Suppression of slow decaying emission in II-VI quantum dots with Förster resonance energy transfer

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Abstract. We report on time-resolved photoluminescence studies of Förster resonance energy transfer (FRET) in structures with two arrays of epitaxial Cd(Zn)Se quantum dots (QDs) of different sizes separated by the ZnSe barrier of a variable width. The acceleration of recombination rate of both fast and slowly decaying components of emission from the energy-donating small QDs with the decrease of the barrier width is well consistent with the FRET mechanism. The found Förster radii turn out to be different for the fast and slow components. The rate acceleration is accompanied by the strong suppression of the slow emission component related, presumably, to the dark excitons. These findings open a way to control the characteristic of QD-based devices.

1. Introduction

Epitaxial Cd(Zn)Se/ZnSe quantum dots (QDs) are very promising as an active region of nano-emitters for the visible range. Recently, it has been demonstrated that the Förster resonance energy transfer (FRET) can take place in arrays of the QDs, possessing high lateral densities [1,2]. It is suggested that the FRET occurs from the ground levels of small QDs (so-called “donors”) towards the excited levels of large QDs (“acceptors”) with fast excitation relaxation to their ground levels. This mechanism can enhance the emission of the large QDs by harvesting the energy from a huge number of the small ones. The efficiency of FRET is strongly dependent on the distance between the donor and acceptor. Therefore, in this study we focus on the heterostructures with double insertions of QDs of markedly different sizes. By variation of the barrier width between these insertions we change the average distance between the donors and acceptors. Using time-resolved photoluminescence (TR PL) measurements we investigate how the decrease of the distance effects the characteristic decay times of exciton transitions. We demonstrate that the FRET apparently controls both the fast and slowly decaying components of excitonic emission related, presumably, to bright and dark excitonic states.

2. Basic consideration

The studied systems with two insertions comprise the donors giving energy to neighboring QDs, acceptors taking this energy, and separated QDs which do not participate in the energy transfer. Details on the peculiarities of the energy transfer, which is controlled by the average donor-acceptor distance and exciton radiative time can be found, e.g., in Ref. [3]. The excitation transfer can occur via FRET if the ground level of the donor-QD coincides in energy with the excited level of the acceptor-QD and if
the condition of close spatial position is satisfied. The acceleration of recombination rate of the donor-QD in the presence of the acceptor-QD located at the distance $R_{da}$ is approximately expressed as

$$\frac{\tau^0}{\tau} = 1 + \left(\frac{R_0}{R_{da}}\right)^6,$$

where $\tau^0$ is the donor-QD lifetime in the absence of the acceptor-QD, $R_0$ is the Förster radius defined as the distance where the transfer efficiency is 0.5.

Previously, it has been well established that the slowly decaying emission component is indicative of emission involving the dark exciton eigenstates in QDs [4,5]. It has been demonstrated also that this emission is promising for qubit application [6]. Because our Cd(Zn)Se/ZnSe QDs have predominantly spheroidal shapes [7], the lowest dark exciton state is characterized by the momentum projection $\pm 2$ on the growth direction and is spin-forbidden. Its radiative recombination, however, can be activated due to the small admixture of the bright exciton states caused by the in-plane asymmetry [8] or by the interaction with acoustic or optical phonons [9]. Such admixtures of the bright exciton dipole moment allows the dark exciton states to be involved into the FRET process as shown by figure 1.

**Figure 1.** Schematic of the energy transitions in a donor-acceptor system. The relaxation and recombination processes are shown by blue and red lines, respectively.

The total PL intensity $I$ can be characterized by the expression $I \sim N_A\Gamma_A + N_F\Gamma_F$, where $N_A$ ($N_F$) and $\Gamma_A$ ($\Gamma_F$) are the exciton population and radiative decay rate, respectively, for the allowed (forbidden) excitonic states. The slow decaying component at low temperatures can be observed only in the case $\Gamma_F \neq 0$. With the temperature increase, the long living dark exciton states populates the bright exciton states and the two exponential decay of the PL can be observed even for $\Gamma_F = 0$. If the relaxation rate between the bright and dark states is faster than $\Gamma_A$, with the rise of temperature $T$, the populations $N_A$ and $N_F$ become related by the thermodynamic equilibrium condition

$$\frac{N_A}{N_F} = \exp\left(-\frac{\Delta E_{AF}}{kT}\right),$$

where $\Delta E_{AF}$ is the energy difference between the forbidden and allowed states. In this case, one can observe at room temperature the PL decay with some average rate which is approximately equal to

$$\Gamma = \frac{1}{2} (\Gamma_A + \Gamma_F).$$
3. Experimental
The Cd(Zn)Se/ZnSe structures were grown by MBE on GaAs substrates. Each of them has two insertions of QDs with a nominal CdSe thickness of ~1.8 and 2.7 monolayers (MLs). The barrier width, \( w \), between them is varied from ~8 nm to 18 nm. Similar structures have been studied previously; however, the arrangement of double insertions was different [10]. TR PL measurements were performed at low temperature (5 K) using a Hamamatsu streak-camera with temporal resolution of ~15 ps. The second harmonics of a tunable Ti: sapphire femtosecond pulsed laser was used for excitation. The laser beam with 2-4 mW averaged power before a cryostat window was focused into a spot of 0.5-1 mm in diameter. At room temperature, the measurements were done using a fast photomultiplier with time-correlated photon counting system.

