Recombination dynamics in heterostructures with two planar arrays of II-VI quantum dots

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Abstract. We present time-resolved photoluminescence studies of epitaxial heterostructures with two arrays of Cd(Zn)Se/ZnSe quantum dots (QDs), which are formed by the successive insertion of CdSe fractional monolayers of different nominal thicknesses into a ZnSe matrix. Our data are suggestive of the appearance of effective channels of the energy transfer from the insertion comprising the array with smaller QDs, emitting at higher energy, towards the array with larger QDs, emitting at lower energy. The effect of dark excitons on characteristic times of radiative recombination is discussed.

1. Introduction

Fractional monolayer (ML) insertions of CdSe within a ZnSe matrix have been successfully used as an active region in green lasers pumped optically or by an electron beam [1]. During molecular beam epitaxy (MBE) growth these insertions are transformed into the planar arrays of quantum dots (QDs). As a rule, the lasers developed for the visible range contain several sheets of such QD arrays. The nominal thickness of each CdSe insertion, d, is in the 1.4-2.7 ML range. As an example, the design of an optically-pumped laser developed for violet–green optical converters includes an active region comprising 5-9 CdSe sheets with d=2.7 ML placed in the center of ZnSe wells [2,3]. These QD arrays are formed at slightly different growth conditions depending on their order in a growth run. The respective variation of the QD sizes and Cd content in each sheet can, in turn, affect the QD transition energies and efficiency of pumping.

On the other hand, it has been recently demonstrated that effective Förster resonance energy transfer (FRET) [4] is possible between subsystems of small and large QDs within an inhomogeneous CdSe/ZnSe QD array [5], where the density of states can have the maximum at higher energy than the photoluminescence (PL) peak [6]. This FRET takes place mainly between the ground states of smaller QDs and the excited states of larger QD, followed by the fast energy relaxation to the ground level of the large QDs. We assume that similar process can be between two arrays comprising small and large QDs when the separation between them does not markedly exceed in order of magnitude the critical Förster radius when this mechanism is still efficient (~10-13 nm). This process can affect the recombination dynamics of the QD arrays [7].

In this paper, we focus on exciton recombination dynamics in structures with two fractional ML insertions separated by a ZnSe barrier. These insertions were intentionally made different by the variation of a nominal CdSe layer thickness to provide the inhomogeneous QD arrays with predominantly either small or large QDs. We demonstrate that there is the energy transfer for
separations between the QD arrays, which are typical for green lasers. Our data are also suggestive of the influence of dark excitons in small QDs on this process.

1. Samples and characterization
Two types of samples were grown by MBE on GaAs substrates. Both comprise two sheets of QDs, which in the first approximation can be considered as the arrays of “small” or “large” QDs, depending on the nominal thickness of the CdSe insertion. In the first-type structures, the insertion of smaller thickness \(d=1.4-2.1\) ML was grown first, followed by the insertion with \(d=2.7\) ML, while in the second type this order was reversed. The basic results of optical studies of these structures turned out to be similar. Here, we present mostly data obtained using the first-type structures, where the array exhibiting PL at lower energy \(E_2\) is located above the array emitting at higher energy \(E_1\) (Figure 1, a).

We believe that this arrangement minimizes the energy transfer between the neighboring arrays via radiation. Two samples of this type were thoroughly studied: Sample A (\(d\) values are 2.1 and 2.7 ML) and sample B (\(d\) values are 1.4 and 2.7 ML). Thus, in each structure a PL band contains the lower energy line (lower line) and the higher energy one (upper line). The QD sheets in these two samples are separated by a barrier with a thickness \(w=12-14\) nm. Note that such QD arrays were considered in previous studies as efficiently separated [8].

![Figure 1](image)

Figure 1. (a) Schematic drawing of the first-type structures with two different arrays of QDs. The inferior array radiates at higher energy \(E_1\). (b) PL (461-nm excitation) and PLE spectra measured at 28 K in sample A with 2.1 and 2.7 ML CdSe insertions. The PLE spectra detected from respective PL lines contain similar peaks at \(\sim 2.6\) eV energy.

The structures were first characterized by cw PL and PL excitation (PLE) spectroscopies in a closed-cycle helium cryostat at low temperature. PL measurements performed using cw lasers show that the ratio of the PL intensities of the two lines depends on the excitation energy. PLE spectra were measured with the excitation by emission of a tungsten lamp, dispersed by a monochromator. In sample B, LO phonon replicas are well pronounced in the PLE spectra recorded from the upper 2.62-eV PL line that indicates phonon-assisted energy transfer to nano-islands. The energy transfer has more complicated character for the lines originated from the arrays with the higher CdSe content (2.1 and 2.7 MLs). Their PLE spectra contain two or three smooth peaks (figure 1, b). Surprisingly, the energy position for some of them is similar in the PLE spectra recorded from upper and lower PL lines in the same structure (compare the peaks near 2.6 eV in the top and bottom panels of figure 1, b). It may indicate that these QD arrays are not completely separated, as assumed previously, but linked via some kind of energy transfer.
3. Recombination dynamics
To elucidate the mechanism of excitation transfer we have performed time-resolved PL studies. Temporal behavior of PL intensity in the structures was investigated at low temperatures (2 K) using a Hamamatsu streak-camera with temporal resolution of ~15 ps. A pulsed femtosecond laser with tunable wavelength was used for excitation. Measured PL decay curves are presented in figure 2 (a, b).

