Fine Structure of Biexciton Emission in Symmetric and Asymmetric CdSe/ZnSe Single Quantum Dots

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The influence of quantum dot (QD) asymmetry on the emission of single three-dimensionally confined biexcitons in II-VI semiconductor nanostructures has been studied by magnetophotoluminescence spectroscopy. Investigating both the biexciton and the single-exciton transition in the same single QD, we obtain a unified picture of the impact of electron-hole exchange interaction on the fine structure and the polarization properties of optical transitions in QDs. The exchange splitting is demonstrated to have a strong influence on the derivation of the biexciton binding energy, which we determine to be about 17 meV, much less than the separation between exciton and biexciton lines (≈24 meV) in the spectra. [S0031-9007(99)08536-1]

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In recent years, optical investigations on single semiconductor quantum dots (QDs), often designated as "artificial atoms," opened a new and exciting field of basic physics studies. In contrast to "real" atoms or molecules, a unique feature of solid state quantum dots is the formation of Wannier excitons giving experimental access to both the Coulomb and the electron-hole (e-h) exchange interaction in three-dimensionally confined solid state systems. Therefore, semiconductor QDs with geometries smaller than or comparable to the bulk exciton Bohr radius can be regarded as a model system in order to study the impact of Coulomb and exchange interaction on the optical properties of zero-dimensional excitons and excitonic complexes [1–5]. Several techniques have been developed to realize semiconductor QDs with high quantum efficiencies. This includes chemically prepared QDs embedded in a matrix [1,6] as well as ensembles of QDs fabricated by means of epitaxy and/or lithography [2,7–15]. A drawback of such QD arrays is a broadening of the optical transitions due to the size dispersion of the dots, which prevents the investigation of, e.g., the fine structure of exciton states [16,17]. In order to suppress the influence of inhomogeneous broadening effects, spectroscopic techniques with a high spatial resolution have been introduced as a powerful experimental tool. This allows one to investigate single quantum dots (SQDs) by means of photoluminescence (PL) spectroscopy [2–5,10,14,18].

In II-VI nanostructures, the e-h exchange interaction is significantly enhanced as compared to the (Ga,In)As system [1,6]. This allows studies of the optical transitions of excitons and multiexcitons without any significant mixing of radiative ("bright") and nonradiative ("dark") excitonic states. Therefore, II-VI materials such as, e.g., CdSe/ZnSe are ideal systems to study the impact of the dot symmetry and the e-h exchange interaction on the fine structure and the polarization properties of excitons and excitonic complexes in SQDs. Until now, the work on e-h exchange interaction in quantum dots has concentrated on single-exciton states, where, e.g., the energy splitting between dark and bright excitons [1,6] or the splitting of the optically allowed single-exciton state into a linearly polarized doublet [2,17] was investigated. To our knowledge, however, there are no studies on the impact of e-h exchange interaction on the emission properties of multiexcitons in QDs until now. However, due to the strong enhancement of the exchange energy expected in low dimensional systems [1,6], a consideration of exchange effects is crucial for, e.g., any spectroscopic determination of multiexciton binding energies in zero-dimensional semiconductors such as, e.g., CdSe/ZnSe QDs.

In the present paper, we investigate for the first time the influence of e-h exchange interaction (i) on the transition energy, (ii) on the PL polarization, and (iii) on the binding energy of zero-dimensional biexcitons. Both weakly and highly asymmetric SQDs have been investigated without and with magnetic field B parallel to the growth axis z. The study of both, the biexciton as well as the exciton transition in the same SQD, gives a unique opportunity to compare the fine structure of (multi)excitonic states in three-dimensionally confined systems with theoretical predictions.

The investigated samples are CdSe/ZnSe structures fabricated by migration enhanced epitaxy, embedding three monolayers (ML) of CdSe between ZnSe barriers [12]. RHEED measurements indicate a 3D growth mode

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for a CdSe layer thickness $L_z > 2.5$ ML. From high resolution transmission electron microscopy data, an estimate of the average QD size has been obtained, yielding a height of about 1.5–2 nm in growth direction and a lateral extension of 5–10 nm. To achieve the high spatial resolution required for SQD spectroscopy, we have prepared square mesas with lateral extensions down to 60 nm by electron beam lithography and wet chemical etching [19]. Continuous wave PL studies were carried out in an optical cryostat with a split-coil solenoid in Faraday configuration using the 363.8 nm line of an Ar^+-ion laser for the excitation and a LN_2-cooled CCD camera for the detection of the QD emission.

