the $\tau_f$ component under a magnetic field is due to the involvement of triplet exciton recombination in a-Si:H, similar to the case of a-$\text{As}_2\text{Se}_3$.

In the absence of an external magnetic field, the spin directions of the distant pair are completely random. That is, the total spin $S$ is not a good quantum number because of the lack of correlation in the pair. When a magnetic field is applied, the spins of the carriers will have a finite polarization [22]. Then, as the spin-aligned state which is energetically favoured under a magnetic field is spin-forbidden to recombine, the recombination rate will decrease. In contrast, the formation of a pair in an anti-parallel spin-allowed state is slightly inhibited by the magnetic field. Overall, the distant-pair recombination rate will be reduced by the application of an external magnetic field, resulting in the weakening of the $\tau_{ng}$ component seen in Fig. 7.

## 4. Conclusions

A triple-peak PL lifetime distribution for a-Si:H, in addition to the well-known double-peak distribution, was observed under the geminate condition at low temperatures, by ultra wide-band
QFRS. The triple-peak lifetime distribution indicates the involvement of a distant pair in recombination events, in addition to singlet and triplet excitons. The lifetime of the distant-pair recombination as a function of the generation rate can be accurately predicted by the balance equation over the full range of $G$, even at higher temperatures. The temperature dependence of the triple-peak lifetime distribution was found to be explicable by a model involving three different types of recombination. At higher temperatures (ca. 100 K), the distribution becomes the double-peak distribution, with geminate and non-geminate recombination peaks. Although excitons are no longer formed above 100 K, the geminate pair persists. These results indicated that Coulomb interaction, essential for the formation of both excitons and geminate pairs, should be included in simulations of the PL lifetime distributions for a-Si:H. The application of a 0.9 T magnetic field was found to weaken distant-pair recombination and enhance triplet exciton recombination, yet was found to have little influence on singlet exciton recombination. These observations were well explained by spin effects on electron-hole pairs.

Acknowledgements

This work was carried out in cooperation with Gifu University (Prof. K. Shimakawa). The authors thank the Promotion and Mutual Aid Corporation for Private Schools of Japan for financial assistance from the Scientific Research Promotion Fund.

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