Polarization dynamics in self-assembled CdSe/ZnSe quantum dots: The role of excess energy

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The polarization dynamics of zero-dimensional exciton emission is studied for CdSe/ZnSe quantum dots going systematically from strictly resonant to nonresonant excitation. Independent on the excess energy, no transient decrease of the polarization is found for ground state exciton emission. However, the absolute value of the polarization degree exhibits a strong nonmonotonic dependence on the excitation energy. We demonstrate that the initial loss of polarization after nonresonant excitation can be minimized if the exciton excess energy corresponds to an integer multiple of LO-phonon energies.

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The idea of using the spin of particles (electrons, holes or, excitons) as information carrier was the ignition of a completely new area of research named *spintronics*.[1,2] In order to use the spin for fast information processing a major requirement is to keep a once prepared spin state as long as possible. In other words, the loss of spin polarization is the most challenging process to be controlled on the way to a well functioning spintronics. It has been shown, that, e.g., the *electron* spin relaxation time can exceed 100 ns in *n*-doped bulk GaAs,[3] while the spin depolarization of *holes* or *excitons* is usually quite fast in higher dimensional structures.[4,5] This is particularly true for wide-band-gap II-VI materials such as ZnSe, where the strong electron-hole exchange interaction results in extremely small spin relaxation times of <10 ps for low temperatures.[6] It is expected that in quantum dots (QD's) spin-flip processes are strongly modified due to the discrete density of states. Indeed, recent time-resolved measurements on epitaxially[7–9] or chemically prepared[10] QD's seem to confirm this prediction, revealing even exciton spin relaxation times up to several nanoseconds, i.e., much larger than in bulk or quantum well samples. This goes hand in hand with spatially resolved photoluminescence (PL) measurements on single QD's, where a spin relaxation time in the nanosecond regime was estimated from time-integrated measurements.[11,12]

However, these experiments were performed under various excitation conditions. Gotoh *et al.*[7] studied the polarization dynamics of exciton recombination in $In_xGa_{1-x}As$ QD's for nonresonant excitation with an excess energy of about 100 meV, while Flissikowski *et al.*[9] used an excess energy comparable to the LO-phonon energy to address a single II-VI QD. To make sure that no relaxation processes influence the spin dynamics in self-assembled InAs/GaAs QDs, Paillard *et al.*[8] applied strictly resonant conditions. No systematic study of the influence of the excess energy on the transient polarization degree and thus the transient change of the spin states is available, although this question is of great importance, as, e.g., in a QD heterostructure in case of electrical injection the electrons and/or holes first have to loose their excess energy before occupying the QD ground state.

We have studied the polarization dynamics in self-assembled CdSe/ZnSe quantum dots. Despite the strong exchange interaction in this system,[13] no depolarization of the PL signal is observed in the time window under investigation, if one excites the eigenstates of the zero-dimensional excitons strictly resonant. By varying the excitation systematically from the resonant (excitation energy $E_{exc}=$ detection energy E_{det}) to the nonresonant($E_{exc}>E_{det}$) case, we are able to extract the role of excess energy on the polarization dynamics of zero-dimensional exciton recombination in an ensemble of QD's.

The samples under investigation have been fabricated by molecular beam epitaxy on a GaAs substrate. On top of a 180 nm nominally undoped GaAs buffer a 53 nm thick ZnSe layer was grown. Subsequently a CdSe layer with a nominal thickness of about 1.3 monolayers was deposited forming the QD layer and a 25 nm ZnSe barrier acts as cap layer. Thus, the total II-VI layer thickness is kept below the critical thickness for strain relaxation, ensuring high sample quality. The PL signal of the QD ensemble is inhomogeneously broadened (full width at half maximum of 43 meV) with the maximum at 2.605 eV. By highly spatially resolved PL spectroscopy[14,15] it has been shown that this sample contains QD's with a density on the order of 10^{11} cm^{-2}. For comparison, a quantum well (QW) sample was grown, consisiting of a 10.5 nm of $Zn_{0.915}Cd_{0.085}Se$ QW sandwiched between ZnSe barriers.

