

Exciton recombination in amorphous chalcogenides

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The total light decay of photoluminescence in amorphous chalcogenides is described empirically by $t^{n-1} \exp[-(t/\tau_0)^n]$, where τ_0 is the effective recombination time and $0 < n < 1$. It is shown that the empirical decay function is replicated well by a Monte Carlo calculation based on a recombination model of localized excitons.

Photoluminescence (PL) has been extensively studied in amorphous (*a*)-chalcogenide semiconductors.¹⁻⁴ In particular, the total-light-decay (TLD) measurement, the spectrally integrated PL intensity as a function of time, is useful for understanding the detailed nature of PL centers. Recent TLD measurements³ show that there are two well-defined recombination times of around 10^{-7} and 10^{-4} s, as shown in Fig. 1. The fast component of PL ($\sim 10^{-7}$ s) is sensitive to the excitation energy (E_x) and retains a polarization memory of the exciting light for low E_x . The retaining of a polarization memory provides the evidence that the excitations are localized at the PL centers. The slow component (10^{-4} s), on the other hand, is excited strongly by higher E_x . This component does not have polarization memory, suggesting that the electron-hole pair produced by the interband excitation diffuse to localized states (PL centers). It is shown in the present Brief Report that the decay is fitted by an empirical law as

$$f(t) = t^{n-1} \exp[-(t/\tau_0)^n], \tag{1}$$

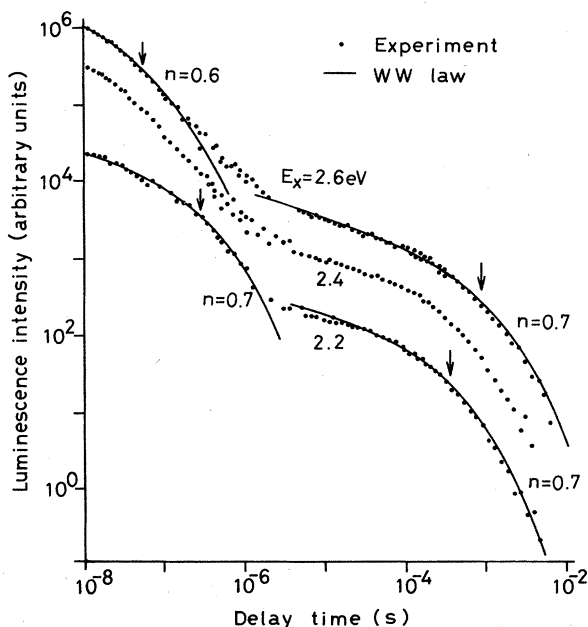


FIG. 1. Total light decay (TLD) in As_2Se_3 film, with data from Murayama *et al.* (Ref. 3). E_x is the excitation energy. Empirical relations (WW law) for $n=0.6$ and 0.7 are shown by the solid curves. The effective recombination time τ_0 is shown by an arrow on each curve.

where τ_0 ($\sim 10^{-7}$ and $\sim 10^{-4}$ s) is the effective recombination time. The value of n lies between 0.5 and 0.8. This relation has been first proposed by Williams and Watts (WW law⁵) to describe dielectric responses in dipolar materials. The empirical relations for $n=0.6$ and 0.7 are shown by the solid lines in Fig. 1. The fitting of Eq. (1) to the decay of monochromatized PL has been first reported in *a-As_2S_3*.⁶ A similar behavior has also been observed in *a-GeSe_2*.⁴ However, it is not clear why the experimental data fit the WW empirical law. As the monochromatized PL is not directly related to the total number of PL centers an analysis of the TLD seems to be better than that of monochromatized PL. Here, the decay kinetics replicated by Eq. (1) are discussed through a Monte Carlo calculation.

