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Redistribution of localised excitons in CdSe/ZnSe quantum dot structures

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Abstract

Population processes and recombination mechanisms of excitons localised in CdSe/ZnSe quantum dot structures are investigated. The photoluminescence (PL) properties are governed by lateral energy transfer within a dense ensemble of quantum dots, which differ in size and Cd concentration, providing for a complex potential landscape with localisation sites of widely varying depth for excitons. At low temperatures, lateral transfer by tunnelling leads to a mobility edge at 2.561 eV. Thermally activated escape and recapture of excitons cause a strong redshift of the PL maximum and the mobility edge.

Keywords: Quantum dots; Time-resolved investigations; Excitons; ZnCdSe

1. Introduction

Structural and compositional fluctuations in semiconductor structures, providing three-dimensional localisation sites for excitons, are dubbed quantum dots (QDs) [1]. Such QD structures differ, depending on the material system and growth conditions, in size, shape and alloy concentration. Therefore, a complex potential landscape with a potentially large variation of the localisation energy is provided. The close proximity of such QDs, e.g. in high density ensembles, renders lateral transfer processes important in the understanding of the exciton dynamics of such quantum structures [2–11]. At low temperatures and excitation densities lateral migration of excitons is limited by tunnel processes. Increasing the temperature thermal escape and recapture provides an additional and often more efficient transfer mechanism. Thus, when the thermal energy becomes sufficient to overcome the localisation provided by the QDs, the mobility of the excitons/carriers is drastically enhanced resulting in a 2D-like behaviour. In photoluminescence (PL) experiments the redistribution of excitons in favour of larger QDs leads to an enhanced redshift of the PL peak as a function of temperature or delay time. Model systems for such complex quantum structures are (In,Ga,Al)(As,N)- and (Zn,Mg,Cd)(S,Se)-based thin ternary and quaternary layers embedded in suitable barrier materials. Inhomogeneous segregation and interdiffusion as well as strain-driven surface migration lead to complex lateral potential landscapes [12].

In the present paper, we report on the lateral redistribution of excitons in a ZnCdSe QD structure. A dense array of QDs with a wide range of localisation energies is provided by lateral inhomogeneities of the Cd concentration and, for suitable growth conditions, by islands formed in a Stranski–Krastanow (SK)-like mode. The resulting complex potential landscape allows studying lateral exciton transfer processes. Despite pronounced Cd-concentration fluctuations, the ZnCdSe layer formed exhibits 2D-like properties [13,14] attributed to their high density. The SK-like islands provide strong exciton localisation as a result of their higher Cd-content, larger volume, and low area density

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($\sim 200\ \mu m^{-2}$) and, thus, allow probing local properties up to elevated temperatures. At low temperatures, lateral exciton transfer by tunnelling is important for 2D-like QDs but inhibited for the larger SK-like QDs. At temperatures above 100 K, thermally activated hopping becomes the dominating transfer process, causing a strong redistribution of the excitons.

2. Experimental set-up

To study transfer processes in an inhomogeneously QD ensemble we choose a quantum dot structure with well-known optical and structural properties [13–15]. The investigated sample was grown by molecular beam epitaxy (MBE) on a GaAs (001) substrate. A single (nominal) CdSe layer with a thickness of 2.8 monolayer (ML) was embedded in pseudomorphically strained ZnSe as described in detail in Ref. [15]. QD-like localisation sites are provided by islands generated by Cd fluctuations (so-called type A islands) and somewhat larger islands formed in a SK-like mode (so called type B islands). The island densities (lateral sizes) are, respectively, some $10^{11}\ cm^{-2}$ (5–10 nm) and $2 \times 10^{10}\ cm^{-2}$ (~ 16 nm) [14,15]. The localisation properties strongly depend on the density and on the Cd content of the islands. Due to their formation conditions, type A islands provide shallow localisation sites with an approximately exponential distribution of localisation energies. Their high density and their shallow localisation energies lead to a 2D-like behaviour of the ZnCdSe layer, which becomes dominant above 100 K. In contrast, the clear 0D-like character of the somewhat larger type B islands is supported by their high Cd content and their smaller density providing deeper localisation sites.

