Exciton transport and nonradiative decay in semiconductor nanostructures

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(Received 19 December 1997; revised manuscript received 26 June 1998)

A phenomenological theory describing the exciton photoluminescence (PL) kinetics in type-II superlattices is proposed herein, which takes into account both the intrinsic exciton radiative decay and nonradiative decay due to exciton trapping by interfacial defects surrounding a ''disordered'' interface. We have thus investigated the effect of system dimensionality on details of these nonradiative-decay kinetics. For effectively three-dimensional and two-dimensional structures, the theory predicts a transition from strongly nonexponential to nearly exponential decay kinetics as the temperature is increased. Contrastingly, for one-dimensional structures the decay kinetics is predicted to be nonexponential at all temperatures. Using these predictions, we have applied this model to explain our observed time-resolved PL on specific short-period type-II GaAs/AlAs superlattices. These PL decays are thus explained both over a wide range of temperatures (2–30 K) and over an observed crossover from nonexponential to exponential behavior. The model allows us to extract a nonradiative-defect density and an average radiative-decay rate from the experimental data.
[S0163-1829(98)03940-X]

I. INTRODUCTION

The recombination kinetics of excitons in bulk and in a variety of semiconductor heterostructures has been investigated experimentally employing optical spectroscopic methods, most particularly the time-resolved photoluminescence technique. The behavior of exciton photoluminescence (PL) decay transients can be fairly complicated. Typically, time-resolved data are analyzed by fitting to some combination of exponentially decaying terms, and then the associated time constants are assigned to the various physical processes occurring within the system.

For various types of excitons in semiconductor structures [three-dimensional (3D), two-dimensional (2D), direct and indirect excitons, etc.] there are a number of physical processes that may govern the PL-decay transient: interaction with a population of nonradiative large-momentum excitons,[1] the relative population of heavy-hole excitons versus light-hole excitons,[2] the formation of biexcitons at low-power excitation,[3] thermalization of excitons with free carriers,[4] and of course, the intrinsic radiative recombination of the exciton.

One important factor in PL kinetics that has often been alluded to, but seldom properly quantified, is the role of nonradiative recombination centers in semiconductor heterostructures. Recent investigations of type-II GaAs/AlAs superlattices have indicated that this phenomenon plays an important role in quenching of the exciton lifetime in these structures.[5] The importance of nonradiative defect centers depends on the specifics of the sample structure; however, we believe that the role of defects must be carefully considered for all semiconductor structures, especially for structures with indirect excitons, since the intrinsic radiative recombination rate is rather small for such excitations.

In this paper we present a model which quantifies the effect of nonradiative-defect centers in photoluminescence time-decay transients. We derive the line shape of the photoluminescence transients for one-, two-, and three-dimensional excitons, and consider the range of validity of this model. Finally, we use this model to explain the results of experimental measurements performed on type-II GaAs/AlAs superlattices.

II. THEORETICAL MODEL

We propose a theoretical model for the photoluminescence time-decay kinetics based on the assumption that both radiative- and nonradiative-decay processes take place in a semiconductor structure. Specifically, we propose the following. (i) At low temperatures all excitons are localized in interfacial disorder and the distribution of these localized states is reflected in the PL spectra. (ii) As the temperature is increased, excitons are thermally detrapped into so-called mobile states. (iii) These mobile excitons thermally diffuse without recombination. (iv) As these mobile excitons diffuse, they may recombine nonradiatively at an unspecified lattice defect. (v) The mobile excitons may spatially diffuse, become again disorder-localized, and subsequently recombine radiatively. These ideas form the basis of our mathematical model.

In order to include diffusion, we approximate the behavior of a mobile exciton by a ''random walker'' on a d-dimensional uniform hypercubic lattice with lattice constant L ($d=1,2,3$, for effectively linear, layered, and bulk microstructures). In this model the lattice sites are identified with localized states and excitons may jump between adjacent sites, but they may also have finite probability to recombine radiatively while occupying a localized state. We assume

that nonradiative recombination occurs when an exciton (random walker) is absorbed by a defect which is considered to be a perfectly absorbing trap located on a lattice site. The defects are randomly distributed among the lattice sites, with q being the fraction of lattice sites occupied by the defects. The lattice constant of the superlattice space over which the exciton performs a random walk is assumed to be equal to the average distance, L, between localized states.