4. Results and discussion
The emission spectra measured in these structures consist of two wide bands related to the donor QDs (higher-energy) and acceptor QDs (lower energy). The typical image of the normalised emission intensity measured at low temperature in the structures with the narrowest \( w \) show the strong suppression of the slow-decaying emission in the donor QD band (figure 2). The remnant part is mostly pronounced at the energies near 2.52 eV, where QDs should be out of the resonance condition between the excited and ground excitonic levels in the donor and acceptor QDs [2]. Generally, the maximum amplitude of the slow-decaying component decreases, respectively, by about 20 and 4 times for the higher-energy and lower-energy PL band, as compared with the maximal amplitude of the corresponding fast component. The decrease is even more pronounced at elevated temperatures.

The PL decay curves derived from the low-temperature TR PL images are modeled using the following expression

\[
I(t) = -I_{\text{rise}} e^{-t/t_{\text{rise}}} + I_1 e^{-t/t_1} + I_2 e^{-t/t_2}
\]

Here, \( t_{\text{rise}} \) is the rise time, \( t_1 \) and \( t_2 \) are the decay times of the fast and slow decaying components, respectively, related presumably to the bright and dark excitonic states; \( I_i \) denotes the corresponding intensity amplitude. Both the fast and slow decay times decrease with diminishing the barrier width.

We use equation (1) to analyse our results focusing on the characteristic decay times measured at the maxima of the PL bands. With data processing, we assume \( R_{\text{d}} \) being equal to the width \( w \); \( t^0 \) is taken equal to either fast or slow decay time value measured in the structure with the maximal \( w \), which is assumed to be not influenced by FRET. The results of the modeling are well consistent with the linear dependence anticipated for FRET (figure 3). The Förster radius \( R_0 \) derived for the bright and dark exciton states turn out to be different: 10.5 nm and 8 nm, respectively. This difference is suggestive of the independent relaxation channels at low temperature for the bright and dark excitonic states. It implies also that the energy transfer channels for these states are different (see Fig.1). Indeed, the theoretical consideration predicted the strong dependence of the Förster radius on the acceptor radiative and nonradiative life times as well as on the detuning between donor and acceptor energy levels [3].

At room temperature, the decay curves are modulated by the strong influence of non-radiative centers and thermally-induced carrier escape. It especially concerns the fastest time which does not reflect more the intrinsic decay. Moreover, the fitting of the room-temperature decay curves needs three decaying exponents instead of two. In such situation, it is difficult to ascribe which component with either “middle” or “slowest” decay times is related to the mixed (bright-dark) excitonic state. Nevertheless, in the structure with \( w = 18 \) nm, which is almost not-influenced by FRET, both respective decay rates are close to the half-sum of the maximal and minimal rates at low temperature in accordance with equation (2). The deviation from the expected half-sum values is much higher in the structure with \( w = 8 \) nm that indicates likely the stronger modification of decay rates by the FRET mechanism.
Figure 3. Acceleration of fast (squares) and slow (triangles) PL decay times with the barrier width decrease at low temperature. Fitting (dashed line) is done with \( R_0 = 10.5 \) nm and \( \tau^0 = 550 \) ps for the fast component and with \( R_0 = 8 \) nm and \( \tau^0 = 1100 \) ps for the slow component.

Summarizing, our studies of recombination dynamics in structures with two QD insertions separated by a barrier of a variable width confirms the existence of FRET between dots of different sizes. This mechanism influences both fast and slowly decaying emission components ascribed, presumably, to the bright and dark excitonic states. This effect is accompanied by the strong attenuation of the slowly decaying emission component in the donor-QDs. The Förster radius \( R_0 \) is found to be different for the bright and dark excitonic states (10.5 nm and 8 nm, respectively). Room-temperature measurements have exhibited the tendency to averaging the decay rate in the mixed (dark-bright) exciton states. We highlight that the results need more thorough analysis which should takes into account the trapping of carriers by non-radiative centres and thermally-induced carrier escape. However, the demonstrated possibility to control the intensity of slow component by FRET may be useful for set of nanophotonic applications.

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