In Fig. 1a, unpolarized PL spectra for two SQDs (QD1 and QD2, respectively) are displayed for different excitation densities. At low excitation densities, the PL spectrum is dominated by the single-exciton transition X. For high excitation, additional features occur in the PL spectrum at about 25 meV lower energy. As will be discussed below in detail, these peaks are due to the recombination of the two-exciton state X_2, the biexciton. Two remarkable features have to be mentioned. First, the energetic difference between the exciton and the biexciton emission is quite large; and, second, the spectral shape of the exciton, which, e.g., is a well resolved doublet for QD2, is exactly reproduced in the PL spectra of the biexciton.

To get a more detailed insight into the symmetry of the QD eigenstates and their consequence on the optical properties of excitonic molecules, the polarization dependence of both, the exciton as well as the biexciton transition, is studied. As can be seen in Fig. 1b, the biexciton and the exciton emission consists of a doublet which is linearly polarized along the [110] and [1$\bar{1}$0] crystal orientation, respectively. The splitting between the two components is small (<0.3 meV) in most (>50%) of the dots investigated (see QD1). However, it changes from one dot to another and, for about 10% of the dots, values of 0.8 meV and larger are obtained (see QD2). Remarkably, the energy sequence of the polarized components is different for the X and X_2 transition: While, for the exciton, the π_x polarized component is the higher energetic one, the situation is exactly the opposite for the biexciton, where the π_x polarized component forms the low energy part of the doublet.

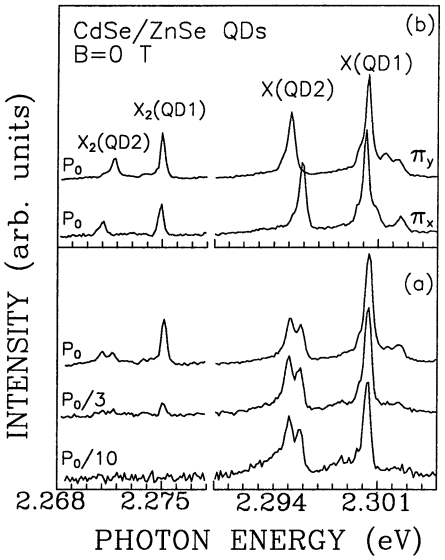

FIG. 1. (a) Unpolarized PL spectra from two QDs for different excitation power. The spectra are taken from a small (diameter of about 100 nm) mesa. X denotes the exciton emission, while X_2 corresponds to the recombination of the two-exciton (biexciton) state. ($P_0 = 10$ W/cm^2). (b) Linearly polarized PL spectra from the two QDs.

The biexciton ground state is a spin-singlet state ($S = 0$). Thus, both the polarization and the fine structure splitting of the biexciton emission are controlled by the final state of the recombination, i.e., the eigenstates of the single exciton. As schematically depicted in Fig. 2, the ground state of the heavy-hole exciton is expected to be fourfold degenerate, if exchange interaction is neglected. To take into account the influence of exchange interaction on the symmetry and the energy of the exciton eigenstates, we have to discuss the spin Hamiltonian for heavy-hole excitons [16,17,20], which is given by

$$H_X = a_z \hat{j}_{h,z} \hat{s}_{e,z} + \sum_{i=x,y,z} b_i \hat{j}^3_{h,i} \hat{s}_{e,i} , \qquad (1)$$

with $\hat{s}_{e,i}$ and $\hat{j}_{h,i}$ as electron and hole spin operators. The eigenvalues are $s_z = \pm 1/2$ and $j_z = \pm 3/2$ for the electron and the heavy-hole spin, respectively. The e-h spin exchange interaction results in a splitting of the X quartet with the angular momentum component $M = s_z + j_z = \pm 1, \pm 2$. Quantum wells (QWs) as well as cylindrical QDs have a D_{2d} point-group symmetry. For this symmetry $b_x = b_y$ and as a consequence the

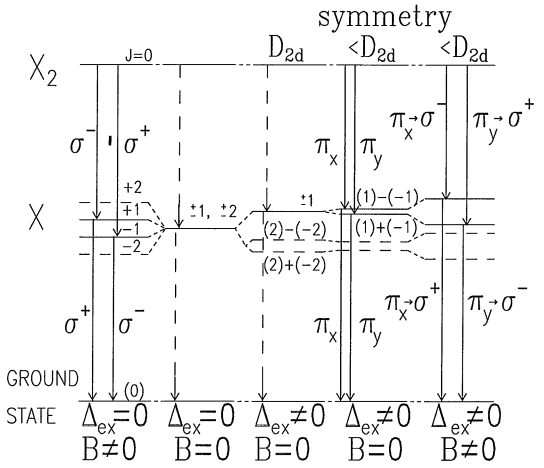

FIG. 2. Schematic illustration of the exciton and the two-exciton states and the allowed optical transitions in QDs of different symmetry.

X quartet splits into a radiative doublet $|\pm 1\rangle$ and two nonradiative singlets formed by linear combinations of $|\pm 2\rangle$ states (see Fig. 2). While in this case the radiative doublet is degenerate, the nonradiative one is split by $\delta_2 = \frac{3}{4}|b_x + b_y|$.

