

Hot exciton relaxation in multiple layers CdSe/ZnSe self-assembled quantum dots separated by thick ZnSe barriers

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Abstract. We have studied PL and PLE spectra of two samples (A and B) of MBE grown CdSe/ZnSe asymmetric double quantum wells with different amount of deposited CdSe layers separated by 14 nm ZnSe barrier. It has been found that PLE spectra of the states forming short wavelength side of the PL spectra of both deep and shallow QWs of the sample A as well as that of deep QW of the sample B demonstrate oscillating structure in the spectral ranges corresponding to exciton states of self-assembled quantum dots only. Meanwhile PLE spectra of the short wavelength states of shallow QW the sample B revealed pronounced oscillating structure with energy period of ZnSe LO phonon under excitation with photons in a wide energy range both in the regions of quantum-dot states and in that of free states in the ZnSe barrier. In these spectra creating of excitons with kinetic energies more than 0.3 eV was observed which considerably exceed the exciton binding energy as well as LO phonon energy (both appr. 0.03 eV). It has been concluded that oscillating structure of the PLE spectra arises due to cascade relaxation of hot excitons. We discuss the model which explains these experimental findings.

1. Introduction

The numerous structural and spectroscopic studies carried out so far have shown that, under certain conditions, epitaxy of several CdSe monolayers into a ZnSe matrix leads to formation of a quantum well (QW) from an inhomogeneous ZnCdSe solid solution with nanosize objects, many properties of which are of 0D nature. Depending on the growth conditions, and primarily on temperature, such self-organized quantum dots (QD) may be of 2D or 3D nature. The most complex structure is observed for 2D objects obtained at $T = 280^\circ\text{C}$. At this temperature the coherent CdSe insertions in ZnSe with CdSe nominal thickness in the range of 1-3 ML are known to generate planar CdSe-enriched QDs incorporated into the body of ZnCdSe QW [1, 2].

In this communication, we discuss the optical spectra of two ZnSe/CdSe/ZnSe double heterostructures grown by MBE at growth $T = 280^\circ\text{C}$ which includes two CdSe quantum wells with different nominal thicknesses separated by a ZnSe barrier with a thickness of 14 nm. The nominal thickness of the first CdSe deposited layer was 1.4 and 1.8 ML (samples B and A, respectively). The thickness of the second layer was $t_{\text{CdSe}}=2.7$ ML in both samples. Other details of the growth conditions as well as design of the samples under study and experimental details can be found in [3].

As it was shown previously, in multilayer ZnSe/CdSe/ZnSe samples with thicknesses of ZnSe barriers exceeding 4 nm there is (i) no correlation of the CdSe QDs in the adjacent layers [4] and (ii) at low temperatures there is no evidence of exciton tunneling between QD states in adjacent QW layers [5].



2. Experimental results and discussion.

Previous study has shown that the main features of the PLE spectrum of heterostructures with planar QDs are the following: (i) the oscillating character of PLE spectra for states on the short-wavelength side of the PL band reflecting exciton cascade relaxation with emission of LO phonons, which practically disappears from the PLE spectrum above a certain photon energy E_{ME} , which is related to the region of transition from states localized within QDs to those distributed over all the QW plane; and (ii) increasing of the PL signal more than an order of magnitude under excitation by photons with energy exceeding the energy gap of the ZnSe barrier material [3]. As one can see from figure 1 a-c both above-mentioned features of PLE spectra can be seen in PLE spectra of both deep and shallow QWs of the sample A as well as that of deep QW of the sample B.