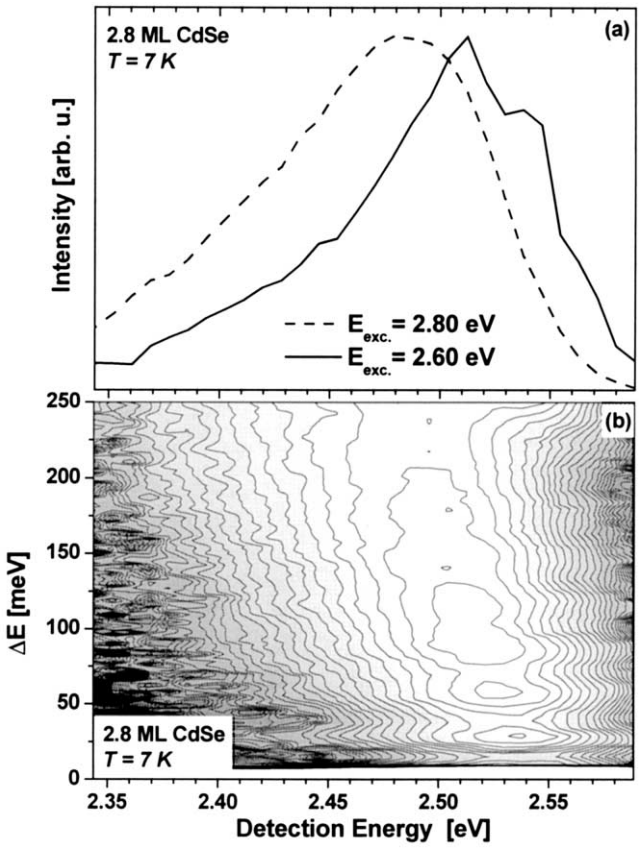

Fig. 1. (a) Photoluminescence spectra of a CdSe/ZnSe quantum dot structure recorded with excitation energies well below (straight line) and resonant to the band edge of the ZnSe matrix (dashed line). (b) Greyscale-coded plot of the logarithmic PL intensity as a function of the detection energy and the excess energy (ΔE, difference between excitation and detection energy).

The optical properties of the CdSe QDs were investigated by PL excitation (PLE) and time-resolved PL (TRPL) spectroscopy at temperatures between 2 and 210 K. PLE was recorded by dispersing the light of a tungsten lamp with a 0.27-m double-grating monochromator with a spectral resolution better than 1 nm. TRPL investigations were performed using a Nd:YAG pumped dye laser with a cavity dumper. Excitation energies were chosen between 2.64 and 2.88 eV to excite below and well above the ZnSe barriers, respectively. The luminescence was detected with a multi-channel plate photo-multiplier attached to a subtractive 0.35-m double-grating monochromator. The laser pulse had a duration of 4 ps, while the temporal resolution of the whole system was determined to be ~ 20 ps. Alternatively, a Hamamatsu streak-camera system in single-sweep mode with a repetition rate of 1 MHz was applied for time-resolved investigations. Here, the excitation was provided by a frequency-doubled Ti:Sa laser with a pulse duration of 3 ps at an energy of 3.07 eV. The temporal resolution of ~ 25 ps was determined by the applied single-sweep mode.