To analyze TLD, a computer-assisted Monte Carlo analysis has been employed. Following the generation of a random number $0 < X < 1$, a recombination time is calculated as

$$t = -\ln(X)\tau, \tag{2}$$

where τ is the average recombination time of electron-hole pairs. The initial term $-\ln(X)$ introduces an approximately random nature to the transition processes,⁷ yielding an exponential distribution which is called the waiting time for the transition. Note that the average of the term $-\ln(X)$ is unity for a large number of random numbers. Hence, the average recombination time $\langle t \rangle$ is given by τ . A successful explanation of dispersive transport of photoexcited carriers in amorphous semiconductors^{8,9} and of the origin of non-symmetric dielectric relaxation in dipolar materials¹⁰ have been obtained by a similar calculation of relaxation times.

There is evidence^{2,3} that PL in amorphous chalcogenides is dominated by localized excitons: The fast component ($\sim 10^{-7}$ s) could originate from singlet recombination and the slow one ($\sim 10^{-4}$ s) from triplet recombination. The recombination time for exciton recombination, τ , is given approximately by¹¹

$$\tau = \tau_r (a_e/a_h)^3, \tag{3}$$

where a_e and a_h are the Bohr radii of electrons and holes, respectively, and τ_r , a constant. The ratio β ($= a_e/a_h$) will fluctuate around a certain mean value β_0 because the excitons are immersed in a disordered medium. A Gaussian distribution of the ratio β is assumed here:

$$G(\beta) = \frac{1}{(2\pi)^{1/2}\Delta} \exp[-(\beta-\beta_0)^2/2\Delta^2], \tag{4}$$

where Δ is the standard deviation. The ratio β for each exciton is selected at random according to Eq. (4). The

number of recombined excitons $n(t)$ at any time, which is proportional to the PL intensity $I(t)$ (TLD), is given by a calculation of t for each exciton ($N=10^5$ in the present calculation) initially created by the excitation. As nonradiative processes could not dominate PL in amorphous chalcogenides at low temperature, these processes were not taken into consideration here.

The solid circles in Fig. 2 show the calculated results of $\log_{10}I(t)$ vs $\log_{10}t$ for the fast component. The data have been displaced vertically for clarity for (a) $\Delta=0$, (b) $\Delta=2$, and (c) $\Delta=3$, where $\tau_r=1 \times 10^{-9}$ s is assumed.² The average ratio $\beta_0=5$ was chosen here to give a calculated τ [Eq. (3)] that fits the effective recombination time τ_0 estimated from experiment (see Fig. 1). These calculations agree well with the solid lines (a), (b), and (c) obtained from the empirical law [Eq. (1)] with $n=1.0, 0.7$, and 0.6 , respectively. Fitting Eq. (1) to simulation data produces the values of τ_0 . These estimated τ_0 are indicated by an arrow on each curve. The curve (a) for $\Delta=0$ gives just the exponential decay ($n=1.0$ in Fig. 1). Curves (b) and (c) in Fig. 2 show that the parameter n decreases with increasing Δ .

The parameter n for the slow component has similar values as for the fast component (see Fig. 1). By assuming the same β_0 as that for singlet excitons (fast component), τ_r is estimated to be $\sim 10^{-6}$ s. This is a plausible value for the triplet excitons (spin forbidden),¹² which is larger three orders than that for singlet excitons (spin allowed). These triplet excitons could be produced after thermalization of electron-hole pairs created by interband excitation. The thermalization of electron-hole pairs does not retain the polarization memory of PL because electrons and holes diffuse randomly during the thermalization.

The PL spectra of the slow component for amorphous chalcogenides are very similar to that of crystalline chalcogenides, suggesting that the PL center related to the slow component of amorphous chalcogenides is the same as that for crystalline (*c*)-chalcogenides.¹³ If charged dangling bonds or valence alternation pairs would be PL centers for both amorphous and crystalline chalcogenides, a broad distribution of recombination times should be observed because the radiative recombination time of such PL centers is described by

$$\tau = \tau_r' \exp(2\alpha R), \quad (5)$$

where R is the pair separation, α an average decay parameter for the electron and hole wave functions, and τ_r' the minimum decay time (10^{-9} s). The distribution of R can be given by

$$G(R) = 4\pi N_p R^2 \exp(-4\pi N_p R^3/3) dR, \quad (6)$$

where N_p is the pair density initially created by photoexcitation. The TLD in synthetic crystals of As_2Se_3 (*c*- As_2Se_3) for interband excitation, however, shows exponential decay with a recombination time of $\tau \approx 10^{-3}$ s,² which is in sharp contrast with the nonexponential decay seen in the TLD for *a*- As_2Se_3 and other amorphous chalcogenides.