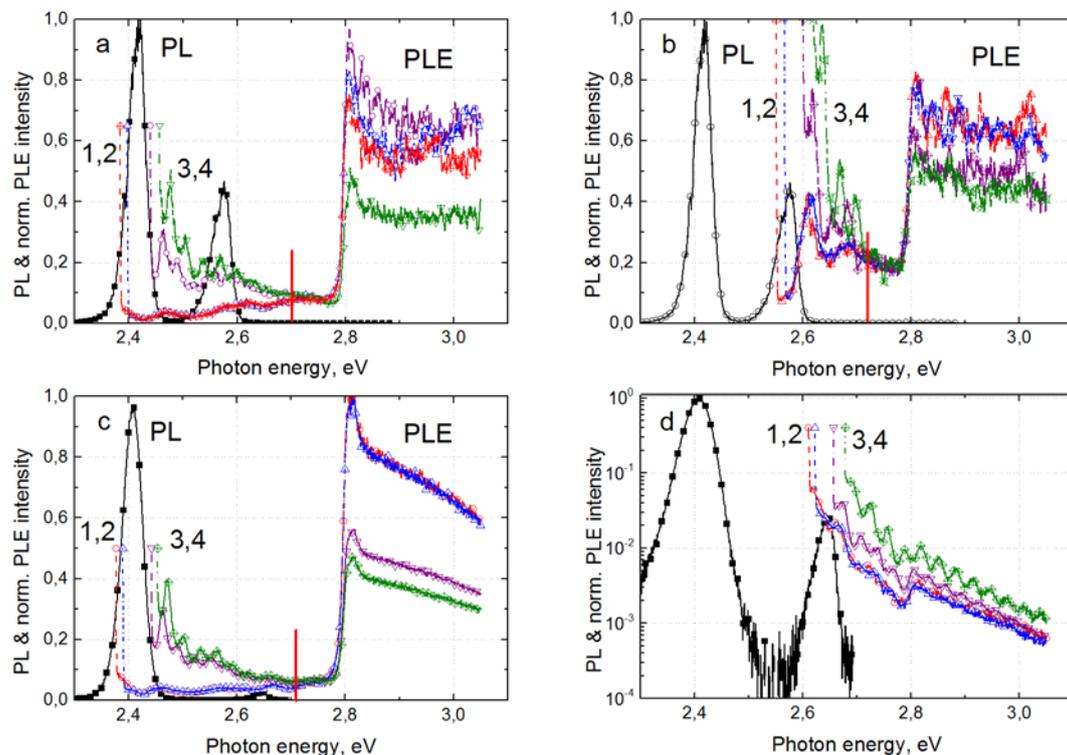


Figure 1. PLE spectra of the long- and short-wavelength parts of PL bands of the samples with nominal CdSe contents $t_{CdSe} = 2.7$ and 1.8 ML (sample A, panels a and b) and 2.7 and 1.4 ML (sample B, panels c and d), respectively. Each panel shows two PLE spectra for each of two detector positions on the long- and short-wavelength parts of the PL band. All the excitation spectra in panels a, b and c are normalized to the amplitude of a spectrum at energy of 2.75 eV. The PL and PLE spectra of the sample B present in panel d in a semilog scale. All PLE spectra of short-wavelength parts of a shallow PL band of sample B are shifted along the vertical axis for clarity. The vertical lines in panels a, b, and c show the position of the exciton percolation threshold E_{ME} .

Unlike abovementioned character of PLE spectra, shown in panels a, b and c, distinct oscillating structure of PLE spectra was found for the states forming short-wavelength side of the PL spectrum of the sample B (see figure 1, panel d) not only within QW states but also at the spectral range above ZnSe fundamental absorption edge where we have detected up to 10 maxima in PLE spectra separated by the energy of ZnSe LO-phonon. It worth pointed out that energy relaxation with emission of LO phonons is a characteristic feature of hot exciton relaxation process [6].

Hot exciton nature of the structure observed in PLE spectra is the most clearly manifested when the excitation spectra are detected in polarized light. Figure 2 shows two PLE spectra obtained under excitation by linearly polarized light and recording in the parallel (solid curve Y1) and crossed (dash

curve Y2) orientations of the polarizer and analyzer. The same figure presents a spectrum of the degree of polarization $Y3 = (Y1 - Y2)/(Y1 + Y2)$ (curve Y3 with symbols).

