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Radiative recombination of excitons in amorphous semiconductors

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Abstract

A theory for calculating the radiative lifetime of excitons in amorphous semiconductors is presented. Four possibilities of excitonic radiative recombination are considered and the corresponding rates are derived at thermal equilibrium. The radiative lifetime is calculated from the inverse of the maximum rate for all the four possibilities. Results agree very well with experiments.

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Much interest has been devoted to study the photoluminescence (PL) in hydrogenated amorphous silicon (a-Si:H) [1] in the last two decades. Using the time-resolved spectroscopy (TRS), Wilson et al. [2] have observed PL peaks in the nanosecond (ns), microsecond (μs) and millisecond (ms) time ranges in a-Si:H at a temperature of 15 K. In contrast to this, using the quadrature frequency-resolved spectroscopy (QFRS), only a double-peak structure PL has been observed in a-Si:H at the liquid helium temperature. One peak appears for a short time in the μs range and the other in the ms range [3–5]. Using the effective mass approach, a theory for the excitonic states in amorphous semiconductors has been developed by Singh et al. [6] 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. However, the controversy over the radiative lifetime has not yet been resolved.

In this paper, a theory is presented for calculating the rate of spontaneous emission and radiative lifetime of excitons in amorphous semiconductors (a-semiconductors). It is assumed that an exciton can be formed between an excited pair of electron

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(e) and hole (h) 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 the tail states, it remains an exciton with 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 as the thermal relaxation of free carriers (not bound in excitons). This results in a peaked excitonic PL as has been observed in several experiments [1]. We have derived the rates of spontaneous emission within two-level approximation, and under both non-equilibrium and equilibrium conditions. However, only the results obtained under thermal equilibrium are presented here. It is shown that when the radiative recombination occurs directly from the extended states it is much faster and has a radiative lifetime in the ns range. When the radiative recombination occurs from the tail-to-tail states, the radiative lifetime gets prolonged due to the localization of charge carriers. This is because, in this case, one of the charge carriers in an exciton has to tunnel across a distance equal to the excitonic Bohr radius for recombining with the other, which prolongs the radiative lifetime.

The exciton–photon interaction operator for radiative recombination by emitting a photon can be expressed as

$$\hat{H}_{xp} = -\frac{e}{\mu_{\rm ex}}\mathbf{A}\cdot\mathbf{P} = \sum_{c,v,v} < c, E_c'|\hat{H}_{xp}|v, E_v' > B_{cv}c_v^+, \quad (1)$$

where $\mathbf{A}$ is the vector potential, $\mu_{\rm ex}$ is the reduced mass of an exciton, $\mathbf{p}$ is the relative linear momentum associated with the relative motion of electron and hole in an exciton. $B_{cv} = d_v a_c$ is the annihilation operator of an exciton and a_c and d_v are the annihilation operators of an electron in the conduction and that of a hole in the valence states, respectively, and c_v^+ is the creation operator of a photon of energy v. The electron creation operator in the conduction states can be defined as [1]

$$a_c^+ = N^{-1/2}\sum_l \exp(i\mathbf{t}_{\rm e}.\mathbf{R}_l^{\rm e})a_{cl}^+,$$

$$|\mathbf{t}_{\rm e}| = t_{\rm e} = \sqrt{\frac{2m_{\rm e}^*(E_{\rm e}-E_{\rm c})}{\hbar^2}}, \quad (2)$$

where $m_{\rm e}^*$ is the effective mass of the electron, $E_{\rm c}$ is the energy of the electron mobility edge, N is the number of atoms in the sample and $\mathbf{R}_l^{\rm e}$ is the position coordinate of an electron at the lth atom in the sample. a_{cl}^+ represents the creation operator of an electron at l in the conduction c states. According to Eq. (3), if the electron energy $E_{\rm e}$ is above the mobility edge, then the electron moves as a free particle in the conduction extended states, but if $E_{\rm e} < E_{\rm c}$the electron gets localized because $t_{\rm e}$ becomes imaginary and the envelope function becomes exponentially decreasing. Likewise the hole creation operator in the valence states can be defined as

$$d_v^+ = N^{-1/2}\sum_l \exp(i\mathbf{t}_{\rm h}.\mathbf{R}_l^{\rm h})d_{vl}^+, \quad d_{vl}^+ = a_{vl},$$

$$|\mathbf{t}_{\rm h}| = t_{\rm h} = \sqrt{\frac{2m_{\rm h}^*(E_v-E_{\rm h})}{\hbar^2}}, \quad (3)$$

where $m_{\rm h}^*$ is the effective mass of the hole, E_v is the energy of the hole mobility edge, and d_{vl}^+ is the creation operator of a hole at l.

For calculating the rate of spontaneous emission due to an exciton, we consider a transition from an initial state with one exciton as $|i\rangle = B_{cv}^+|0\rangle$ to a final state with a photon as $|f\rangle = c_v^+|0\rangle$, where $|0\rangle$ denotes the vacuum state with fully occupied valence states and completely empty conduction states. For amorphous solids, it is important to distinguish whether the excited charge carriers are created in the extended states or tail states. This is because charge carriers have different wave functions, effective masses, and hence different excitonic Bohr radii in their extended and tail states. There are four possibilities: (i) both excited e and hole h are in their respective extended states, (ii) e in its extended and h in its tail states, (iii) e in its tail and h in its extended states, and (iv) both e and h are in their respective tail states.

Using Eq. (1) as the interaction operator and applying Fermi's golden rule, the rate $R_{\rm sp}$ (s^{-1}) of