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Femtosecond dephasing in CdS quantum dots determined by nondegenerate four-wave mixing

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Nondegenerate four wave mixing (NDFWM) has been proven to be a useful tool to investigate femtosecond phase relaxation processes in II-VI quantum dots. The range of application covers dephasing times between 10 fs and some picoseconds. By means of NDFWM the intensity- and temperature-dependent dephasing has been studied in CdS quantum dots with radii larger than the Bohr radius.

Quantum dots (QD's) are very attractive and interesting objects for scientific research of three-dimensionally confined systems. During the past few years the discussion of the confinement-induced changes of the electronic properties has been concentrated so far on the energy positions and the weights of the optical transitions. However, the complete understanding of the observed linear and nonlinear absorption spectra of QD's needs the additional information about the mechanisms determining the homogeneous linewidth. Therefore, the investigation of dephasing processes in zero-dimensional systems is a central point of present research work. In analogy to bulk materials the phase-destroying processes can be divided in dephasing (i) by coupling to different types of phonons, (ii) by scattering at defects or interfaces, and (iii) by scattering within a many-particle system of interacting electrons and holes. The present knowledge of the mutual contributions and the size dependence of these types of scattering in QD's is rather poor. The experimental attempts to study the dephasing processes in II-VI QD's started with the direct determination of the phase relaxation time by use of femtosecond pulses. As a further interesting method four-wave mixing experiments with incoherent light have been performed.[1–4] Recently a detailed study of quantum size dependent dephasing has been published for CdSe QD's with small sizes below the Bohr radius in Ref. 5, applying a three-pulse photon echo technique. However, the majority of published dephasing studies is based on methods working in the frequency domain, such as the hole burning spectroscopy.[6–9]

In this paper we investigate the phase relaxation of CdS QD's with radii larger than the Bohr radius. As an experimental method we apply the nondegenerate four-wave mixing to obtain femtosecond time resolution via the frequency domain. We determine the phase relaxation time T_2 and compare the relative contributions arising from the carrier-phonon scattering and the carrier-carrier scattering to the dephasing process by measuring the temperature dependence and intensity dependence of the dephasing time.

The CdS QD's used in the experiments have been grown in a borosilicate glass matrix as desribed in detail in Ref. 10. The average radius of the QD's is $\bar{R}=7.5$ nm ($\sim 2.5 a_B$). Figure 1 shows the linear absorption, luminescence, and differential absorption spectra measured at low temperature. The weak confinement produces only small energy separations between the quantum-confined states and the structures merge into shoulders. The steps in the linear absorption correspond to the splitting between the $J=3/2$ and the $J=1/2$ valence-band states. From differential absorption at $T=20$ K the first absorption maximum related to the electron-hole-pair ground state of the uppermost valence band has been found at 2.64 eV and at 2.72 eV starts the series of confined states arising from the next lower valence band. The efficient narrow-band luminescence, redshifted by only 20 meV compared to the absorption, is a sign for a high sample quality. Since the dots have a small surface to volume ratio, the elastic scattering at imperfections introduced by the dot/matrix boundary is supposed to be of minor importance and present in the spectra as a small constant contribution only, independent of temperature and intensity. Likewise, no resonance is expected between an interior exciton state and a surface state as reported for small CdSe QD's in Ref. 11.

The experimental method of nondegenerate four-wave mixing (FWM) uses extremely narrow-band nanosecond dye lasers to determine dephasing times in the femtosecond range and is therefore an interesting alternative concept to

