Lateral redistribution of excitons in CdSe/ZnSe quantum dots

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Lateral redistribution processes of excitons localized in CdSe/ZnSe quantum dot structures are investigated by time-integrated and time-resolved spectroscopy. The photoluminescence properties are governed by lateral energy transfer within a dense ensemble of quantum dots. The quantum dots differ in size and Cd concentration and provide a complex potential landscape with localization sites for excitons. At low temperatures, lateral transfer by tunneling leads to a redshift with increasing delay after pulsed excitation. The mobility edge was determined to 2.561 eV. Above 100 K, thermally activated escape and recapture of excitons cause a strong redshift of the PL maximum in the first 500 ps. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1432743]

The self-organized formation of quantum dot (QD) structures strongly depends on the growth conditions and the material system. Pronounced differences in size, shape, density, and alloy concentration have been demonstrated.[1] Ensembles of such QDs and even more the coexistence of distinct types of QDs provide a complex potential landscape which limits the localization properties for excitons/carriers. Such ensembles are regarded as nonisolated QDs, where transfer processes were observed, e.g., by tunneling as well as thermal escape and recapture.[2–11] In particular for II–VI QD and quantum well structures, localization properties for excitons/carriers were intensively studied applying models for disordered systems.[12] Under adequate conditions the induced mobility of excitons/carriers results in a 2D-like behavior. In photoluminescence (PL) experiments the redistribution of excitons in favor of larger QDs leads to an enhanced redshift of the PL peak as a function of temperature or delay time.

The purpose of this letter is to show that lateral redistribution of excitons determines the population and recombination properties in a ZnCdSe QD structure. The QD ensemble consists of islands formed by lateral Cd fluctuations (2D-like QDs) with a density of $\sim 5000\ \mu m^{-2}$ and by islands formed in a Stranski–Krastanow (SK) like mode ($\sim 200\ \mu m^{-2}$).[13] We find that lateral exciton transfer by tunneling is important for 2D-like QDs but inhibited for the SK-like QDs at low temperatures. With rising temperature thermally activated hopping becomes the dominating transfer process, causing a strong redistribution of the excitons.

To investigate lateral transfer processes in an inhomogeneously QD ensemble we chose a system with well-known optical and structural properties.[13–15] A single (nominal) CdSe layer with a thickness of 2.8 monolayer (ML) embedded in pseudomorphically strained ZnSe was grown by molecular beam epitaxy on a GaAs (001) substrate as described in Ref. 13. 2D-like islands generated by lateral Cd fluctuations and larger islands with increased height and Cd concentration formed in a Stranski–Krastanow-like mode provide for 3D confinement, i.e., QD states. Despite pronounced Cd-concentration fluctuations, the formed ZnCdSe layer exhibits 2D-like properties.[13,15] The SK-like islands provide strong exciton localization as a result of their higher Cd content, larger volume, and low area density and, thus, allow probing local properties up to elevated temperatures. From an exciton point of view, a complex potential landscape with localization sites of widely varying depth and an approximately exponential distribution of localization energies is provided.

The CdSe QD ensemble was examined by photoluminescence (PL), PL excitation (PLE) and time-resolved PL (TRPL) spectroscopy at temperatures between 2 and 300 K. PLE was recorded by dispersing the light of a tungsten lamp with an 0.27 m double-grating monochromator with a spectral resolution better than 1 nm. TRPL investigations were performed using a Hamamatsu streak-camera system in single-sweep mode with a repetition rate of 1 MHz. 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.

Figure 1(a) shows the maximum of the PL emission band at ~ 2.5 eV depends on the excitation energy. PL investigations for excitation of the ZnSe barrier of the very same sample were published in Ref. 14. Decreasing the excitation energy well below the band gap of the ZnSe matrix results in a blueshift of the PL maximum by ~ 30 meV. This blueshift is attributed to the competition of the population processes of shallow and deep QDs on the high- and low-energy tail of the PL emission band, respectively. To study this process in more detail PLE spectroscopy was applied. Figure 1(b) shows a gray-scale 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. Localized excitons