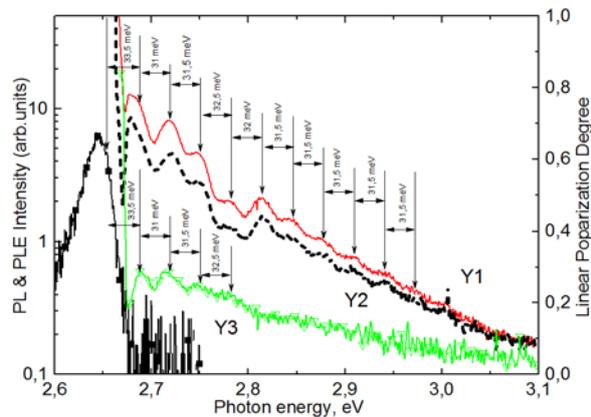


Figure 2. Black solid line with symbols shows the PL spectrum of sample B. Solid line Y1 and dashed line Y2 represents linearly polarized PLE spectra of the same sample in polarizations with parallel and crossed orientations of polarizer and analyser, respectively. Curve Y3 indicates the spectrum of the linear polarization degree (see text).

It can be concluded that both above-mentioned features of PLE spectra reflect the role of two main channels of the population of the QD emitting states, namely, (i) direct capture of excitons from the barrier states to the QD states and (ii) initial capture of electronic excitations in QW states with the following diffusion along QW states and consequent capture in QD states. The simple estimation of the relative role of these two ways of populations of QD emitting states is given by total square of QDs in QW plane. For 10 nm of mean lateral QD size and QD density states of 10^{11} cm^{-2} it gives 10 percent for direct capture from the barrier states and 90 percent for the capture to QW states followed by diffusion and capture in QD states. So, in normal conditions direct capture of excitons from the barrier states gives a small correction to the population of QD states.

Nevertheless if one supposes that due to some reasons excitation channel of the QD emitting states through QW states is suppressed, then the only possible way for population of QD states would be direct capture of excitons from the barrier states. In this case cascade relaxation of hot excitons with the emission of LO phonons is dominant mechanism of the population of the emitting QD states (the direct capture of free e-h pairs from the barrier to QD states can be neglected due to built-in electric fields available in the samples under study [5]).

Thus, the clue point in the discussion of the differences in the shapes of PLE spectra of the samples A and B is the understanding of the negligible role of QD states population via the states of shallow QW in the sample B.

One of the possible ideas was suggested in paper [3] according to which all amount of CdSe in shallow QW of the sample B (1.4 ML) accumulates into QDs. In this case QDs will be surrounded by ZnSe barrier material in all three dimensions and thereby QDs are spatially isolated from each other. To check this idea we have studied the PLE spectra of specially grown sample ZnSe/CdSe/ZnSe with single CdSe QW with the same nominal thickness $t_{\text{CdSe}} = 1.4 \text{ ML}$ and have found that the shape of its PLE spectra looks very similar to that shown in Figure 1 a-c. This result indicates that any possible explanation should take into account multilayer character of the samples under study. In the following we discuss the model which is based on this idea and explains available experimental findings.

3. Model description

3.1. Quantum well states in growth direction.

High resolution transmission electron microscopy of the samples grown in similar conditions shows [1, 2] that the Cd distribution in the growth direction with a good accuracy can be approximate by the function

$$C(z) = \frac{4C}{\left[\exp(-z/l) + \exp(z/l) \right]^2}, \quad (1)$$

where the point of reference for z is taken in the middle point of distribution. A parameter l defines the width of the Cd distribution, and C is the Cd concentration in the center monolayer of the QW at some point of the lateral QW plane. The function $C(z)$ in Eq.(1) is considered as a continuous function and presents the averaged two dimensional Cd concentration.

The knowledge of the Cd distribution allows us to construct the potential profile of the QW in growth direction of heterostructure. We consider the limit of strong confinement of exciton in z direction [7] and a large lateral size of island in comparison with exciton radius a_B in the plane of QW. Using $C(z)$ we can present the averaged potential profile $U_e(z)$ for electrons and $U_h(z)$ for holes of the QW as

$$\begin{aligned} U_e(z) &= -C(z)\Delta_e, \\ U_h(z) &= -C(z)\Delta_h, \end{aligned} \quad (2)$$

where z is the particle coordinate in the growth direction, Δ_e and Δ_h are the conduction and valence bands offsets, respectively. The quantization levels for exciton in the QW with potential profile given by $U_e(z)$ and $U_h(z)$ and corresponding wave functions can be found as eigenvalues and eigenfunctions of the Schrödinger equation.