For excitons direct in both real and momentum space, the radiative component of the decay may be exponential, but for indirect-gap excitons in type-II structures, due to disorder-induced randomness at the interfacial boundaries in the system, excitons at different localized states have different radiative-decay rates, the distribution of these rates being approximated by the Klein-Sturge-Cohen (KSC) theory for the radiative decay in a random alloy.[6]

Let $I_R(t)$ be the PL intensity at time t in the absence of nonradiative defects and $P_{\mathrm{NR}}(t)\,[P_{\mathrm{NR}}(0)=1]$ be the probability of an exciton survival at time t for the purely nonradiative recombination. If we assume that the radiative and nonradiative recombination processes are not correlated, then the total PL intensity in the presence of nonradiative defects is a product of $I_R(t)$ and $P_{\mathrm{NR}}(t)$. The total PL intensity $I_T(t)$ at time t is then given as

$$I_T(t)=I_R(t)P_{\mathrm{NR}}(t). \tag{1}$$

In the KSC theory,[6] the radiative-decay component in the presence of lattice disorder is given by

$$I_R(t)=I_0(1+2\langle W_R\rangle t)^{-3/2}, \tag{2}$$

where $\langle W_R\rangle$ is the mean radiative rate in the system.

In our model, it is assumed that an exciton decays nonradiatively whenever it strikes a defect and gets absorbed. Obviously, in the limit $q\ll 1$ the survival probability $P_{\mathrm{NR}}(t)$ entirely depends on the number of different lattice sites visited by an exciton. This fact is known as the Rosenstock approximation for absorption of random walkers on a lattice by randomly distributed perfect traps,[7]

$$P_{\mathrm{NR}}(t)=(1-q)^{\langle S(t)\rangle}, \tag{3}$$

where $\langle S(t)\rangle$ is the mean number of distinct lattice sites visited by a random walker in time t. It has been shown[8] that this Rosenstock approximation works well for small values of q and for relatively small times, such that $P_{\mathrm{NR}}(t)>10^{-4}$, and this approximation is usually valid for most systems of interest.

The mean number of distinct sites $\langle S(t)\rangle$ visited by a random walker in time t is a function of the lattice dimensionality and was evaluated in Ref. 9.

For a one-dimensional case,

$$\langle S(t)\rangle\approx\left(\frac{8n}{\pi}\right)^{1/2}; \tag{4}$$

for a two-dimensional case,

$$\langle S(t)\rangle\approx\frac{\pi n}{\ln(\alpha n)}; \tag{5}$$

and for a three-dimensional case,

$$\langle S(t)\rangle\approx(1-R)n; \tag{6}$$

where n is the number of random walks completed by a walker in time t, R is the probability of the walker's return to the start in the absence of traps ($R\approx 0.34$ in three dimensions), and α is a constant which was determined in Ref. 8 ($\alpha=5.7$). Equations (4)–(6) are asymptotic expressions for $\langle S(t)\rangle$ in the case $n\gg 1$, even though all of them, except Eq. (5), are good approximations for $\langle S(t)\rangle$ for any $n\geqslant 0$. Equation (5) may also be modified to take into account the correct asymptotic behavior for $n\to 0$, namely, $\langle S(t)\rangle\to 0$. Thus, we propose the following form of $\langle S(t)\rangle$ in two dimensions:

$$\langle S(t)\rangle\approx\frac{\pi n}{\ln(\beta+\alpha n)}, \tag{7}$$

where $\beta=17.5$ is a constant that is determined from the condition $\langle S(t)\rangle=1$ for $n=1$.

Considering $q\ll 1$, one can derive from Eqs. (4)–(7) the expressions for nonradiative decay due to the absorption on traps in one, two, and three dimensions. Let n_d denote the linear, sheet, or bulk density of the defects in 1D, 2D, and 3D cases, respectively, and L denote the average distance between localized states. In order to derive the expressions for the nonradiative-decay probability, we use the following expressions for the number of random walks n performed by the walker in time t and for the fraction of lattice sites q occupied by the defects:

$$n=\frac{2D_E t d}{L^2} \tag{8}$$

and

$$q=n_d L^d, \tag{9}$$

where d is the system dimensionality ($d=1,2,3$) and D_E is the effective exciton diffusivity.