For a lower symmetry, all of the coefficients in Eq. (1) have a different magnitude and the radiative doublet is split by $\delta_1 = \frac{3}{4}|b_x - b_y|$. In QDs with $L_z \ll L_x, L_y$, the splitting between bright and dark excitons ($\delta_0 = \frac{3}{2}a_z + \frac{27}{8}b_z$) is expected to be much larger than the energy splitting of the bright exciton doublet. Therefore, the mixing of $|\pm 1\rangle$ and $|\pm 2\rangle$ states is small, and the radiative states are a symmetric and antisymmetric combination of $|+1\rangle$ and $|-1\rangle$ states, X_+ and X_-, respectively. Thus, the optical transitions of both the X and the X_2 transitions are expected to be linearly polarized along the principal in-plane axes, i.e., the $[110]$ and $[1\bar{1}0]$ directions. This is exactly what we observe in our experiments (see Fig. 1b). Moreover, the energy sequence of the π_x and π_y polarized components observed in the experiment nicely confirms the theoretical expectation.

In order to calculate the energy splitting of the exciton ground state due to exchange interaction, we have applied the theory introduced by Blackwood and Ivchenko [16,17], assuming the simplest form of the exciton envelope function, namely, the full confinement of the exciton in the QD [21]. From our calculations, we find that the exchange splitting between bright exciton states increases with increasing dot asymmetry and decreasing size. For cylindrical QDs (D_{2d} symmetry), the exchange splitting is expected to be zero. Thus, we mainly attribute the variation of the exchange splitting between different dots to a dot dependent deviation from cylindrical shape (i.e., $|L_x - L_y| > 0$) [22]. A splitting between the X_+ and X_- states of 0.8 meV as obtained, e.g., for QD2 (note that the number of such dots is very small) is possible only in small enough (few nm) and highly anisotropic QDs. For example, with $L_z \approx 1.5$ nm and $L_x \times L_y \approx 10$ nm $\times$ 2.5 nm, we obtain $\delta_1 \approx \delta_2 \approx 0.8$ meV. In this case, the dark-bright splitting is about $\delta_0 = 3.2$ meV, i.e., significantly enhanced as compared, e.g., to ZnSe/ZnCdSe QWs, where a splitting of $\delta_0 \approx 0.5$ meV is found for $L_z = 10$ nm [23]. This enhancement is attributed to quantum confinement effects, in good agreement with results on CdS/ZnS nanostructures reported by Woggon *et al.* [6].

The fine structure of the exciton and the biexciton emission has an important impact on the determination of the biexciton binding energy in QDs. The energetic distance between the emission of the single-exciton and the two-exciton complex, Δ_M^*, is typically about 23–25 meV and depends strongly on the PL polarization (see Fig. 1b). In QDs with a large exchange splitting of excitons, however, Δ_M^* and the biexciton binding energy Δ_M are different entities. As indicated in Fig. 2, the allowed X_2 transition corresponds to the transition from X_2 to the excited ($|\pm 1\rangle$) rather than to the ground ($|\pm 2\rangle$) X state. Thus, in QDs, Δ_M should be defined by the following equation:

$$\Delta_M = \Delta_M^* - 2\delta_0 \mp \delta_1 - \delta_2 , \qquad (2)$$

for π_x and π_y polarization, respectively. For example, for QD2 we obtain $\Delta_M^* = 24.9$ meV (23.3 meV) for π_x (π_y) polarization and, with the above estimated values of $\delta_0 \approx 3.2$ meV and $\delta_1 \approx \delta_2 \approx 0.8$ meV, one obtains $\Delta_M \approx 16.9$ meV, which is significantly smaller than Δ_M^*. Thus, the commonly used energetic difference between the exciton and the biexciton emission results in a strong overestimate of the biexciton binding energy. Nevertheless, the biexciton binding energy determined here including exchange effects is strongly enhanced as compared to II-VI quantum wells, a direct consequence of the three-dimensional confinement of the biexciton in the QD.

The symmetry and the energy of the dot eigenstates can be systematically varied by applying a magnetic field. For $B \parallel z$, the Zeeman interaction is given by

$$H_B = \mu_B(g_{e,z}\hat{s}_z - g_{h,z}\hat{j}_z)B , \qquad (3)$$

where $g_{e,h}$ are the electron and hole g factors and μ_B is the Bohr magneton. The energy eigenvalues E_i of the two radiative heavy-hole states derived from the corresponding Hamiltonian $H = H_X + H_B$ are ($g_1 = g_e + 3g_h$)

$$E_{1,2} = \frac{1}{2}\left(\delta_0 \pm \sqrt{(g_1\mu_B B)^2 + \delta_1^2}\right). \qquad (4)$$

As shown in Fig. 3a, for the symmetric QD1 the exciton line splitting, $\Delta_1(B) = E_1 - E_2$, increases almost linearly with B with a g factor of $g_1 = 1.56$. For the asymmetric QD2, in contrast, $\Delta_1(B)$ strongly differs from the linear dependence. This deviation is related to the large zero-field splitting δ_1 of the radiative exciton state due to e-h exchange interaction. The experimental dependence (symbols) is in excellent agreement with the calculated one using Eq. (4) (solid lines).

