

Switching of resonance energy transfer mechanism in a dense array of II-VI quantum dots

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Abstract. We report on Förster resonance energy transfer (FRET) in a dense array of II-VI epitaxial quantum dots (QDs). Besides FRET between the ground states of QDs of different sizes, we observe the energy transfer via the excited levels of large QDs which are in resonance with the ground levels of small QDs. The switching of dominant energy transfer mechanism, revealed by photoluminescence excitation spectroscopy, takes place at the energy controlled by the architecture of quantum levels in these arrays.

Introduction

Epitaxial CdSe/ZnSe II-VI quantum dots (QDs) have great potential for nanolaser application. One of main features of the arrays of such QDs, which have high lateral densities $>10^{10} \text{ cm}^{-2}$, is a relatively narrow width of photoluminescence (PL) band (40-50 meV) that contradicts the broad distribution of QD sizes, revealed by transmission electron microscopy (TEM) studies [1,2]. Besides, our recent micro-PL spectroscopy studies exhibited narrow exciton lines of single QD emission instead of an expected smooth PL band [3]. These findings evidence the spectral selection of a limited number of radiating QDs. To explain such features it has been proposed that Förster resonance energy transfer (FRET) [4] between the smaller QDs (“donors”) and larger ones (“acceptors”) takes place in such QD ensembles [5]. The FRET mechanism between QDs can be realized in different ways. First, it can take place between the ground states of the “donor”-QDs and “acceptor”-QDs, provided their absorption and emission contours are overlapped (FRET¹). This mechanism is realized in an ensemble of colloidal QDs [6], between sheets of vertically coupled direct and indirect bandgap QDs [7], and in Si nanocrystals [8]. In the dense and inhomogeneous array of epitaxial II-VI QDs, the energy transfer can be performed by other way, namely, from the ground levels of smaller QDs towards the excited levels of larger QDs, followed by the fast excitation relaxation to their ground levels (FRET²) [5]. The coincidence of the ground and excited levels in the QDs of different sizes is the necessary prerequisite for such mechanism. It can provide emission from a limited number of selected large QDs, while the emission from a huge number of small QDs will be completely suppressed [9]. Note that both FRET processes can act in competition and coexistence with radiative, tunneling, and hopping mechanisms of energy transfer.

2. Experimental

To prove this concept, we have performed the comprehensive studies of structures containing CdSe fractional monolayer (ML) insertions in a ZnSe matrix, which are spontaneously transformed into the QD arrays during growth by molecular beam epitaxy [10]. The structure A contains one CdSe insertion with a 2.7-ML nominal thickness. Structures with two insertions (B and C) contain 1.4 and



2.7 ML sheets. In these structures, the sheet with lower Cd content, and hence smaller QDs, can act as a donating array, while the sheet with higher Cd content will accept the energy. These two insertions are separated by a ZnSe barrier of a different width to control the FRET efficiency. The nominal barrier widths were 7 nm in the structure B and 15 nm in the structure C; their gradient along a substrate allows us to elucidate precisely the effect of width variation on the efficiency of energy transfer.

PL and PL excitation (PLE) measurements were performed at low temperature (20 K) using detection by a nitrogen-cooled CCD camera and excitation by a halogen lamp dispersed by a monochromator. The hyper-PLE spectra comprise the PL spectra measured at continuously changed excitation energy. Thus, the tracks of PL in the coordinates “excitation energy – detection energy” are obtained synchronously with the excitation energy variation. The TEM studies have shown that the structure A consists of distinct nano-islands with the lateral density of 10^{11} - 10^{12} cm $^{-2}$ and average distance between them about 5-10 nm (sufficiently small for FRET). The QD characteristic lateral sizes are distributed within the 2-12 nm range with maximum at 2-4 nm [3,5]. In contrast to that, the PL maximum position is near 2.42 eV (Figure 1, a). In accordance with preliminary modeling [5,9], it corresponds to the emission from the QDs with the lateral sizes of 5-7 nm and Cd content about 85%. Thus, a significant part of QDs is out of radiation process.