3. Results and discussion

The radiative recombination of localised excitons leads to a broad emission band around 2.5 eV at $T = 7$ K in the investigated sample. Time-integrated PL investigations with excitation above the ZnSe bandgap of the very same sample were published in Ref. [13]. Decreasing the excitation energy well below the bandgap of the ZnSe matrix results in a blue shift by ~ 30 meV of the PL maximum as shown in Fig. 1(a). This blue shift increases with decreasing excess energy ($E_{exc} - E_{det}$) and is attributed to a small capture cross-section and the abundant 2D-like localisation centres on the high-energy tail [16]. With increasing excess energy, lateral carrier motion leads to a preferential capture into larger QDs, providing strong localisation. PLE investigations indeed support the competition of the population processes for shallow and deep localising QDs on the high-

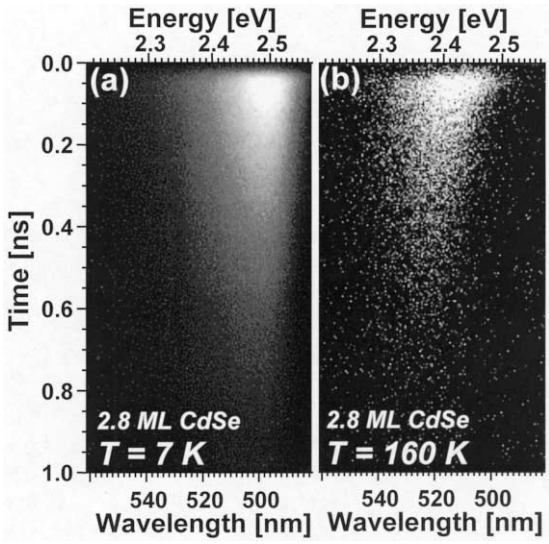

Fig. 2. PL dynamics recorded with a streak camera at 7 K (a) and 160 K (b). The intensity is greyscale-coded with white indicating high intensity.

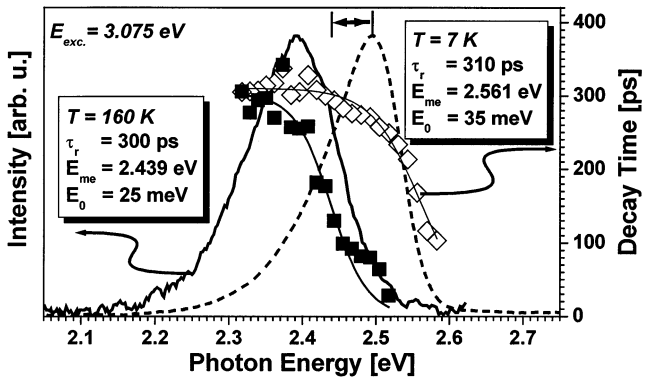

Fig. 3. Time-integrated photoluminescence and decay constants as a function of the detection energy. Eq. (1) was applied to determine the parameters τ_{rad}, E_{me} and E_0. For further explanation, see the text. The data were recorded at 7 and 160 K, respectively. The arrow marks the redshift due to the temperature dependence of the bandgap.

and low-energy tail of the logarithmic PL emission band, respectively. Fig. 1(b) shows a greyscale-coded map of the PL intensity as a function of the excess excitation energy and the detection energy recorded at $T = 7$ K. Vertical line scans correspond to PLE spectra and diagonal cuts to PL spectra. Localised excitons in the QDs are efficiently excited via the ZnSe matrix (not shown in Fig. 1(b)).

The PLE spectra detected on the high-energy tail exhibit equidistant maxima with a period of ~ 31 meV corresponding to the LO-phonon energy of ZnSe or Zn-rich ZnCdSe as expected for the deposited CdSe layer. While above ~ 2.52 eV a continuous band of excitation channels is provided by the 2D-like density of states of the shallow localisation sites, the transfer of excitons between deep localisation sites during their relaxation is almost completely suppressed. This is attributed to deeper localisation provided by the SK-like islands and their smaller density. As a consequence of the population mechanisms, time-integrated PL, as shown for example in Ref. [14] and Fig. 3, does not represent the inhomogeneous distribution of the QD distribution but is modified by the redistribution of excitons.