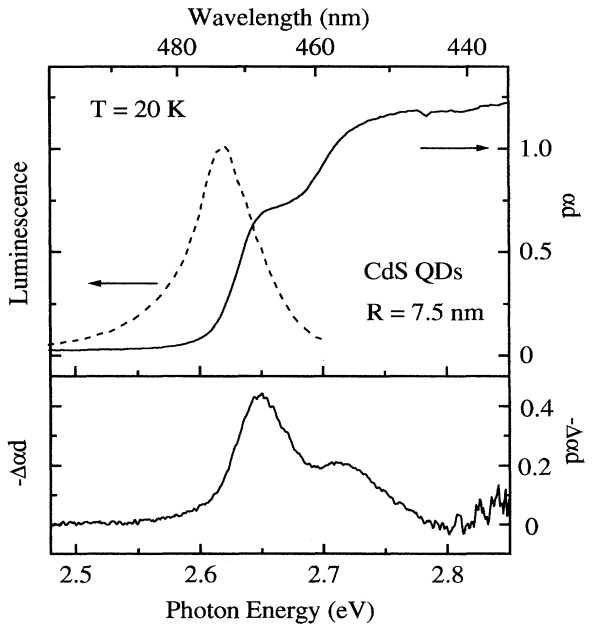

FIG. 1. Linear absorption, luminescence, and differential absorption of CdS quantum dots grown at 600 °C/60 h, $R=7.5$ nm.

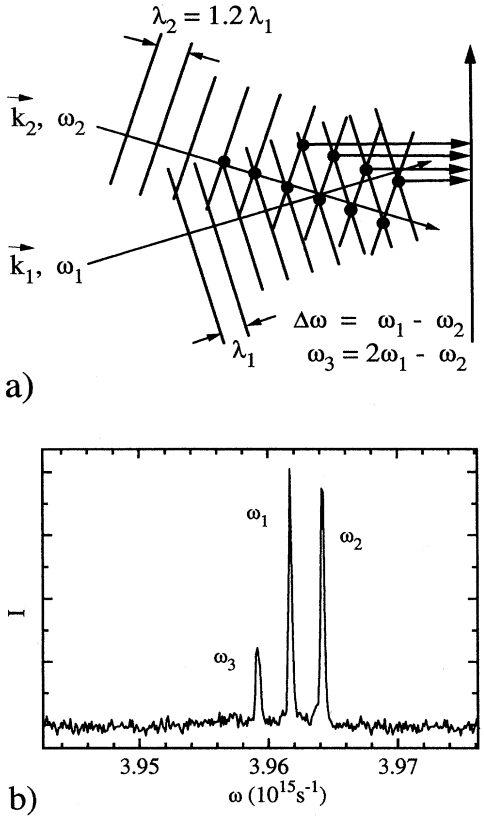

FIG. 2. Scheme of the method and signals detected in the NDFWM setup: ω_1 and ω_2 are the scattered light of the two exciting laser pulses forming the grating and ω_3 is the frequency-shifted diffracted signal. The sample is the CdS-doped glass with $R=7.5$ nm quantum dots.

the direct probing by fs lasers. In the nondegenerate case (NDFWM), the frequencies of the two laser beams, forming the light-induced grating, are different. If one of the pump beams is detuned by a small difference $\Delta\omega$ compared to the other, then the interference results in a "moving grating" structure and produces a nonstationary intensity distribution in the sample. The third-order nonlinearity of the material produces a signal at $\omega_3=2\omega_1-\omega_2$. When the two incident frequencies are both resonant with the inhomogeneously broadened optical transition and $\Delta\omega=|\omega_1-\omega_2|$ is in the range of the homogeneous linewidth, NDFWM can serve for the determination of the dephasing time T_2. Figure 2 shows a scheme of the method together with the signals detected by an optical multichannel analyzer system in the NDFWM setup: ω_1 and ω_2 are the scattered light signals of the two exciting laser pulses, and ω_3 is the frequency-shifted diffracted signal. The diffracted signal has been produced in the CdS-doped glass with the 7.5 nm QD's. The inhomogeneous broadening here is realized by the size deviation of the QD's of about 20% determined by x-ray scattering.