3.2. Numerical characteristic of energy transfer rates between asymmetrical QW pairs.

Potential profile in growth direction of samples A and B with asymmetrical quantum wells based on optical spectroscopy data are shown in Figure 3. Wavy and thick arrows indicate energy transfer from the ground QD and QW states to corresponding states in deep QW (we suppose that rates of all exciton energy relaxation processes in barrier and quantum well states are much exceed that of recombination and energy transfer processes).

Some important conclusions can be made from the data presented in Figure 3:

(i) in sample A energy transfer from QD ground states of shallow well is possible only to QD states of deep well but this process looks improbable due to random spatial occupation of QDs in adjacent QW layers;

(ii) similar process in sample B includes as final states continuous spectra of QWs and probability of this process is determined by overlap integral between corresponding wave functions only.

Features listed in (i) and (ii) explain differences in relative intensities of emission bands from shallow and deep QWs in PL spectra of samples A and B

In order to explain different shapes of PLE spectra of the samples A and B shown in Figure 1 *b* and *d*, we should be mostly interesting in comparison of the energy transfer rates from ground state of shallow QW and corresponding states of deep QW in these samples shown by thick arrows in Figure 3. We estimate probability of transition from the ground state of shallow QW to a state of deep QW which is proportional to the overlap integral between corresponding wave function:

$$I_{1,2} = \int \Psi_{QW_1} \Psi_{QW_2} dr. \quad (3)$$

Transition rates between two layers of QWs in samples A and B can be compared by parameter

$$\beta = \left| I_1^2 \right| / \left| I_2^2 \right|.$$

We have shown that in the samples under study this parameter is $\beta \ll 1$ for $\Delta_e/\Delta_h = 3$ [8], which explains the peculiarities of the energy transfer in the samples A and B.

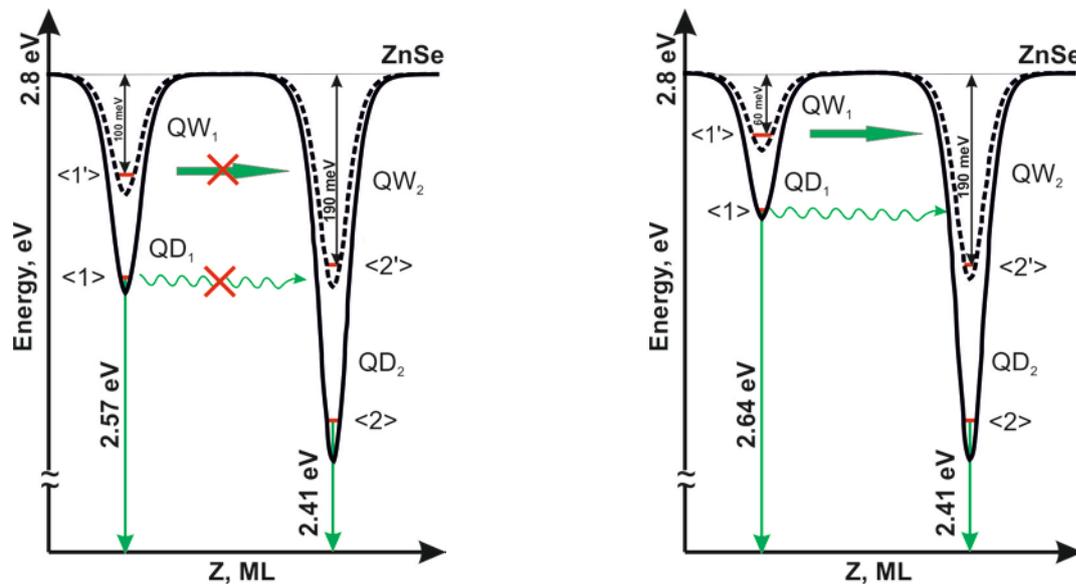


Figure 3. Energy diagram of samples A and B (left and right panels, respectively) for the average potential in the growth direction (Z). Dashed and solid lines indicate QW potential profile in Z direction between and within quantum dots, respectively. <1> and <2> - percolation thresholds of shallow and deep QWs, <1> and <2> - emitting states of QDs of shallow and deep QWs, respectively, (ground states of QWs and QDs in valence bands set as an energy points of reference).