In order to excite the QDs we used a tunable frequency doubled and mode-locked titanium-sapphire-laser providing 1.5 ps pulses with a repetition rate of 82 MHz. The PL signal was spectrally dispersed by a 0.46 m monochromator equipped with a 1200 mm^{-1} line grating. Before being detected by a Peltier cooled charge coupled device (CCD) the PL signal was temporally resolved by a streak camera. The overall temporal and spectral resolution of the setup was 20 ps and 0.4 meV, respectively. To adjust the linear polarization of the laser beam we used a Glan laser prism followed by a $\lambda/2$ rhombus. A dichroic sheet polarizer was used in the detection path to select between the π^Y and π^X polarization (the linear polarizations are chosen to be parallel to the [110]

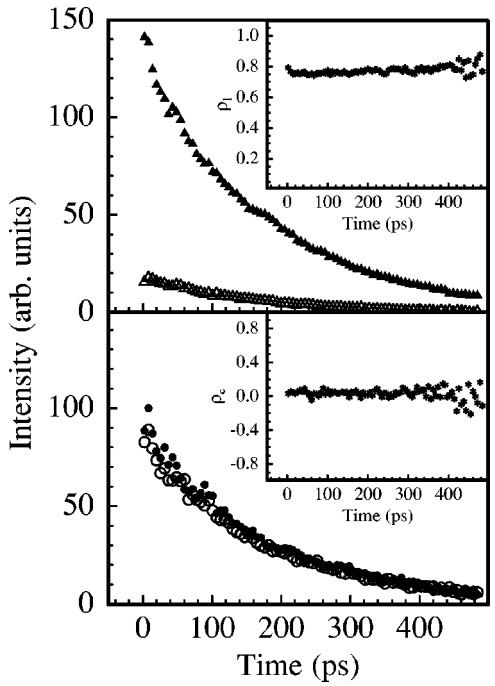

FIG. 1. PL-transients obtained after linear polarized excitation (π^Y) (upper part) and after excitation with circular polarized light (σ^+) (lower part). Filled symbols indicate parallel polarization of the exciting laser beam and the detected PL signal, while open symbols indicate the opposite one. The insets show the polarization degrees defined as $\rho_l=(I^Y-I^X)/(I^Y+I^X)$ and $\rho_c=(I^+-I^-)/(I^++I^-)$ for linear and circular polarized excitation, respectively.

and $[1\bar{1}0]$ crystal orientation, respectively) of the emitted PL signal. For experiments with circular polarization a $\lambda/4$ rhombus and a $\lambda/4$ plate were placed in the excitation and the detection path, respectively. All the measurements were done at a temperature of 2 K and the excitation density was kept low enough to ensure that only single electron-hole pairs occupy the QD ground state, i.e., biexciton or multiexciton formation was avoided.

Figure 1 shows typical PL transients after excitation with linear (π^Y, upper part of the figure) and circular (σ^+, bottom) polarized light, respectively. The experiments are performed under strictly resonant excitation of the QD ground state, i.e., the detection energy is chosen to be identical to the excitation energy of 2.599 eV. No transient energy shift of the PL signal is seen, demonstrating that we are really probing zero-dimensional states.[16] In case of linear polarized excitation, no decay of the remarkably high polarization degree of $\rho_l=(I^Y-I^X)/(I^Y+I^X)\approx 0.8$ is obtained (see inset of Fig. 1). In contrast, a circular polarization degree of $\rho_c=(I^+-I^-)/(I^++I^-)\approx 0$ is measured if one goes from linear polarized to circular polarized excitation (see lower part of the figure). Similar measurements performed on the QW reference sample showed for both, linear as well as circular polarized excitation a rapid depolarization within our temporal resolution of 20 ps, in good agreement with data obtained for ZnSe/ZnMgSSe quantum wells.[6] It is important to note that these findings do not change if one varies the excitation density (between 0.5 W/cm^2 and 100 W/cm^2) or the excitation/detection energy if one stays resonant to the QD ground state.

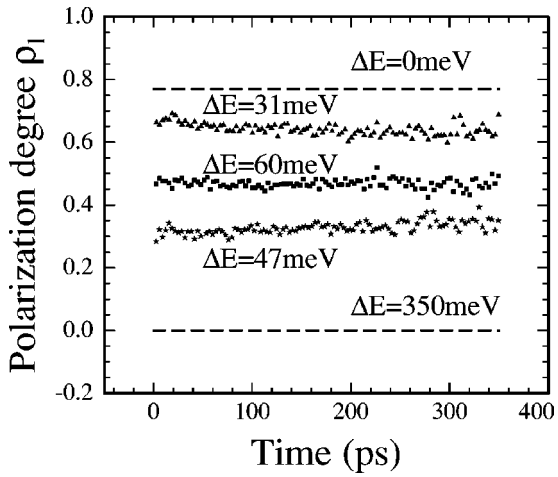

FIG. 2. Transient polarization degree for three different excess energies [$\Delta E=31$ meV (triangles), 47 meV (stars) and 60 meV (squares)]. For comparison the polarization degree for strictly resonant excitation ($\Delta E=0$) and for excitation above the barrier ($\Delta E=350$ meV) are plotted versus time (dashed lines).

