

RADIATIVE LIFETIME AND SPONTANEOUS EMISSION IN AMORPHOUS SEMICONDUCTORS

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A theory for the spontaneous emission due to radiative recombination of excitons in amorphous semiconductors is presented. Four possibilities are considered: (i) both the excited electron and hole are in their extended states, (ii) the electron is in the extended and the hole in tail states, (iii) the electron is in tail and the hole in extended states and (iv) both are in their tail states. It is found that the singlet excitonic radiative recombination for possibilities (i)-(iii) occurs in the nanosecond (ns) range, and that for possibility (iv) occurs in the microsecond (μ s) range. Results are compared with recent experiments and other theories.

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1. Introduction

Much interest has been devoted to the study of the photoluminescence (PL) in hydrogenated amorphous silicon (a-Si:H) in the last two decades [1], because it provides direct information about the electronic states and carrier dynamics in the material. Some controversies have recently occurred, concerning the magnitude of the radiative lifetime in a-Si:H. Using time-resolved spectroscopy (TRS), Wilson *et al.* [2] observed PL peaks with radiative lifetimes in the nanosecond (ns), microsecond (μ s) and millisecond (ms) time ranges in a-Si:H, at a temperature of 15 K. In contrast to this, using quadrature frequency resolved spectroscopy (QFRS), other groups [3-6] have observed only a double peak structure of PL in a-Si:H at liquid helium temperature. One peak appears at a short time, in the μ s range, and the other in the ms range. Using an effective mass approach, a theory for the excitonic states in amorphous semiconductors has been developed by Singh *et al.* [7] and the occurrence of the double peak structure has successfully been explained. The theory also enables one to calculate the energy difference between the singlet and triplet states, and it has been successfully applied to both a-Si:H and a-Ge:H.

In this paper, a theory for the spontaneous emission and radiative lifetime due to recombination of excitons in amorphous semiconductors is presented. Four possibilities are considered: (i) both the excited electron and hole are in their extended states, (ii) the electron is in the extended and the hole in tail states, (iii) the electron is in tail and the hole in extended states and (iv) both are in their tail states. It is assumed that an exciton can be formed between an excited electron (e) and hole (h) pair, by a photon of energy higher than the optical gap energy, such that initially both the charge carriers are in their extended states. It is further assumed that as an exciton so created relaxes downward to tail states, it retains its identified excitonic Bohr radius and binding energy, until the charge carriers recombine radiatively by emitting a photon. Thus, the excitonic relaxation is restricted by the excitonic internal energy quantum states and therefore it is not as fast

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as the thermal relaxation of free carriers (not bound in excitons). We have derived the rates of spontaneous emission within the two-level approximation, and under both non-equilibrium and equilibrium conditions. It is found that the rates derived are not applicable for studying the excitonic PL radiative lifetime in amorphous semiconductors. Rates derived under equilibrium are used to calculate the PL radiative lifetime in a-Si:H. It is shown that the radiative recombination directly from the extended-to-extended states is much faster than the radiative recombination from the tail-to-tail states. The radiative lifetime is prolonged for tail-to-tail state transitions, due to the localization of the charge carriers.

2. Transition matrix element for recombination

We consider an exciton excited such that its electron (e) is in the conduction states and hole (h) in the valence states, and then they recombine radiatively by emitting a photon due to the exciton-photon interaction. Using the centre of mass, $\mathbf{R}_x = \frac{m_e^* \mathbf{r}_e + m_h^* \mathbf{r}_h}{M}$ and relative $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$ coordinate transformations, the interaction operator between a pair of excited e and h and a photon can be transformed into:

$$\hat{H}_{xp} = -\frac{e}{\mu_x} \mathbf{A} \cdot \mathbf{p}, \quad (1)$$

where $\mathbf{A} = \sum_{\lambda} \left(\frac{\hbar}{2\epsilon_0 n^2 V \omega_{\lambda}} \right)^{1/2} [c_{\lambda}^+ \hat{\epsilon}_{\lambda} + c.c.]$ is the vector potential, n the refractive index, V the volume of the material, ω_{λ} the frequency, c_{λ}^+ the creation operator of a photon in a mode λ , and $\hat{\epsilon}_{\lambda}$ the unit polarization vector of photons. $\mathbf{p} = -i\hbar \nabla_r$ is the linear momentum associated with relative motion between e and h in an exciton, and μ_x is the excitonic reduced mass ($\mu_x^{-1} = m_e^{*-1} + m_h^{*-1}$). The operator in Eq. (1) does not depend on the centre of mass motion of the exciton. The second term of $\mathbf{A}$ corresponds to the absorption, and will not be considered hereafter.