From these data, we can conclude that both the Zeeman energy as well as the splitting between the bright states

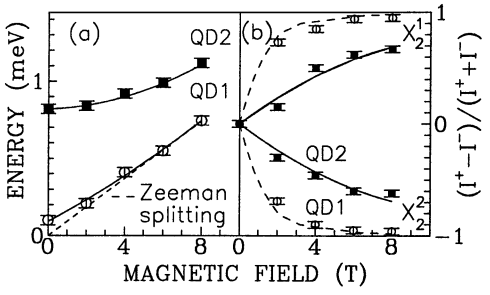

FIG. 3. (a) Energy splitting between the bright exciton states, $\Delta_1(B)$, and (b) degree of circular polarization, $[I(\sigma^+) - I(\sigma^-)]/[I(\sigma^+) + I(\sigma^-)]$, of the X_2 transition versus magnetic field.

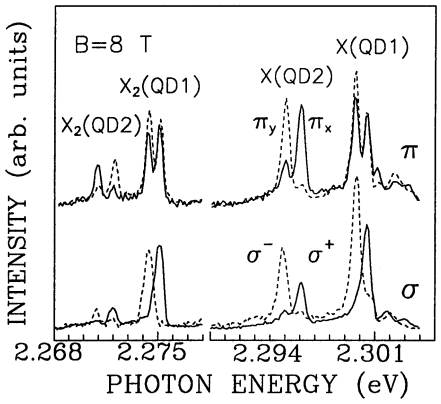

FIG. 4. σ and π polarized PL spectra from SQDs at a magnetic field $B = 8$ T and an excitation power of $P_0 = 10$ W/cm^2.

are much smaller than the dark-bright splitting, δ_0. For that reason, a magnetic field in Faraday geometry results in a redistribution of the circular polarized $|+1\rangle$ and $|-1\rangle$ states between the two bright exciton levels $X^{1,2}$ according to ($\alpha = g_1 \mu_B B/\delta_1$)

$$|X^{1,2}\rangle = \frac{1}{\sqrt{2}} \frac{|+1\rangle \pm (\sqrt{1+\alpha^2} \mp \alpha)|-1\rangle}{\sqrt{1+\alpha^2 \mp \alpha\sqrt{1+\alpha^2}}}, \quad (5)$$

without mixing bright and dark exciton states.

As an external magnetic field does not split the biexciton spin-singlet state, both the polarization and the transition energies of the lines X_2 are controlled by the energy and the symmetry of the exciton levels. This means that, first, the splitting of the biexciton lines should coincide with that of the exciton emission, in agreement with our experimental data. Second, the linear polarization of both the X and X_2 lines at zero magnetic field should transform into a circular one in a high magnetic field. While for the exciton transition the effective exciton temperature and/or the spin flip process between the bright states are expected to influence the polarization degree significantly, the X_2 transition should directly reflect the magnetic field induced change of the symmetry of the exciton eigenstates according to Eq. (5). This is shown in Fig. 3b, where the degree of circular polarization of the X_2 line is plotted versus magnetic field. Indeed, a very good agreement between the experimental data (symbols) and the theory (lines) is found.

In Fig. 4, polarized PL spectra at 8 T are shown. For QD1 ($\alpha \gg 1$), the exciton and the biexciton emission consist of two components of σ^+ and σ^- polarization, respectively. In contrast, for the asymmetric QD2, the Zeeman splitting is comparable to δ_0 ($\alpha \approx 1$). This results in a degree of linear polarization, which even for $B = 8$ T is still rather large.

Most interesting, however, is the change of the polarization sequence of the X_2 and the X lines at high magnetic field compared to the zero magnetic field data. As already mentioned, for $B = 0$, the X_2 emission has the same magnitude of the fine structure splitting, but the opposite sequence of polarized components than the emission of the exciton (see Fig. 1b). In contrast, at high magnetic fields, the energy sequence of the σ^+ and σ^- transitions is the same for excitons and biexcitons, as demonstrated in the magneto PL spectra depicted in Fig. 4. Comparing Figs. 1b and 4, it can be clearly seen that, if the $\pi_{x(y)}$ components of the line X transform with increasing magnetic field B into the $\sigma^{+(-)}$ lines, the biexciton emission component π_x transforms into σ^- and, vice versa, π_y into σ^+, in full agreement with theory.

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