It is well known that in self-assembled CdSe/ZnSe QD's the heavy hole exciton eigenstates are quite frequently linear superpositions of $J_Z=|\pm 1\rangle$ and $J_Z=|\pm 2\rangle$ states[17] due to the exchange splitting caused by the QD asymmetry[13,18] and/or the interface anisotropy.[19] Thus, while circular polarized excitation creates a superposition of the eigenstates, in the case of linear polarized excitation, the excitons are generated in their eigenstates. The observation that the (linear) polarization degree does not reach unity is most likely due to the fact that a part of the QD's have eigenstates of different symmetry. As in our ensemble measurements the exchange splitting varies from dot to dot a superposition of spin precession with different frequencies is obtained in case of circular polarized excitation and thus a vanishing polarization degree is expected within our finite time resolution.[20]

It has to be emphasized that observing a linear polarization degree which does not decrease in time means that the coherent superposition of the spin-up and the spin-down exciton state isn't destroyed. According to Paillard *et al.*[8] this means that neither the electron nor the hole spin state change within the time scale under investigation.

It is supposed that only under strictly resonant excitation conditions it is possible to study the intrinsic polarization dynamics.[8] In the case of nonresonant excitation carrier scattering and relaxation processes as well as the excitation of states with different symmetry and thus different selection rules may affect the transient polarization degree of the QD ground state emission. However, a systematic investigation of the influence of the excess energy on the polarization dynamics is still missing. For this purpose we performed a kind of time resolved photoluminescence excitation (PLE) spectroscopy: We fix the detection energy (here to 2.599 eV) and systematically vary the excess energy of the exciting laser pulse.

In Fig. 2 the transient polarization degree for excitation

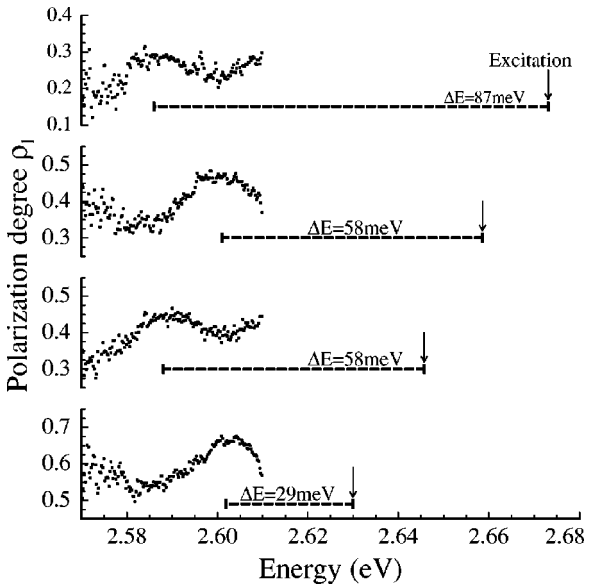

FIG. 3. The degree of linear polarization, ρ_l, is plotted versus PL energy for four different excitation energies (indicated by the arrows). ΔE gives the excess energy, i.e., the energy separation between the exciting laser and the maximum of the polarization degree.

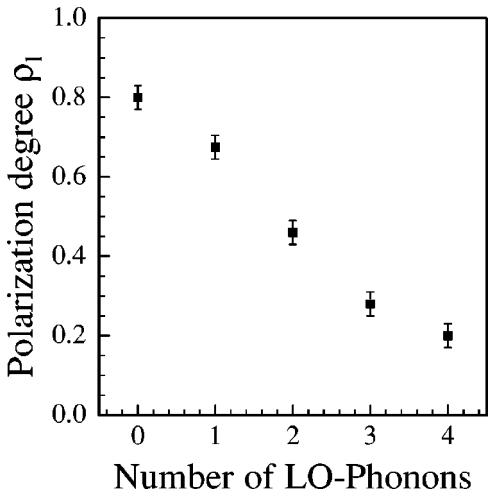

FIG. 4. Polarization degree ρ_l obtained in the center of the LO phonon resonances plotted in Fig. 3 versus the number of LO phonons required for relaxation into the QD ground state.