For amorphous solids, it is important to distinguish whether the excited charge carriers are created in the extended states or tail states [7-9]. For studying PL, therefore, it is important to identify which one of the above four possibilities we are dealing with. This is because charge carriers have different wave functions, effective masses, and hence different excitonic Bohr radii in their extended and tail states [7-9].

The field operator $\hat{\psi}_c(\mathbf{r}_e)$ of an electron in the conduction states can be written as:

$$\hat{\psi}_c(\mathbf{r}_e) = N^{-1/2} \sum_l \exp(i\mathbf{t}_e \cdot \mathbf{R}_l) \phi_l(\mathbf{r}_e) a_{cl}, \quad (2)$$

where N is the number of atoms in the sample, $\mathbf{R}_l$ is the position vector of an atomic site at which the electron is created, $\phi_l(\mathbf{r}_e)$ is the wave function of an electron at the excited site l , $\mathbf{r}_e$ is the position coordinate of the electron with respect to site l , and $\mathbf{t}_e$ is given by:

$$|\mathbf{t}_e| = t_e = \sqrt{2m_e^*(E_e - E_c)}/\hbar, \quad (3)$$

where E_e is the energy of the electron and E_c is that of the electronic mobility edge. a_{cl} is the annihilation operator of an electron at a site l in the conduction c states. According to Eq. (3), if the electron energy E_e is above the mobility edge, then the electron moves as a free particle in the conduction extended states, but if $E_e < E_c$ the electron gets localized as t_e becomes imaginary and the

envelope function becomes exponentially decreasing. Likewise, the field operator, $\hat{\psi}_v(\mathbf{r}_h)$, of a hole excited with an energy E_h in the valence states can be written as [1,7-9]:

$$\hat{\psi}_v(\mathbf{r}_h) = N^{-1/2} \sum_l \exp(-i\mathbf{t}_h \cdot \mathbf{R}_l) \phi_l(\mathbf{r}_h) d_{vl}, \quad d_{vl} = a_{vl}^+, \quad (4)$$

where $|\mathbf{t}_h| = t_h = \sqrt{2m_h^*(E_v - E_h)}/\hbar$, with E_v being the energy of the valence band mobility edge, and d_{vl} annihilation operator of a hole in the valence states, v , with energy E_h .

We now consider a transition from an initial state with one exciton created by exciting an electron at site, say, l and a hole at site m (any other site is assumed to have zero excitons), and no photons to a final state with no excitons but one photon emitted in a mode λ . The initial state, $|i\rangle$ can be expressed in terms of the occupation numbers as: $|i\rangle = |0, 0, \dots, 1_{\{cl, vm\}}, 0, 0, \dots, 0\rangle$ and the final state as: $|f\rangle = |0\rangle|0, 0, \dots, 1_\lambda, 0, 0, \dots, 0\rangle = |0\rangle|1\rangle$. Using Eqs.(1), (2) and (4), the transition matrix element is then obtained as:

$$\langle f | \hat{H}_{xp} | i \rangle = -\frac{e}{\mu_x} \sum_\lambda \left(\frac{\hbar}{2\epsilon_0 n^2 V \omega_\lambda} \right)^{1/2} p_{cv}, \quad (5)$$

where

$$p_{cv} = N^{-1} \sum_l \sum_m \exp[-i\mathbf{t}_e \cdot \mathbf{R}_l^e] \exp[-i\mathbf{t}_h \cdot \mathbf{R}_m^h] Z_{lm\lambda}, \quad (6)$$

and

$$Z_{lm\lambda} = \int \phi_l^*(\mathbf{r}_e) \hat{\epsilon}_\lambda \cdot \mathbf{p} \phi_m^*(\mathbf{r}_h) d\mathbf{r}_e d\mathbf{r}_h. \quad (7)$$

Two approaches have been used to evaluate the integral $Z_{lm\lambda}$ in amorphous solids. In the first approach, it is assumed to be a constant and independent of the photon energy as, $Z_{lm\lambda} = Z_1 = \pi\hbar(L/V)^{1/2}$, where L is the average bond length in a sample. In the second approach, the integral is evaluated within the dipole approximation [1] as, $Z_{lm\lambda} = Z_2 = i\omega \mu_x r_{eh}$, where $\hbar\omega = E'_c - E'_v$ is the emitted photon energy and r_{eh} is the average separation between the excited electron-hole pair, which can also be assumed to be site independent. In the case of excitons, it can be easily assumed that $r_{eh} = a_{ex}$. Thus, through both approaches the integral becomes site independent and can be taken out of the summation.