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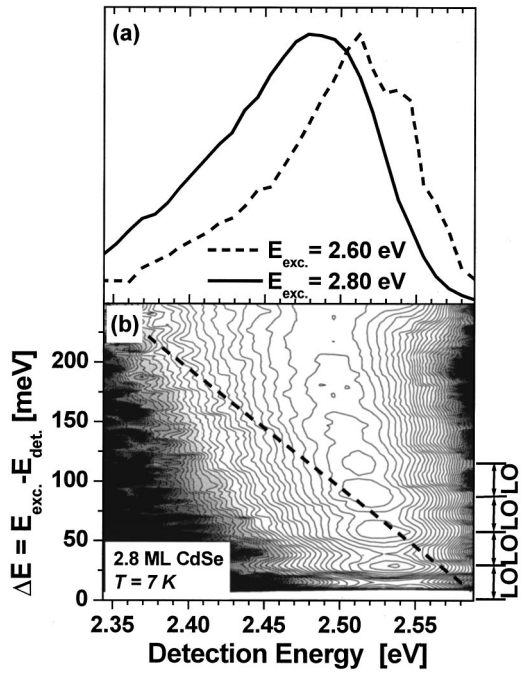

FIG. 1. (a) Photoluminescence (PL) spectra of a CdSe/ZnSe quantum dot structure recorded with excitation energies well below (dashed line) and resonant to the band edge of the ZnSe matrix (straight line). (b) Gray-scale coded plot of the logarithmic PL intensity as a function of the detection energy and the excess energy (ΔE, difference between excitation energy $E_{\mathrm{exc.}}$ and detection energy $E_{\mathrm{det.}}$). White areas indicate high intensity. The dashed line marks the PL spectra with an $E_{\mathrm{exc.}}$ at 2.60 eV in (a).

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 localization sites, the transfer of excitons between deep localization sites during their relaxation is almost completely suppressed. This is attributed to deeper localization provided by the SK-like islands and their smaller density. Hence, the blueshift of the PL [see Fig. 1(a)], which increases with decreasing excess energy ($\Delta E = E_{\mathrm{exc}} - E_{\mathrm{det}}$), is assigned to a small capture cross section of the host of 2D-like QDs on the high-energy tail.[16] With increasing excess energy, lateral carrier motion leads to a preferential capture into larger QDs, which provide strong localization. Excitation-density dependent studies (not shown here) revealed a filling of states and the presence of localization sites with transition energies above 2.6 eV. The high density of shallow localizing QDs allows for lateral motion of carriers resulting in a 2D-like behavior. In consequence of the population mechanisms time-integrated PL, as shown, e.g., in Ref. 15 and Fig. 4, does not represent the inhomogeneous distribution of the QDs but is modified by the redistribution of excitons.

Redistribution processes in the QD ensemble strongly influence the temperature dependence of the PL. The energy of the maximum and the full width at half maximum (FWHM) of the emission band are depicted in Fig. 2. Above 100 K, the redshift of the PL maximum becomes significantly larger than that of the ZnSe band edge.[17] Simultaneously, the FWHM increases [see Fig. 2(b)]. As proposed

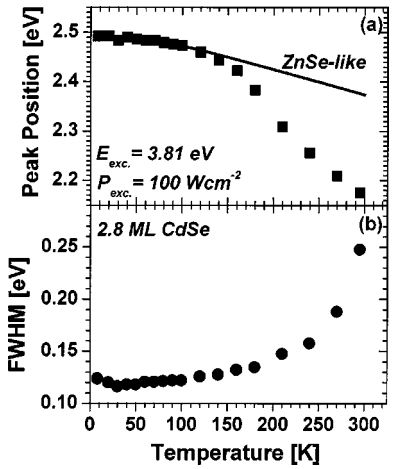

FIG. 2. PL emission maximum (a) and half width (FWHM) of the emission band (b) as a function of the temperature between 2 and 300 K. The solid line shows the temperature dependence of the ZnSe band gap.

for interacting InGaAs QDs (Ref. 2 and references therein), we attribute the observed effects to tunnel processes and thermally activated transfer between QDs within the ensemble. The exciton transfer occurs at low temperatures via tunneling among the shallow localizing 2D-like QDs. Hence, the redshift of the PL band follows the ZnCdSe band gap and the FWHM remains approximately constant. Above 100 K more and more excitons are thermally activated and transferred to deeper localizing SK-like QDs with smaller transition energies. The complex potential landscape also allows for a transfer from large to small QDs, which becomes important only for temperatures above 160 K. Despite the high density of the small QDs, the significant redshift remains until room temperature. This behavior is studied in detail by time-resolved investigations shown in Figs. 3 and 4.