We may now derive an expression for the nonradiative-decay probability $P_{\mathrm{NR}}(t)$ for a one-dimensional case. Thus, by inserting Eqs. (4), (8), and (9) into Eq. (3), we obtain

$$P_{\mathrm{NR}}(t)=(1-n_d L)^{(4/L)\sqrt{D_E t/\pi}}. \tag{10}$$

Now, using the fact that $q=n_d L\ll 1$, we may employ the following additional approximation:

$$1-n_d L\approx e^{-n_d L}. \tag{11}$$

Then, substituting Eq. (11) into Eq. (10), we obtain the expression for $P_{\mathrm{NR}}(t)$ for a one-dimensional case,

$$P_{\mathrm{NR}}(t)=\exp\left[-4n_d\left(\frac{D_E t}{\pi}\right)^{1/2}\right]. \tag{12}$$

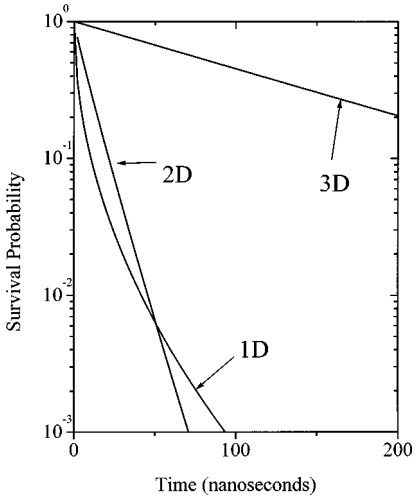

FIG. 1. Time dependence of nonradiative survival probability $P_{NR}(t)$ for effectively one-dimensional, two-dimensional, and three-dimensional structures. For the sake of illustration, the average distance between localized states $L=20$ nm, the average defect separation distance $r_1=1000$ nm, and the exciton diffusivity $D_E=0.1$ cm^2/s are assumed to be the same in all three cases.

The expressions for two- and three-dimensional cases are obtained in a similar fashion. For instance, for a two-dimensional case, we get

$$P_{NR}(t)=\exp\left(-\frac{4\pi D_E n_d t}{\ln(\beta L^2+4\alpha D_E t)-\ln(L^2)}\right) \tag{13}$$

and for a three-dimensional case, we get

$$P_{NR}(t)=\exp[-6(1-R)LD_E n_d t]. \tag{14}$$

III. DISCUSSION

In Fig. 1 we plot the nonradiative-decay kinetics for excitons in effectively 1D, 2D, and 3D systems. The average distance between the defects (r_1), the average distance between the localized states (L), and the diffusivity (D_E) are assumed to be the same for all three systems for the sake of illustration. One may then see that in the initial stages of exciton recombination, the decay in the 1D system is the fastest, while the decay in the 3D system is the slowest. The nonradiative decays in 1D and 2D systems are nonexponential, although the deviation from exponential behavior in 2D systems is logarithmically small. Also in 3D systems, the decay rate is found to depend strongly on the average distance between the localized states (L), while in 1D systems there is no such dependence at all (for $q \ll 1$). Contrastingly, in 2D systems the dependence on L is very weak (logarithmic).

The radiative-decay kinetics may vary for different types of structures and for different temperatures. As noted above, we have used the Klein-Sturge-Cohen (KSC) theory[6] for radiative decay in an alloy to approximate the radiative decay of excitons due to a random potential induced by a heterointerface disorder (although the exact shape of this potential is unknown). The KSC theory is applicable at relatively low temperatures (small diffusivities) and for spatially inhomogeneous defect distributions. For high diffusivities and homogeneous defect distributions, the excitons visit many different localized sites before they decay radiatively, and as a result, the radiative lifetimes for different localized states become averaged out and the decay kinetics only then become exponential. We note that radiative decay dominates nonradiative decay only at low temperatures; hence, the exact line shape of the radiative decay is not important for higher temperatures ($T>10$ K for the superlattice discussed in the next section). For this reason, we use Eq. (2) for the radiative decay over the range of temperatures considered in this paper.

Equation (2) is also a good approximation over a wide range of temperatures for the radiative-decay kinetics of a system with spatially inhomogeneous (but smooth on the scale of intersite distances) distributions of radiative-decay rates. In this case, an exciton may diffuse only to the sites with approximately equal radiative-decay rates.