3. Rate of recombination

Using Eq. (5) and applying Fermi's golden rule, the rate of spontaneous emission R_{sp} (s^{-1}) can be written as [10,11]:

$$R_{sp} = \frac{2\pi e^2}{\mu_x^2} \left(\frac{1}{2\epsilon_0 n^2 V \omega_\lambda} \right) \sum_{E'_c, E'_v} |p_{cv}|^2 f_c f_v \delta(E'_c - E'_v - \hbar\omega_\lambda), \quad (8)$$

where f_c and f_v are the probabilities of occupation of an electron in the conduction and a hole in the valence states, respectively. Eq. (8) can be evaluated under several conditions, as described below.

3.1. The two level approximation

This is valid only for atomic systems where an electron takes a downward transition from an excited state to the ground state; no energy bands are involved. In this case, $f_c = f_v = 1$ and then denoting the corresponding rate of spontaneous emission by R_{sp12} , we get:

$$R_{sp12} = \frac{4\kappa e^2 \sqrt{\epsilon} \omega^3 |r|^2}{3\hbar c^3}, \quad (9)$$

where $\hbar\omega = E_2 - E_1$, which is the energy difference between the excited E_2 and ground E_1 states, $|r|$ is the average dipole length, $\kappa = 1/(4\pi\epsilon_0)$, c is the velocity of light and ϵ is the static dielectric constant. In this case, the transition matrix element is derived using the dipole approximation that gives $Z_{lm\lambda} = Z_2$, as obtained above. The rate in Eq. (9) is well known [2], and is independent of the electron and hole masses and temperature. As only two discrete energy levels are considered, the density of states is not used in the derivation. Therefore, although using $|r| = a_{ex}$, the excitonic Bohr radius, the rate R_{sp12} has been applied for a-Si:H [2] it should only be used for calculating the radiative recombination in isolated atoms, not in condensed matter.

3.2 Recombination in amorphous solids in non-equilibrium

It may be argued that the short-time photoluminescence can occur before the system reaches thermal equilibrium, and therefore no equilibrium distribution functions can be used for the excited charge carriers. In this case, one should also use $f_c = f_v = 1$ in Eq. (8). However, as the carriers are excited by the same energy photons, even in a short time delay, they may be expected to be in thermal equilibrium among themselves, but not necessarily with the lattice. Then they will relax according to an equilibrium distribution. As the electronic states of amorphous solids include the localized tail states, it is more appropriate to use the Maxwell-Boltzmann distribution for this situation. We will first consider radiative recombination in non-equilibrium, and then in equilibrium.

For the possibilities (i)–(iii), using Eq. (6) we obtain $|p_{cv}|^2 = |Z_i|^2$, $i = 1, 2$, from the two approaches and then the corresponding rates of spontaneous emission, denoted by R_{spni} , become:

$$R_{spn1} = \frac{\pi^2 \hbar^2 e^2 L}{\epsilon_0 n^2 \omega \mu_x^2 V^2} \sum_{E'_c, E'_v} \delta(E'_c - E'_v - \hbar\omega), \quad (10)$$

$$R_{spn2} = \frac{\pi^2 e^2 a_{ex}^2 \omega}{\epsilon_0 n^2 \hbar^2 V} \sum_{E'_c, E'_v} \delta(E'_c - E'_v - \hbar\omega), \quad (11)$$

where the subscript spn denotes the rate of spontaneous emission under non-equilibrium conditions. For evaluating the summations over E'_c and E'_v in Eqs. (10) and (11), the normal approach is to convert it into an integral by using the excitonic density of states, which can be obtained as follows. Using the effective mass approximation, the joint excitonic density of states is obtained as

$$g_x = \frac{V}{2\pi^2} \left(\frac{2\mu_x}{\hbar^2} \right)^{3/2} (E_x - E_0)^{1/2}, \text{ where } E_x \text{ is the energy of an exciton state. Using this, the}$$

summation in Eqs. (10) and (11) can be converted into an integral, which can be easily evaluated.