with linear polarized light, ρ_l, is shown for three different excess energies ($\Delta E = 31$ meV, 47 meV, and 60 meV, respectively). For comparison, the time evolution of the polarization degree in the case of strictly resonant excitation ($\Delta E = 0$) and above barrier excitation ($\Delta E = 350$ meV) is indicated in the figure (dashed lines). The polarization degree is virtually constant in time, independent on excitation energy. This means that once the exciton occupies the ground state of the QD, no transient change of the polarization occurs within the time window under investigation. However, a general feature seems to be the lower initial degree of polarization as compared to the strictly resonant case. For above barrier excitation, the polarization degree is even zero, i.e., the polarization information initially imprinted to the electron-hole pairs by the exciting laser beam is completely lost.[21]

Interestingly, the loss of polarization is not simply a monotonic function of the excess energy ΔE, e.g., while for an excess energy of 47 meV the polarization degree is reduced to about $\rho_l = 0.3$, a much higher degree of linear polarization is obtained by increasing the excess energy to about $\Delta E = 60$ meV. In order to identify the origin of this behavior, the degree of polarization ρ_l is plotted versus the PL energy for different excitation energies in Fig. 3. In order to discuss predominantly the polarization degree of the PL signal originating from excitons recombining in the QD ground state, we restrict ourselves to energies below ≈ 2.61 eV. In general, the average polarization degree decreases for increasing excess energy. However, there are pronounced resonances in the degree of polarization at certain PL energies. The maxima of these resonances are separated by about 29 meV from each other and by a multiple of this energy from the energy of the exciting laser. This clearly demonstrates a reduced loss of polarization information if one creates electron-hole pairs with well-defined excess energies above the QD ground state.

Calling into mind that the LO-phonon energies in bulk CdSe and ZnSe are 26.5 meV and 31.6 meV, respectively,[22,23] this suggests that the resonances in the polarization degree are related to carrier relaxation into the ground state via LO-phonon scattering: If the excess energy of the electron-hole pairs fits to a multiple of LO-phonon energies, the relaxation process is expected to be quite fast. The width of those resonances becomes slightly larger with increasing number of phonons contributing to the relaxation process and is most likely determined by the composition fluctuations between the QD's, which in turn leads to a distribution of LO-phonon energies.[9]

It is interesting to compare the degree of polarization at the maximum of the resonances for different excess energies, i.e., different numbers of LO phonons contributing to the relaxation process (Fig. 4). While for strictly resonant excitation a polarization degree of almost 0.8 is obtained, ρ_l decreases with the number of phonons, reaching about 0.2, if four LO phonons are required for the exciton to reach the QD ground state. Still, however, a significant degree of polarization is obtained with rather large excess energies.

At this point, we would like to discuss briefly some possible reasons for the depolarization effect found with increasing excess energy. First, the energy splitting between heavy and light hole excitons is expected to be on the order of 100 meV for this structure[24] and the split-off band is even further above in energy.[25] Thus, the involvement of these additional branches of the valence band can be ruled out, at least for excess energies, which are clearly below 100 meV. In addition, at least for small excess energies (e.g., the one LO-phonon resonance) the population of extended states seems to be negligible, as can be concluded from PL excitation measurements on single CdSe/ZnSe QD's.[9,26]

In order to account for the overall reduction of polarization degree with increasing excess energy both, phonon scat-

tering as well as the excitation of QD states or superposition of QD states[9] with different symmetry and thus different selection rules have to be considered. While we cannot discriminate quantitatively between these different mechanism, the fact that the polarization degree can be minimized by adjusting the excess energy to a multiple of LO-phonon energies is quite important. For these excitation energies, the carrier relaxation time to the QD ground state is significantly shortened due to the efficient carrier–LO-phonon interaction. This decrease of the relaxation time to the QD ground state is related to a reduced initial loss of polarization. Thus, one has to conclude that in case of nonresonant excitation at least a part of the loss of initial polarization is connected to the energy relaxation process. That is, the loss of polarization cannot purely be explained by assuming different selection rules for excited states. Note that the broadening of the distribution of N LO-phonon energies cannot account for the overall reduction of the peak polarization degree.

In conclusion, we studied the polarization dynamics in self-assembled CdSe/ZnSe QD's for various excitation conditions. Exciting strictly resonant the eigenstates of the QD ground state, no loss of polarization is found within the time scale of recombination. Even in the case of nonresonant excitation, no transient decrease of the polarization degree is obtained for ground state exciton emission, while however the absolute value of the polarization degree strongly depends on excess energy. In the case of nonresonant excitation, the effect of depolarization can be minimized if the excess energy is equal to a multiple of LO-phonon energies. Although we have not yet a complete theoretical understanding of the mechanism behind the initial loss of polarization for increasing excess energy, we hope that our experimental data can give some input for corresponding calculations.

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