IV. COMPARISON WITH EXPERIMENTAL DATA

The usefulness of this model is demonstrated by its ability to explain experimental time-resolved PL data in type-II GaAs/AlAs superlattices. Type-II heterostructures are characterized by the spatial and k-space separation of the electron and the hole in AlAs and GaAs layers, respectively. Electrons and holes hence bind into excitons via their mutual Coulomb interaction across the interface of AlAs and GaAs. Therefore, we expect the experimentally observed kinetics of these excitons to be particularly sensitive to the interfacial quality, i.e., the interfacial defect density. Typically in these samples, the exciton recombination lifetime ranges from tens of microseconds at 2 K to nanoseconds at 30 K. The decay curve itself is found to be nonexponential at low temperatures, while becoming strictly exponential at higher temperatures. Thus, the exciton decay kinetics is experimentally observed to be a strong function of temperature. Hence we apply our model to these experimental time-decay kinetics at several temperatures, and thereby extract both the concentration of defects in the 2D interface and the mean radiative-decay rate of type-II excitons.

The sample studied is an undoped molecular-beam-epitaxy (MBE)-prepared GaAs/AlAs superlattice with 55 periods; each period consists of a 35-Å GaAs layer followed by a 50-Å AlAs layer. To help ''smooth'' the interface, a 45-sec growth interruption was employed between the AlAs layer and the GaAs layer (sample was grown at 590 °C atop a 0.5-μm-thick GaAs buffer layer on a GaAs substrate). Between the superlattice layer and the buffer layer is a 200-Å stop layer, and on top of the superlattice layer is a 35-Å GaAs cap layer. The sample was excited by a cw mode-locked Ti^{3+}: sapphire laser which was frequency-doubled (350–430 nm) and pulse-picked to lower the repetition rate (variable from 400 Hz to 82 MHz). The resulting emission was dispersed by a 0.85-m double spectrometer and recorded by the time-correlated single-photon counting technique, yielding a temporal resolution of about 500 ps. Further, exciton transport was measured using an all-optical time- and space-resolved confocal-imaging technique described

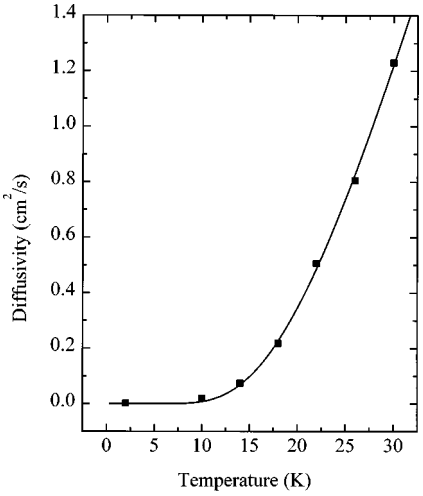

FIG. 2. Temperature dependence of the diffusivity D_E. Solid squares represent the experimental data obtained from our time-resolved confocal PL-imaging technique; solid line is a fit of the experimental data to the theoretical dependence given by Eq. (16).

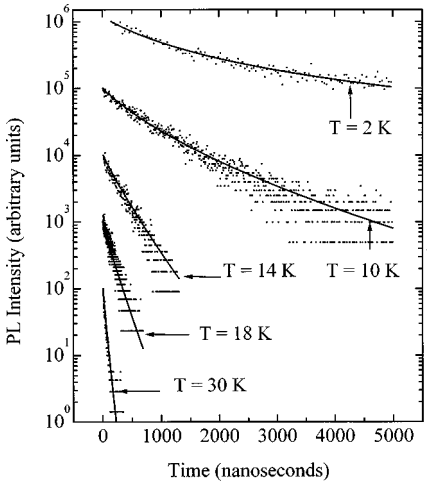

FIG. 3. Time-resolved PL intensity for the type-II GaAs/AlAs superlattice. Dots represent the experimental data; solid lines are obtained using Eq. (15).

elsewhere[5] to determine the exciton diffusivity at various temperatures.[10]

We compare our experimental data on PL-decay kinetics in type-II GaAs/AlAs short-period superlattice with our model. According to Eqs. (1), (2), and (13), the decay kinetics in such systems may be described as

$$I_T(t)=I_0\ \exp\left(-\frac{4\pi D_E n_d t}{\ln(\beta L^2+4\alpha D_E t)-\ln(L^2)}\right)\times(1+2\langle W_R\rangle t)^{-3/2}. \tag{15}$$

As noted earlier, in a two-dimensional system the PL intensity depends weakly on the average distance (L) between the localized states. Hence, the actual choice of L is not important except that the condition $L\ll(n_d)^{-1/2}$ should be satisfied to ensure that $q\ll 1$. In our calculations we used the value of L equal to the exciton diameter ($\sim$230 Å for the GaAs/AlAs superlattice).