The rates are then obtained as: $R_{spn1}^J = \frac{\pi e^2 L}{\epsilon_0 n^2 \omega V \hbar} \left(\sqrt{\frac{2}{\mu_x}} \right) (\hbar\omega - E_0)^{1/2} \Theta(\hbar\omega - E_0)$ and

$$R_{spn2}^J = \frac{\sqrt{2} \mu_x^{3/2} e^2 a_{ex}^2}{\pi \epsilon_0 n^2 \hbar^4} \hbar\omega (\hbar\omega - E_0)^{1/2} \Theta(\hbar\omega - E_0), \text{ where } \Theta(\hbar\omega - E_0) \text{ is a step function used to}$$

indicate that there is no radiative recombination for $\hbar\omega < E_0$, and J denotes that these rates are derived through the joint density of states. It is important to remember that the use of such a joint density of states for amorphous semiconductors does not give the well known Tauc relation [1] in the absorption coefficient. Therefore, by using it in calculating the rate of spontaneous emission, one would violate the Van Roosbroeck and Shockley relation [12] between the absorption and emission. For this reason, the product of the individual electron and hole densities of states is used in evaluating the summations in Eqs. (10) and (11) for amorphous semiconductors [1,13-14].

Using the product of the individual densities of states as $g_q(E) = \frac{V}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E_q^{1/2}$,

$q = c$ (conduction), v (valence), the integrals can be evaluated and the rates in Eqs. (10) and (11) are, respectively:

$$R_{spn1} = \frac{e^2 L \mu_x}{4\epsilon_0 \hbar^3 n^2 (\hbar\omega)} (\hbar\omega - E_0)^2 \Theta(\hbar\omega - E_0), \quad (12)$$

and

$$R_{spn2} = \frac{\mu_x^3 e^2 a_{ex}^2}{2\pi^2 \epsilon_0 n^2 \hbar^7 \nu \rho_A} \hbar\omega (\hbar\omega - E)^2 \Theta(\hbar\omega - E_0), \quad (13)$$

where m_e^* and m_h^* in the electron and hole density of states have been replaced by μ_x for excitonic transitions. It may be emphasized here that E_0 , defined as the energy of the optical gap, is not always the same for amorphous solids. It depends on the lowest excitonic state formed before the radiative recombination, and it is not easy to determine; either theoretically or experimentally.

For the possibility (iv), where both e and h have relaxed down into the tail states before their radiative recombination, p_{cv} in Eq. (6) is obtained as $|p_{cv}|^2 = |Z_i|^2 \exp(-2t'_e a_{ex})$, $i = 1, 2$, where $t'_e = \sqrt{2m_e^*(E_c - E_e)} / \hbar$. Using this and the individual densities of states, the rates of spontaneous emission are obtained as:

$$R_{spnti} = R_{spni} \exp(-2t'_e a_{ex}), \quad i = 1, 2, \quad (14)$$

where the subscript *spnt* stands for the spontaneous emission under non-equilibrium conditions from tail-to-tail states. $a_{ex} = (5\mu\epsilon a_0)/(4\mu_x)$ is the excitonic Bohr radius in the tail states, where μ is the reduced mass of the electron in the hydrogen atom and $a_0 = 0.529 \text{ \AA}$ is the Bohr radius. The above rates do not have any peak structures, hence they cannot be used to determine E_0 . However, unless one knows the relevant effective masses of charge carriers and the value of E_0 , these rates cannot be calculated. The effective mass of charge carriers in amorphous solids has recently been derived [1] but E_0 is not known. For this reason, it is useful first to derive these rates under thermal equilibrium as well, as shown below:

3.3 Recombination in thermal equilibrium

Assuming that the excited charge carriers are in thermal equilibrium among themselves, the distribution functions f_c and f_v , can be given by the Maxwell-Boltzmann distribution functions as $f_c = \exp[-(E_e - E_{Fn})/\kappa_B T]$ and $f_v = \exp[-(E_{Fp} - E_h)/\kappa_B T]$, where E_{Fn} and E_{Fp} are the electron and hole Fermi energies. This gives $f_c f_v \approx \exp[-(\hbar\omega - E_0)/\kappa_B T]$, and using this in Eq. (8) we get the two rates denoted by R_{spi} , ($i = 1, 2$) at equilibrium for the possibilities (i) - (iii) as:

$$R_{spi} = R_{spni} \exp[-(\hbar\omega - E_0)/\kappa_B T], \quad i = 1, 2, \quad (17)$$

and for the possibility (iv), tail-to-tail states transitions, we get the two rates R_{spti} as:

$$R_{spti} = R_{spnti} \exp[-(\hbar\omega - E_0)/\kappa_B T], \quad i = 1, 2 \quad (18)$$

The rates derived in Eqs. (15) and (16) have a maximum value, which can be used to determine E_0 as described below.

We assume that the peak of the observed PL intensity is proportional to that of the rate of spontaneous emission obtained in Eqs. (15) and (16). The PL intensity as a function of $\hbar\omega$ has been

measured in a-Si:H [2,15,16]. By comparing the experimental energy thus obtained with the energy corresponding to the maximum of the rate, we can determine E_0 . Defining $x = \hbar\omega - E_0$ ($x > 0$) and $\beta = \kappa_B T$, and then setting $dR_{spi}/dx = 0$ ($i = 1, 2$), we can derive the corresponding E_0 from Eq. (15) as:

$$E_{01} = \frac{E_{mx}(-1 + \beta E_{mx})}{1 + \beta E_{mx}} \text{ and } E_{02} = \frac{E_{mx}(-3 + \beta E_{mx})}{1 + \beta E_{mx}}, \quad (17)$$

where E_{mx} is the emission energy at which the PL maximum is observed experimentally. The radiative lifetime, τ_r , is then obtained from the inverse of the maximum rate ($\tau_r = 1/R_{\max}$) calculated at $\hbar\omega = E_{mx}$.

4. Results

The effective masses of e and h, required for calculating the rates in Eqs. (15) and (16), have recently been derived for amorphous solids [1]. Accordingly, one gets different effective masses for a charge carrier in its extended and tail states, and for sp^3 hybrid systems the electron effective mass is found to be the same as the hole effective mass. Thus, in a sample of a-Si:H with 1 at.% weak bonds contributing to the tail states, we get the effective mass of a charge carrier in the extended states as $m_{ex}^* = m_{hx}^* = 0.34 m_e$ and in the tail states as $m_{et}^* = m_{ht}^* = 7.1 m_e$ [1].

For finding E_{01} and E_{02} from Eq. (17), we need to know the value of E_{mx} and the carrier (exciton) temperature T . Wilson *et al.* [2] have measured the PL intensity as a function of the emission energy for three different samples of a-Si:H at 15 K. Stearns [15] and very recently Aoki [16] have also measured it at 20 K and 3.7 K, respectively. The values of E_{mx} estimated from these three measurements at 3.7 K, 15 K and 20 K are obtained as 1.360 eV, 1.401 eV and 1.450 eV, respectively. These values of E_{mx} are below the mobility edge E_c by about 0.44 eV at 3.7 K, 0.40 eV at 15 K and 0.35 eV at 20 K. This means that most excited charge carriers have relaxed down below their mobility edges in these experiments, and are not hot carriers anymore. They can be assumed to be in thermal equilibrium with the lattice. Substituting the above values of E_{mx} and the corresponding lattice temperatures in Eq. (17), the values of E_{01} and E_{02} are found to be the same, i.e. $E_{01} = E_{02} = E_0 = 1.359$ eV, 1.398 eV and 1.447 at 3.7 K, 15 K and 20 K, respectively.

Table 1. The maximum values of rates calculated at $\hbar\omega = E_{mx}$ from Eqs. (15) and (16) and the corresponding lifetimes at temperatures 3.7 K, 15 K and 20 K. The results are indicated by superscripts a, b and c for possibilities (i), (ii)-(iii) and (iv), respectively.