3.3. Estimations of exciton capturing rates

The PLE spectra of shallow QW of the sample B at the spectral range above ZnSe fundamental absorption edge shows pronounced oscillation and exponential decay. To explain these phenomena we consider cascade relaxation of hot excitons with consequent direct capture from the barrier states to the QD states. During single LO phonon emission there are two competing processes: exciton transition as whole particle from 1s state to 1s state with lower kinetic energy and non-radiative exciton decay on free electron and hole, which are then separated by the built-in electric field. Therefore, the higher photon excitation energy the higher probability of exciton decay in the process of cascade relaxation.

The details of calculations are as follows. Wavefunction of the exciton initial state is given by

$$\Psi_{1s,k}(\mathbf{r}_e, \mathbf{r}_h) = \exp(i\mathbf{k} \cdot \mathbf{R}) \exp(-r/a_B) / (\pi V a_B^3)^{1/2}, \quad (4)$$

where \mathbf{r}_e and \mathbf{r}_h are electron and hole coordinates respectively, $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$, \mathbf{R} is coordinate of the center of mass, V is normalizing volume, \mathbf{k} is exciton wavevector. The final state is described either by the wavefunction of 1s with smaller momentum or by wavefunction $\Psi_{\mathbf{k}_e, \mathbf{k}_h}$ of free electron and hole with wavevectors \mathbf{k}_e and \mathbf{k}_h , respectively. The rates of the transitions are given by Fermi's golden rule

$$W_c = (2\pi / \hbar) \sum \left| \langle \Psi_{\mathbf{k}_e, \mathbf{k}_h} | H_{Fr} | \Psi_{1s,k} \rangle \right|^2 \delta(E_f + \hbar\Omega_{LO} - E_i), \quad (5)$$

$$W_{1s} = (2\pi / \hbar) \sum \left| \langle \Psi_{1s,k} | H_{Fr} | \Psi_{1s,k} \rangle \right|^2 \delta(E_f + \hbar\Omega_{LO} - E_i),$$

where W_c is the rate of exciton decay, W_{1s} is the rate LO phonon emission by exciton as whole particle, summation is taken over all final states, δ is Dirac delta function, E_f and E_i are energies of final and initial states, respectively, and the exciton-phonon interaction is described by Fröhlich mechanism

$$H_{Fr} = i e \left[2\pi \hbar \Omega_{LO} / V (\epsilon_{\infty}^{-1} - \epsilon_0^{-1}) \right]^{1/2} \hat{c}_q^{\dagger} \left[\exp(i\mathbf{q} \cdot \mathbf{r}_e) - \exp(i\mathbf{q} \cdot \mathbf{r}_h) \right] + c.c. \quad (6)$$

where e is electron charge, Ω_{LO} is LO phonon frequency, \mathbf{q} is phonon wavevector, \hat{c}_q^{\dagger} is phonon creation operator, ϵ_{∞} and ϵ_0 are the high- and low-frequency dielectric constants. Straightforward calculations yield the probability of bulk exciton decay in the process of single LO phonon emission $W_c / (W_c + W_{1s}) \approx 0.4$, which is in a good agreement with experimental findings.

4. Summary and conclusions.

We have studied energy transfer between electronic states in MBE grown double CdSe/ZnSe asymmetrical quantum wells with self-assembled quantum dots in dependence of nominal thicknesses of deposited CdSe in adjacent layers. It was found that in the samples of proper design the situation can be realized when the rate of energy transfer from ground state of shallow QW to all states of deep QW is much larger than energy transfer rate between QW and QD states within the shallow QW itself. We have shown that in this case the only channel of population of QD exciton states participated in the emission spectrum of shallow QW is direct capture of free excitons from ZnSe barrier through the mechanism of cascade relaxation of hot excitons. We put forward the model which explains the shape of PLE spectra of the samples with such features.

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