The enhanced delocalization at elevated temperatures is

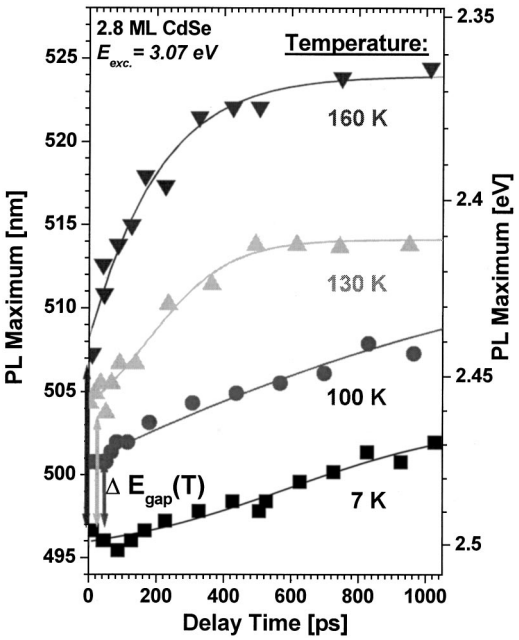

FIG. 3. PL maximum as a function of the delay time. The data were recorded at 7, 100, 130, and 160 K, respectively. The least-square root fits are introduced to guide the eye. The vertical arrows near $t = 0$ ps mark the redshift due to the temperature dependence of the band gap at the corresponding temperatures.

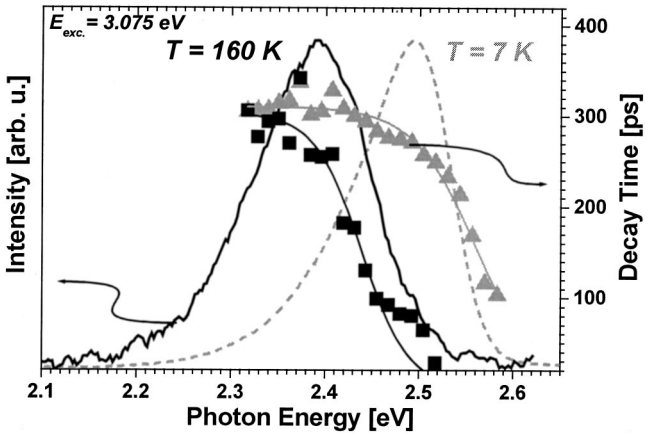

FIG. 4. Time-integrated photoluminescence and decay constants as a function of the detection energy recorded at 7 and 160 K. Equation (1) was applied to fit the decay-time dependence.

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. 3. At 7 K the PL experiences a redshift of ~25 meV after a delay of 1 ns, which is attributed to the tunnel processes. With increasing temperature the situation is changed. The redshift rises continuously. For example, at 160 K the PL maximum undergoes a redshift by ~50 meV during the first 200 ps. In general, the redshift of the PL maximum observed in cw PL (Fig. 2) is established 500 ps after the excitation pulse. At $\Delta t = 0$ the difference of the PL energies at 7, 100, 130, and 160 K agrees closely to the expected band-gap decrease (see arrows in Fig. 3). This behavior is typical for thermally activated redistribution of carriers or excitons and supports the described transfer processes.

Figure 4 shows the time-integrated PL at 7 and 160 K and the decay constants recorded at various detection energies. Generally, with increasing detection energy the decay time decreased. The decay time of excitons localized in CdSe/ZnSe QDs ranged between 100 and 320 ps at 7 K and between 30 and 300 ps at 160 K. The decrease of the decay time is attributed to the rising contribution of nonradiative recombination and thermally activated escape of localized excitons. To determine the radiative lifetime of the localized 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 proportional to $\exp(-E/E_0)$ the PL decay time for excitons in localized states as a function of the spectral position can be described by

$$\tau(E) = \frac{\tau_{\mathrm{rad}}}{1+\exp[(E-E_{\mathrm{me}})/E_0]}, \tag{1}$$

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 localization energy of the QDs. Above E_{me} the transfer of excitons has a higher probability than the radiative decay. Applying Eq. (1) by a least-square fit (solid lines in Fig. 4) yields a radiative lifetime of $\tau_{\mathrm{rad}} \sim 310$ ps (~300 ps), an average binding energy of $E_0 \sim 35$ meV (~25 meV) and an $E_{\mathrm{me}} \sim 2.561$ 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. In our structure, this energy 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. 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 nonradiative processes. The evolution of the average localization energy E_0 is determined by the complex potential landscape, the thermally activated redistribution of the excitons among the QDs, and the rising contribution of deep localizing QDs.

In conclusion, we have demonstrated that in ternary ZnCdSe QD structures the mobility of excitons is strongly limited by the existence of Cd fluctuations, formed by segregation and interdiffusion, and by the presence of SK-like QDs. Lateral exciton transfer within the dense ensemble of QDs determines the population and recombination dynamics of localized excitons. The observed PL emission band does not represent the inhomogeneous distribution of the QDs but is strongly modified by the redistribution of excitons. This redistribution is enabled by tunnel processes dominating at low temperatures and thermally activated transfer processes.

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