T (K)	R_{sp1} (s^{-1})	τ_{r1}	R_{sp2} (s^{-1})	τ_{r2}
3.7 ^a	7.77×10^6	$0.1 \mu s$	8.38×10^6	$0.1 \mu s$
15 ^a	1.58×10^8	6.3 ns	2.05×10^8	4.9 ns
20 ^a	2.77×10^8	3.6 ns	3.72×10^8	2.7 ns
3.7 ^b	1.47×10^7	$0.1 \mu s$	1.62×10^7	$0.1 \mu s$
15 ^b	2.97×10^8	3.4 ns	3.43×10^8	2.9 ns
20 ^b	5.22×10^8	1.9 ns	1.08×10^8	0.9 ns
3.7 ^c	0.51×10^6	$1.9 \mu s$	0.55×10^6	$1.8 \mu s$
15 ^c	1.04×10^7	1.04×10^7	1.18×10^7	$0.1 \mu s$
20 ^c	1.08×10^7	$0.1 \mu s$	2.14×10^7	$0.1 \mu s$

For calculating the rate for the possibility (i), the excitonic reduced mass is obtained as $\mu_x = 0.17 m_e$ and the excitonic Bohr radius as 4.67 nm. For the possibilities (ii) and (iii), where one of the charge carriers of an exciton is in its extended states and the other in its tail states, we get $\mu_{ex} = 0.32 m_e$, and the corresponding excitonic Bohr radius is 2.5 nm. For the possibility (iv), we

get $\mu_{ex} = 3.55 m_e$, $a_{ex} = 2.23 \text{ \AA}$ and $t'_e = 1.29 \times 10^{10} \text{ m}^{-1}$. Using these in Eqs. (15) and (16), we can calculate the rates of radiative recombination for the possibilities (i) - (iv) at any photon energy $\hbar\omega$. However, for calculating the radiative lifetime, we will calculate the rates only at $\hbar\omega = E_{mx}$. In Table 1, we have listed the maximum values of the rates calculated at $\hbar\omega = E_{mx}$ for the possibilities (i), (ii)-(iii) and (iv) from both the approaches of evaluating the integral in Eq. (7). For the possibilities (i) –(iii), the rates are of the order of 10^8 s^{-1} from both the approaches for E_0 , E_{mx} and temperature obtained from Wilson *et al.* [2] and Sterns' [15] experiments, but one to two orders of magnitude less for E_0 , E_{mx} and temperature obtained from the recent measurements of Aoki *et al.* [16]. For the possibility (iv), the rates are one to two orders of magnitude slower.

According to Table 1, the radiative lifetimes for the possibilities (i)-(iii) are found to be in the ns time range for the experiments of Wilson *et al.* and Sterns, which agree very well with their experimental results. Also the radiative lifetimes calculated for the data of Aoki *et al.*, for the possibilities (i) – (iii) are found to be of the order of $0.1 \mu\text{s}$, which agrees very well with their measured lifetimes in the μs time range. Aoki *et al.* have not observed any peak in the ns region. The lifetimes for the possibility (iv) are found to be an order of magnitude longer than those for possibilities (i) – (iii).

5. Discussion

A comprehensive theory for calculating the rate of spontaneous emission from excitons in amorphous semiconductors has been presented. It was applied to calculate the rate of spontaneous emission for three samples of a-Si:H for which the PL spectra have been measured at 3.7 K [16], 15 K [2] and 20 K [15]. The rate is independent of the excitation density but it increases (and hence the radiative lifetime becomes shorter) as the PL energy increases, which is quite consistent with the observed results [4]. Eq. (19) produces different values of E_0 for different values of E_{mx} . Such a change in E_0 can only be possible in amorphous solids, which do not have a well defined energy gap. Therefore the excited charge carriers can relax down to different E_0 through the four different possibilities.

In order to understand the PL mechanism, it is important to know the value of the exciton binding energy in the possibilities (i) – (iv). The ground state singlet exciton binding energy E_s in

amorphous solids is obtained as [7]: $E_s = \frac{9\mu_{ex}e^4}{20(4\pi\epsilon_0)^2\epsilon^2\hbar^2}$. This gives $E_s \sim 16 \text{ meV}$ for the