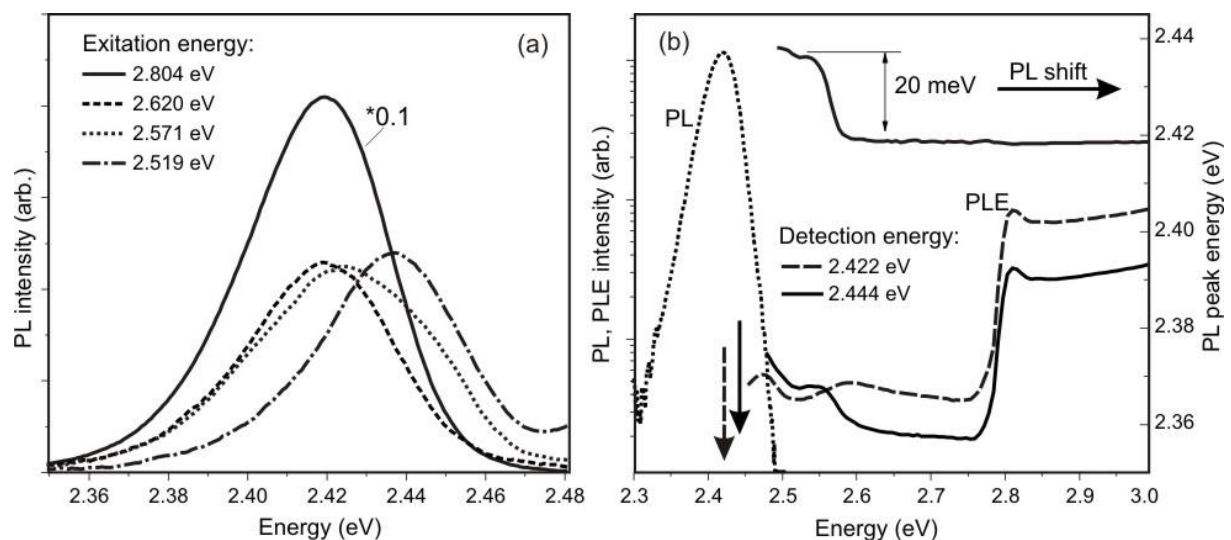


Figure 1. (a) PL spectra measured in the structure A at different excitation energies. (b) PLE spectra recorded in the same structure at two detection energies corresponding to the PL maximum positions with above-barrier (dashed line) and under-barrier (solid line) excitations. On the top, the solid line shows the shift of PL maximum.

In the studied structures, we observe an unusual feature – the modification of PL spectra when the excitation energy changes. Namely, the PL maximum shifts toward higher energies by 10-25 meV at ~2.55-2.6 eV energy with respect to the position corresponding to the excitation above the ZnSe barrier energy gap (2.8 eV). In particular, this shift approaches 20 meV in the structure A (Figure 1, a). The PLE spectra recorded from the shifted PL maximum differ from those registered at the initial PL peak position. Namely, no features are observed above the 2.6-eV boundary. Thus, the states in the 2.6-2.8 range do not supply any excitation for this shifted PL peak. These peculiarities look even more pronounced in the hyper-PLE spectra (Figure 2). Besides, the hyper-PLE spectroscopy shows that the value of the shift depends on the distance between two QD sheets (the closer sheets, the stronger shift). Moreover, in the case of the small barrier width between these sheets (7-10 nm) the “donor” QD array has dramatically decreased PL intensity (Figure 2, a). Apparently, this QD array transfers the most part of excitation to the lower-energy states in the “acceptor” sheets. We highlight that the

insertions with small Cd content do not exhibit such blue shift at all (see PL tracks of the 1.4 ML CdSe insertions in the hyper-PLE spectra shown in Figure 3). It is also essential that the blue shift of PL peaks takes place at the same energy around 2.6 eV in different structures.

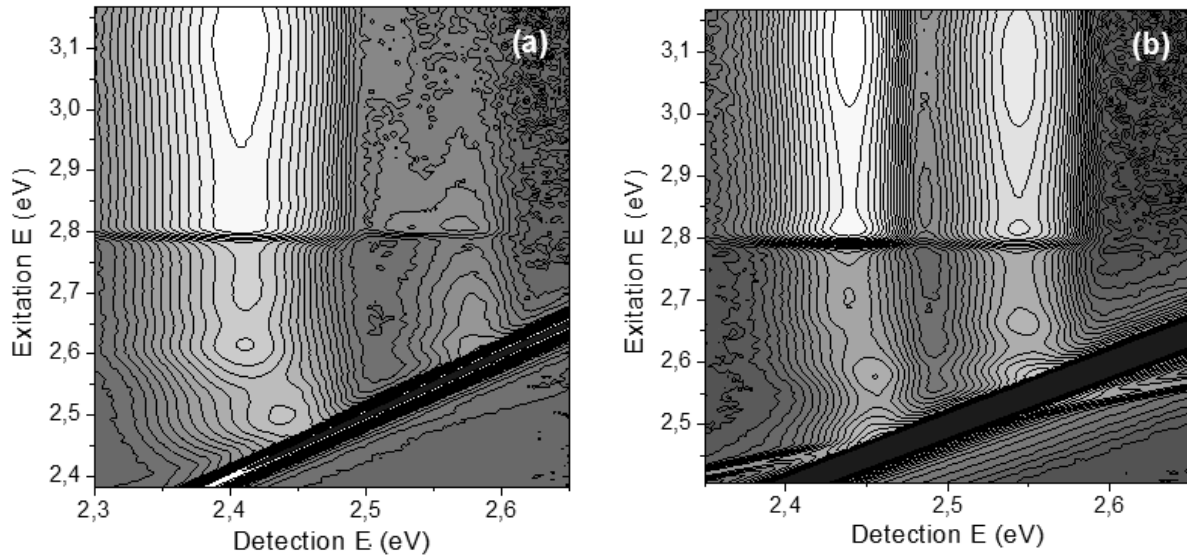


Figure 2. Hyper-PL excitation spectra measured at 20 K in the B (a) and C (b) structures with two insertions. The brightness represents the PL intensity, decreasing from white to black, shown in logarithmic scale. Contours connect the points of equal intensity. Inclined black line in bottom part of the images is the track of excitation with continuously changed energy.