We have measured PL-decay kinetics in this superlattice at several different temperatures between 2 and 30 K. At lowest temperatures the decay is strongly nonexponential, whereas for increasing temperature the decay becomes exponential. Using our time-resolved confocal PL-imaging technique, we have obtained the time-dependent spatial profile of the radiating excitons, which allows us to calculate the temperature dependence of the diffusivity $D_E(T)$ (see Fig. 2). The functional dependence of diffusivity on temperature supports our assumption that an exciton diffuses between localized states and that recombination occurs from these localized states. The theoretical dependence of diffusivity on temperature for the exciton transport between localized states is given in Ref. 11 by

$$D_E(T)=D_E^0\ \exp\left(-\frac{E_a}{kT}\right) \tag{16}$$

and is in excellent agreement with our experimental data (see Fig. 2). In Eq. (16), E_a is the exciton activation energy from the localized state and D_E^0 is a constant. A plot of the logarithm of diffusivity versus inverse temperature yields an exciton activation energy of 6.8 meV for our sample. A remarkable temperature invariance of the PL line shape for type-II GaAs/AlAs superlattices[5] also supports our assumption that the excitons recombine from the localized states. This temperature invariance of the PL line shape also implies that the mean radiative-decay rate in the presence of interfacial disorder $\langle W_R\rangle$ is independent of temperature.[12]

The condition $q\ll 1$ is consistent with our experimental data. If this condition is not satisfied, then the diffusion of excitons in the system is effectively suppressed because of the high concentration of traps. This is not the case for the system of interest. A near-Gaussian shape of the time-dependent spatial profile of the radiating excitons is observed that demonstrates that the diffusion is not suppressed and, hence, the condition $q\ll 1$ is satisfied.

We have found that using only two adjustable parameters—namely, concentration of defects n_d and mean radiative decay rate $\langle W_R\rangle$, together with measured diffusivity D_E—we can fit PL-decay data with our model at several different temperatures (see Fig. 3). We have thus found that for our sample $n_d=(2.7\pm 0.6)10^7$ cm^{-2} and $\langle W_R\rangle=(0.40\pm 0.05)\ \mu$s^{-1}. For low temperatures the diffusivity is small and the radiative-decay component dominates, while at high temperatures the main contribution to the decay comes from the nonradiative part. The crossover from the nonexponential decay to almost exponential decay is observed between 10 and 14 K. From the determined value of n_d and the condition $q\ll 1$, we find an upper bound for the average distance between localized states for our system as being $L\ll 2\ \mu$m. The relatively small sheet density of nonradiative defects found is consistent with otherwise reported possibility of heterointerfacial oxygen incorporation or the presence of interfacial dislocations.[13]

V. SUMMARY

In summary, we have developed a phenomenological theory that describes exciton time-decay kinetics in 3D, 2D, and 1D semiconductor structures—taking into account both

intrinsic radiative decay and nonradiative decay due to defect centers. This theory may be particularly useful for systems with ''indirect'' (real and *k*-space) excitons, because for such systems both radiative and nonradiative decays play an equally important role, while for systems with ''direct'' (real and *k*-space) excitons the radiative-decay component is usually dominant. The theory predicts an exponential character for nonradiative decay in 3D systems, almost exponential character in 2D systems, and a strongly nonexponential character in 1D systems. We have used this theory to explain the results of our time-resolved measurements of PL decay in type-II GaAs/AlAs superlattices. The theoretical PL-decay line shapes fit the experimentally measured ones very well at all temperatures using only two adjustable parameters (the density of nonradiative defects and the average radiative lifetime). The experimentally observed crossover from a nonexponential decay regime at low temperatures to almost exponential decay at high temperatures is also predicted by the theory. The theory allows us to extract important characteristics of the sample, such as nonradiative defect density and average radiative-decay rate from experimental PL-kinetics data.

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