To study these transfer processes in more detail, TRPL investigations were performed. Fig. 2 compares the decay of the PL emission bands at 7 K (a) and at 160 K (b). Two significant effects are resolved in the greyscale-coded maps. The redshift of the PL maximum (horizontal linescans) is larger than is to be expected for the ZnSe- or CdSe-like bandgap temperature dependence [14,17]. Furthermore, especially on the high-energy tail the decay constants are drastically reduced. We attribute this to thermally-activated evaporation of excitons from weakly localising QDs and hence the increasing 2D-like character of the ZnCdSe layer. Excitons remain localised only in the SK-like QDs leading to PL emission below 2.4 eV. A quantitative evaluation of these results is shown in Figs. 3 and 4.

Fig. 3 shows the time-integrated PL at 7 and 160 K and the decay constants recorded at various detection energies. The decay constants were determined by the convolution technique. Generally, with increasing detection energy the decay time decreased. The decay time of the excitons localised in CdSe/ZnSe QDs range between 100 and 320 ps at 7 K and between 30 and 300 ps at 160 K. To determine the radiative lifetime of the localised excitons as well as their average binding energy and mobility properties, we evaluated the results with a model introduced by Gourdon and Lavallard [18] accounting for lateral energy transfer in a high-density QD ensemble. Assuming the density of tail states is

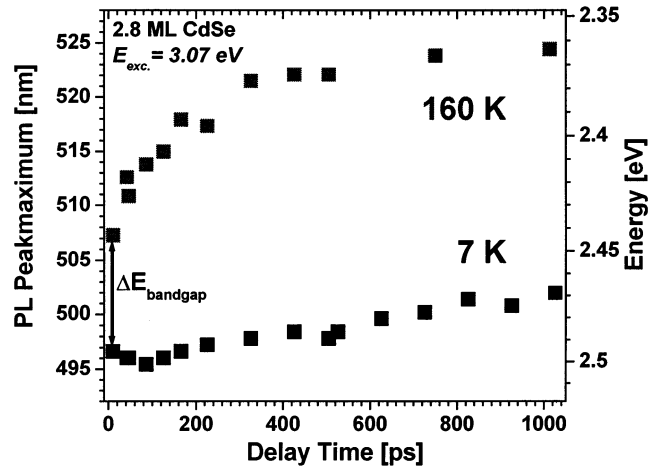

Fig. 4. The peak energy as a function of the delay time. The data were recorded at 7 and 160 K, respectively.

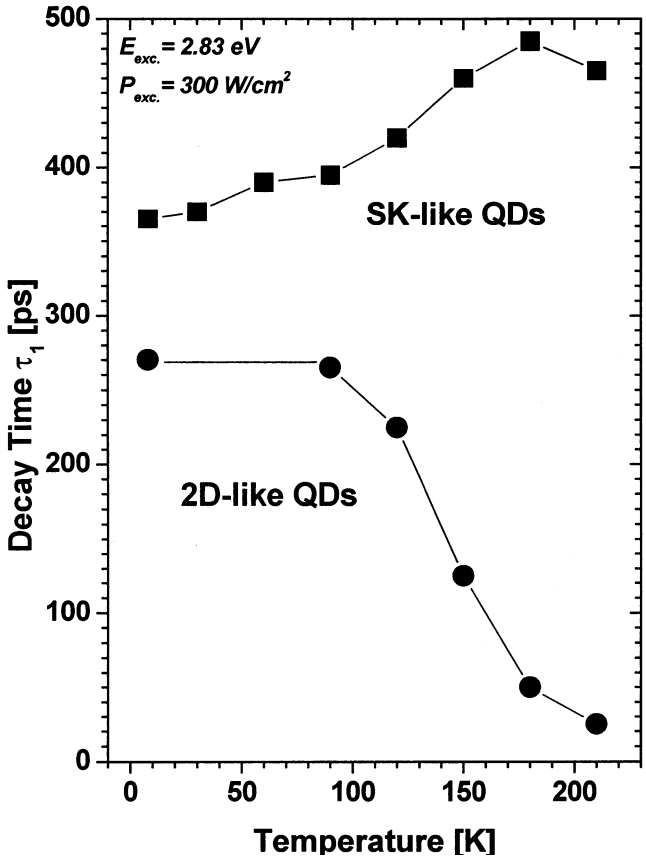

Fig. 5. Temperature dependence of decay constants obtained for detection energies according to 2D-like and Stranski–Krastanow-like quantum dots.