The single recombination time observed for *c*- As_2Se_3 has been interpreted in terms of triplet exciton recombination,² which could be explained by a constant ratio β for crystals. It is suggested that the broad distribution of recombination times observed for amorphous chalcogenides is due to a distribution of β for localized excitons.

Returning to the fast component, a donor-acceptor pair

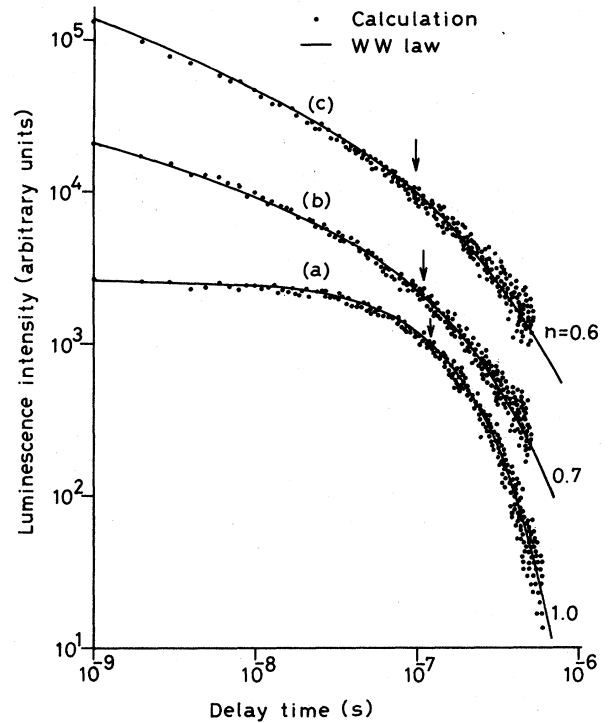


FIG. 2. Calculated TLD's (solid circles) for (a) $\Delta=0$, (b) $\Delta=2$, and (c) $\Delta=3$. The data are displaced vertically for clarity. The empirical relations for $n=1.0, 0.7$, and 0.6 are shown by the solid lines. τ_0 is shown by an arrow on each curve.

(DA pair) model² has been suggested for amorphous chalcogenides. If the pairs are randomly distributed in space, the radiative recombination time can be represented by Eqs. (5) and (6), leading to an excitation intensity dependence of PL lifetime. Such excitation dependence of τ has not been observed.² If a cutoff in the long-distance pair is assumed ($4\pi N_p R^3/3 < 1$),¹⁴ τ would be independent of N_p , as observed in experiments. However, it is not clear whether or not the assumption of a cutoff in the pair distribution is valid. It is also not clear whether or not the DA pairs retain the polarization memory.

We conclude that both the fast and slow components of PL in amorphous chalcogenides are dominated by localized excitons. The decay kinetics of PL were well explained by a combination of the exponential distribution of $\ln(X)$ and the fluctuation of $\beta (= a_e/a_h)$.

Note added in proof. It should be mentioned here that the luminescence intensity $I(t)$ from the present Monte Carlo calculation gives the same $I(t)$ from the analytical calculation, $I(t) = \int \nu P(\nu) \exp(-\nu t) d\nu$, with $\nu = \nu_0 \beta^{-3}$. As far as the present problem is concerned, the Monte Carlo calculation cannot be a fascinating approach. However, if the complex physical situation such as diffusion of electrons and holes and/or nonradiative processes should be taken into consideration, the present approach could become quite useful.

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