The theoretical description of the NDFWM for resonant excitation of an inhomogeneously broadened optical transition has been developed by Yajima and co-workers.[12,13] The most simple model to introduce the phase relaxation is based on the optical Bloch equations formulated for the two-level

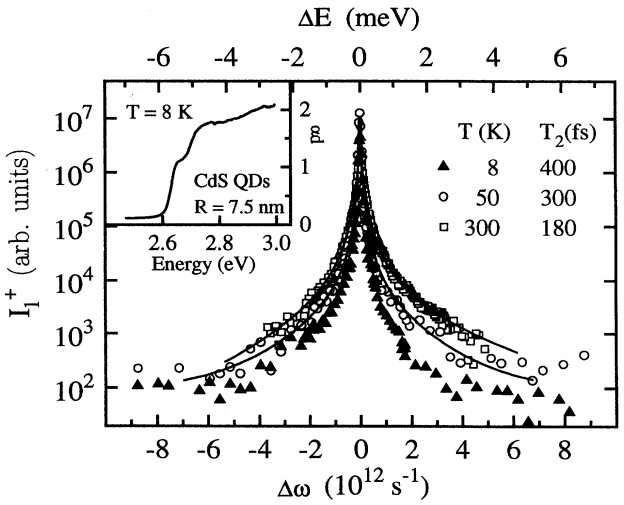

FIG. 3. Intensity of the first diffracted order measured at ω_3 versus detuning of the two laser beams $\Delta\omega$ with the temperature as a parameter.

system. Although the correct treatment of an optically excited semiconductor requires a many-body formalism, the simple two-band model has been often applied for a qualitative understanding of the relaxation dynamics. In QD's with their discrete level structure the two-level model is the best developed description in the present stage of application of NDFWM to quantum-confined structures and therefore used for the fitting procedure of the experimental results and the determination of the T_2 time.

In the weakly confined CdS QD's the temperature dependence of the dephasing time has been investigated at an excitation energy resonant to the lowest optical transition of the quantum-confined electron-hole-pair states. The NDFWM experiments have been performed at moderate excitation intensities and by adjusting the laser frequencies for $\Delta\omega=0$ according to the temperature-dependent shift of the linear absorption spectrum. Figure 3 shows the intensity of the first diffracted order at ω_3 versus the detuning of the two laser frequencies for three different temperatures of 8, 50, and 300 K. The signal around $\Delta\omega=0$ is determined by the lifetime T_1 of the underlying population grating. A sharp peak is expected if T_1 is large compared to T_2. In our experiment the difference between T_1 and T_2 is certainly more than one order of magnitude. Then the width of the tails in the detuning curves is a direct measure for the value of the dephasing time T_2. From the fitting procedure according to Refs. 12 and 13 a faster dephasing, i.e., a decrease in T_2 has been found if the temperature increases. The corresponding data for the results of Fig. 3 are $T_2=400$ fs (8 K), 300 fs (50 K), and 180 fs (300 K).

This change in T_2 with temperature is significant, but not dramatically. Comparing with the results obtained for strongly confined CdSe QD's,[5,7] the temperature-dependent dephasing of the weaker-confined CdS QD's investigated here is considerably smaller, in particular, in the range of higher temperatures between 50 K and room temperature. In strongly confined CdSe QD's with radii between 1 and 2 nm a linear decrease of the dephasing times by a factor of about

0.75 has been found starting at very low temperatures around 10 K up to values around 50 K. However, in the higher temperature range above 50 K the dephasing times show a more distinct decrease of more than a factor of 0.3, e.g., for CdSe QD's with ~2 nm radius.[5,7] The temperature-dependent phase loss has been ascribed to the interaction of the electron-hole pairs with the heat bath formed by a variety of acoustic phonons (e.g., intrinsic confined acoustic modes, surface modes, etc.), in particular, at very low temperature.[5,7,14–16] Due to the small dimensions of the dots, a significant increase of the coupling via the deformation potential interaction is expected for radii below the Bohr radius. At higher temperatures additionally the polar interaction with LO phonons contributes to the temperature-depending dephasing in strongly confined QD's. However, the concrete value of the coupling constant is very sensitive with respect to the dipolar character of the electron and hole wave functions. In these small dots the localization of one of the carriers near the interface is very likely which results in a large charge separation and polarity of the electron and hole wave functions.[11,17] The variation in the overlap of the wave functions given by the dot/matrix interface properties might be responsible for the great variety of the experimentally observed values for the electron-hole-pair–LO-phonon coupling constant, the Huang-Rhys parameter S.