proportional to $\exp(-E/E_0)$, the PL decay time for excitons in localised states as a function of spectral position can be described by:

$$\tau(E) = \frac{\tau_{rad}}{1 + \exp\{(E - E_{me})/E_0\}} \quad (1)$$

where τ_{rad} is the radiative lifetime, E_{me} the energy for which the radiative lifetime equals the lateral transfer time and E_0 is a characteristic energy for the density of states. The latter parameter is in a measure for the average localisation energy of the QDs and E_{me} might be interpreted as the mobility edge for excitons. Applying Eq. (1) by a lead square fit (solid lines in Fig. 3) yields a radiative lifetime of $\tau_{rad} \sim 310$ ps (~ 300 ps), an average binding energy of $E_0 \sim 35$ meV (~ 25 meV) and the mobility edge at $E_{me} \sim 2.561$ eV (~ 2.439 eV) at 7 K (160 K). The most striking result is the strong redshift of E_{me}, which is comparable to that of the PL maximum (Fig. 3). In our structure, the mobility edge is determined by the 2D-like character of the ZnCdSe layer, i.e. lateral exciton transfer. The exciton transfer at low temperatures is limited to tunnel processes, whereas thermally activated hopping becomes the dominant transfer process with rising temperatures. The observed decrease of the lifetime τ_{rad} at 160 K is attributed to exciton escape from SK-like QDs but might also be influenced by non-radiative processes. The evolution of the average localisation energy E_0 is determined by the complex potential landscape and the thermally activated redistribution of the excitons among the QDs. The contribution of the low-density of deep localising QDs increases and a pronounced redshift of E_{me} occurs.

The enhanced delocalisation at elevated temperatures is supported by time-delayed and temperature-dependent TRPL investigations. The pronounced difference of the transfer processes is underlined by the evolution of the PL maximum as a function of the delay time, shown in Fig. 4. Time-delayed spectra were determined by horizontal scans in Fig. 2. At 7 K, the PL exhibited a redshift of ~ 25 meV after a delay of 1 ns, which is attributed to the tunnel processes. The situation is changed completely at 160 K, when the PL maximum undergoes a redshift by ~ 50 meV during the first 200 ps after pulsed excitation. At $\Delta t = 0$ the difference of the PL energies at 7 and 160 K agrees closely with the expected bandgap decrease. This behaviour is typical for thermally activated redistribution of carriers or excitons and supports the transfer processes described above.

Further investigations at higher temperatures are summarised in Fig. 5. Here, the decay constants at selected detection energies are plotted as a function of temperature. The energies were chosen to detect the decay of shallow and deep localising QDs. To investigate a certain QD state, the temperature dependence of the ZnSe matrix [17] was applied to determine the detection position on the high-energy tail. The derived decay constants for the 2D-like QDs in the high-energy tail reflect the thermally activated delocalisation of excitons above 100 K. The stability for the decay time observed for the low-energy PL tail indicates stable localisation up to 210 K. The slight enhancement and subsequent decrease of the decay time with increasing temperature are assigned to the described lateral transfer processes from the high-energy tail and thermal escape from the SK-like QDs.

4. Conclusion

In ternary ZnCdSe QD structures, the mobility of excitons is strongly limited by the existence of Cd fluctuations, formed by segregation and interdiffusion and the presence of SK-like QDs. The population and recombination processes of excitons localised in the ZnCdSe layer were investigated, demonstrating lateral exciton transfer within the dense ensemble of QDs. At low temperatures lateral transfer by tunnelling leads to a mobility edge at 2.561 eV. Thermally activated escape

and recapture of excitons cause a strong redshift of the PL maximum and the mobility edge.

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