possibility (i), 47 meV for the possibilities (ii) and (iii), and 0.33 eV for the possibility (iv) for a-Si:H. The known optical gap for a-Si:H is 1.8 eV [1] and E_{mx} estimated from experiments is about 1.36 eV [16], 1.401 eV [2] and 1.45 eV [15] measured at 3.7 K, 15 K and 20 K, respectively. Considering the PL in a-Si:H originating from the excitonic states, we find a Stokes shift of about 0.44 eV, 0.40 eV and 0.35 eV at temperatures of 3.7 K, 15 K and 20 K, respectively, which are close to each other. Such a large Stokes shift cannot only be due to the exciton binding energy, which is at most in the meV range for possibilities (i) - (iii). As the non-radiative relaxation of excitons is very fast in a-Si:H, not much PL may occur through the possibility (i). It is more likely to occur from transitions involving the possibilities (ii) - (iv). As the charge carrier-lattice interaction is much stronger in a-Si:H than in crystalline Si [1], an excited hole gets self-trapped very fast in the tail states. Thus a Stokes shift of about 0.4 eV in all three experiments can be expected to be due to relaxation of holes in excitons to the tail states plus the excitonic binding energy. Small discrepancies in the experimental Stokes shift may be attributed to the different temperatures of the three measurements. Thus, the PL observed in the three experiments originates from the possibility (ii), for which the radiative lifetime is in the ns range at 15 K and 20 K and in the μs range at 3.7 K. The radiative lifetime is sensitive to the time delay, E_0 , E_{mx} and the measurement temperature.

Wilson *et al.* [2] have also observed the lifetime to be in the μs range, which may be attributed to the possibility (iv). However, according to Table 1, the data of Aoki *et al.* also gives a

radiative lifetime in the μs from the possibility (iv), but the Stokes shift is too small to have both charge carriers in the tail states bound in excitonic states. As an exciton relaxes into the tail states, its Bohr radius is retained but not its excitonic motion due to localization. It becomes a geminate pair. Thus, in a-Si:H two types of geminate pair are possible, i) from excitons and ii) from other excited e and h. The latter is likely to have larger separation and hence a slower radiative lifetime. Such a slower lifetime has recently been observed [16].

6. Conclusions

It is shown that the excitation density independent PL observed in amorphous semiconductors arises from the radiative recombination of excitons. Both the Stokes shift and the radiative lifetimes should be taken into account in determining the PL energy states. Although the radiative lifetimes for possibilities (i) to (iii) are of the same order of magnitude, the Stokes shift observed in the PL at higher temperatures ($>15\text{ K}$) suggest that these recombinations occur from extended-to-tail states (possibility (ii)) in a-Si:H.

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References

- [1] J. Singh, K. Shimakawa, *Advances in Amorphous Semiconductors*, Taylor and Francis, London and New York, 2003, and references therein.
- [2] B. A. Wilson, P. Hu, J. P. Harbison, T. M. Jedju, *Phys Rev Letters* **50**, 1490 (1983).
- [3] R. Stachowitz, M. Schubert, W. Fuhs, *J. Non-Cryst. Solids* **227-230**, 190 (1998).
- [4] T. Aoki, S. Komodoori, S. Kobayashi, C. Fujihashi, A. Ganjoo, K. Shimakawa, *J. Non-Cryst. Solids* **299-302**, 642 (2002).
- [5] S. Ishii, M. Kurihara, T. Aoki, K. Shimakawa, J. Singh, *J. Non-Cryst. Solids* **266-269**, 721 (1999).
- [6] T. Aoki, S. Komodoori, S. Kobayashi, T. Shimizu, A. Ganjoo, K. Shimakawa, *Nonlinear Optics* **29**, 273 (2002).
- [7] J. Singh, T. Aoki, K. Shimakawa, *Phil. Mag.* **B82**, 855 (2002).
- [8] J. Singh, *J. Non-Cryst. Solids* **299-302**, 444 (2002).
- [9] J. Singh, *J. Materials Sci.* **14**, 171 (2003).
- [10] G. Lasher, F. Stern, *Phys. Rev.* **133**, A553 (1964).
- [11] H. Barry Bebb, E. W. Williams, in *Semiconductors and Semimetals*, Eds. R. K. Willardson and A. C. Beer, Academic, London, 1972, vol. 8, p. 18.
- [12] W. Van Roosbroek, W. Shockley, *Phys. Rev.* **94**, 1558 (1954).
- [13] N. F. Mott, E. A. Davis, *Electronic Processes in Non-crystalline Materials*, Clarendon Press, Oxford, 1979.
- [14] S. R. Elliott, *The Physics and Chemistry of Solids*, John Wiley & Sons, Sussex, 1998.
- [15] D. G. Stearns, *Phys. Rev.* **B30**, 6000 (1984).
- [16] T. Aoki, T. Shimizu, D. Saito, K. Ikeda, *J. Optoelectron. Adv. Mater.* **7**(1), 137 (2005).