To fit PL intensity decay with time, \( t \), we use the following expression

\[
I(t) = A_1 \left( \exp \left( \frac{-t}{t_1} \right) - \exp \left( \frac{-t}{t_{\text{rise}}} \right) \right) + A_2 \exp \left( \frac{-t}{t_2} \right),
\]

where \( t_1 \) and \( t_2 \) are the decay time constants characterizing, respectively, fast and slow decaying PL components; \( A_i \) (i=1,2) is a respective amplitude; \( t_{\text{rise}} \) is the rise time constant (~15-25 ps). The PL decay curves turn out to be almost similar for both the upper and lower emission lines at the above-barrier excitation by a 266-nm (4.66 eV) laser line. Their decay can be fitted by a single exponent with the time constant \( t_1=280-300 \) ps, while the contribution of the other (slower) component is negligible.

With under-barrier excitation by a 461-nm line (2.69 eV), the decay curves are strongly modified. In both structures, we observe shortening of the PL decay time of the upper lines. It is especially strong in sample B, where \( t_1 \) of the 2.62-eV line decreases down to 130 ps; the \( t_1 \) variation for the 2.54-eV line of sample A is much smaller. We assume that the fast PL decay in sample B indicates the efficient energy transfer from the small QDs in the 1.4-ML array towards the larger QDs in the 2.7-ML array which exhibits lower-energy emission. This energy transfer can be done via dipole-dipole interaction between QDs of different sizes, in other words, via the FRET [5]. It takes place when the ground and excited levels of these dots are close to be in resonance (Figure 2, c). Such energy transfer (and acceptable detuning) depends on the exciton radiative time. When its value is less than 1 ns, this process can be efficient at a distance up to 13 nm between interacting QDs [7]. Such a distance is comparable with the barrier width in our structures. The PL decay variation is less pronounced in the sample A, because the excited and ground QD levels in the neighbouring arrays are out of resonance.

\[ \Delta E_{A-F} \] is the splitting of allowed-forbidden exciton states.

Other intricate finding is the enhancement of the slow decaying components with under-barrier excitation in both the lower and upper PL lines. These slow components are characterized by \( t_2=1.0-1.9 \) ns. To understand this phenomenon, let us remind that the fine structure of exciton ground states

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**Figure 2.** PL decay curves measured in samples A (a) and B (b) in the maxima of the upper and lower PL lines at different energies of excitation: 2.69 eV (solid lines) and 4.66 eV (dash-dotted lines). (c) Schematic drawing of possible resonance energy transfer (shown by dashed arrow) between excitonic levels in the small and large QDs. \( \Delta E_{A-F} \) is the splitting of allowed-forbidden exciton states.
comprise optically allowed (AX) and forbidden (FX) dark excitons (see figure 2, c), separated by the energy $\Delta E_{A,F}$ defined by the electron-hole exchange interaction [9]. The FX radiative recombination reveals itself as an appearance of slowly decaying component in time-resolved PL spectra [10-12]. Actually, such FX contribution is observed due to its mixing with the AX state. The efficiency of the mixing depends on the $\Delta E_{A,F}$ value, which is strongly dependent on a QD size. For bulk CdSe, this value is 0.12 meV; for QDs, it ranges between 1.3 and 3.8 meV, increasing with the decrease of the QDs size [10]. When $\Delta E_{A,F}$ is $\leq$ 1 meV, as in the large QDs, the mixing is effective and the recombination rate is high. In the small QDs with large $\Delta E_{A,F}$ separation, the mixing is hampered and the rate of recombination goes down. This explains the appearance of the slow component in the PL band originating from the small QDs. The recombination rate in the large QDs is decreased as well, because it is controlled by the resonance energy transfer via the dipole-dipole interaction with the allowed states of the small QDs, which are slowly and insufficiently populated with the large $\Delta E_{A,F}$ value.

Summarizing, we demonstrate that QD planar arrays formed by CdSe fractional monolayer insertions into a ZnSe matrix cannot be considered as isolated with barrier widths typical for lasers. Effective energy transfer to one of these arrays can be realized if the ground level of small QDs is in resonance with the excited level of large QDs. This conclusion is supported by the results of time-resolved studies demonstrating the acceleration of PL decay in small QDs which transfer the energy to the large ones. The enhancement of slow decaying components evidences the influence of dark excitons on the recombination process. Our finding can be used for optimization of II-VI laser design.

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