3. Modelling and discussion

Theoretical modeling of excitonic levels, considering the QDs as spheroids with a Gaussian potential profile, is performed as described in Refs. [7,8].

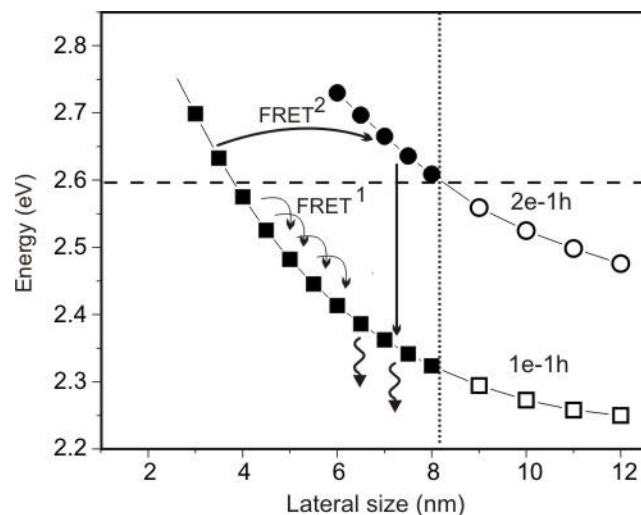


Figure 3. Dependences of exciton energies on QD lateral sizes calculated for CdSe QDs with 85% Cd content in their center. Possible energy transfer processes are marked by arrows. The white marks denote data for largest QDs which are presumably defective; they are separated from radiating QDs by a vertical dotted line. Horizontal dashed line separates the energy ranges where different FRET mechanisms dominate.

The calculated electron (hole) levels in the QDs of different lateral sizes are used to compose the excitonic levels, whose symmetry allows their participation in the process of excitation transfer. Figure 3 presents the simplified scheme of possible energy transfer channels, which involve only 1e-1h and 2e-1h excitonic levels. Here, 1e (1h) corresponds to the first electrons (holes) level, 2e denotes excited electron level. The existence of other excitonic states such as 1e-2h is neglected. We consider the FRET² via the excitonic states 1e-1h of the small QDs (lateral size of 2-4 nm) and 2e-1h states of the larger ones (lateral size of 6-8 nm). The 1e-1h states of these 6-8-nm-sized dots are radiating, while the CdSe islands of larger sizes are usually defective and cannot participate in emission process [11,12]. Therefore, the FRET² can exist only until the energy is higher than 2.6 eV, since below there are no suitable states. Underneath this 2.6-eV boundary, the FRET¹ can dominate. This mechanism acts via the ground states 1e-1h in two closely situated QDs which have small energy detuning. In our inhomogeneous systems, the FRET¹ can be a multistep process, which includes several steps of energy transfer from a “donor” QD to a next “acceptor” dot, which plays a role of the “donor” for the next step. The required closeness of QD energies for such mechanism results in the blue shift of the PL band as a whole. Note that involvement of 1e-2h states to the energy transfer process will provide some blue shift of PL maximum as well. In any case, we assume that the basic reason of observed PL modification near 2.6 eV in the studied structures is the change of the energy transfer mechanism.

The modeling also shows that in the case of low Cd content the excited levels exist only in the too large QDs which are optically inert. Therefore, the blue shift cannot be pronounced in the QD arrays formed from thin CdSe insertions. Indeed, the 1.4 ML CdSe sheets, which have lower Cd content in the dots, do not exhibit the PL blue shift at all. The modeling predicts also the sharpest FRET² cutoff for bimodal QDs size distribution. On the contrary, with large dispersion of QD sizes the cutoff must be more smooth. This is also consistent with experimental data obtained from structures with different QD size statistics (compare 2.7-ML insertion PL tracks in Figure 3, (a) and (b)).

In conclusion, we demonstrate that both FRET¹ and FRET² can be dominating energy transfer mechanisms in CdSe/ZnSe QDs at helium temperatures. Switching between these resonance mechanisms takes place at certain energy of excitation, which depends on the architecture of quantum levels in an array. Our data provide a new insight into unusual optical properties of fractional monolayer CdSe/ZnSe insertions studied from the end of the last century. The FRET² can be used for the spectral selection of single QDs in combination with spatial isolation to fabricate efficient nano-emitters.

Acknowledgments

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