Theoretical calculations revealed for the electron-hole-pair–LO-phonon coupling constant a nonmonotonic function in dependence on the size of the crystallites.[18] In small QD's the difference in the spatial distribution of the electron and hole wave functions is mainly governed by the nonparabolicity of the conduction band and the mixing of states from the different valence bands. For larger dot sizes the polarity of the wave functions is caused by the influence of the Coulomb interaction and the differences in the effective masses of the electron and hole.

Considering now CdS QD's of larger sizes, it is expected that the charge separation introduced by interface effects becomes smaller due to the smaller surface/volume ratio. Likewise, the influence of low-frequency acoustic phonons via the deformation potential coupling is reduced in larger QD's. As the radius of the QD's becomes larger, the influence of the confining barriers is less important and the properties approach that of the bulk semiconductor with the dominance of excitonic effects via the Coulomb potential. Generally speaking, compared to strongly confined QD's, in the case of CdS QD's with radii considerably larger than the Bohr radius, a smaller influence of the temperature on the homogeneous line broadening and a smaller electron-hole-pair–LO-phonon coupling constant are expected, i.e., Huang-Rhys parameters below 1. This behavior has been confirmed in the experiments. The value for the homogeneous line broadening obtained in NDFWM yields $S \approx 0.1$. For comparison, the corresponding values from the luminescent Stokes shift $\Delta_{\text{Stokes}} = 20$ meV and from the linewidth $\Delta_{\text{FWHM}} = 35$ meV obtained in differential absorption (see Fig. 1) (where FWHM denotes full width at half maximum) give Huang-Rhys parameters in the same order of magnitude, namely $S = 0.28$ and $S = 0.25$, respectively ($\hbar\omega_{\text{LO}} = 35$ meV). These small Huang-Rhys parameters and the more gradual change of the dephasing times with temperature observed in the experiments are in agreement with the discussion above.

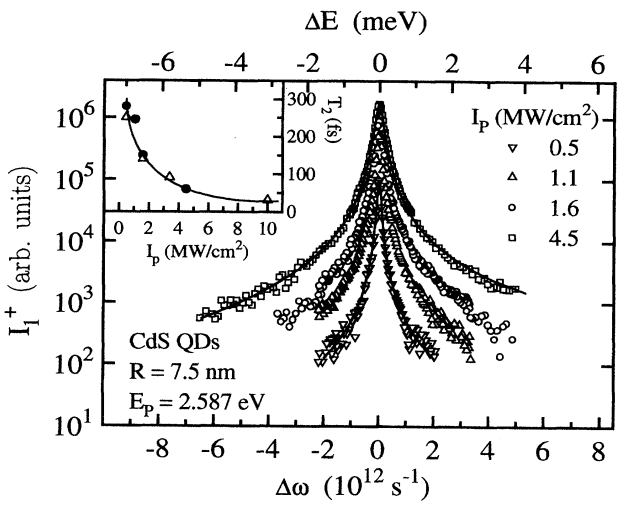

FIG. 4. Intensity of the first diffracted order measured at ω_3 versus detuning of the two laser beams $\Delta\omega$ with the intensity as a parameter. The inset shows the dephasing times as a function of excitation density, measured at the quantum dot energy states at 2.587 eV (circles) and 2.680 eV (triangles); $T = 300$ K.

The influence of high carrier densities on the dephasing time T_2 has been studied with the aim to find (i) the carrier density, where the interparticle interaction starts to be the dominant process and (ii) the lowest limit of the time T_2 if increasing the excitation intensities. It is expected to be in the range of some femtoseconds.

Dealing with that problem by NDFWM, the dephasing times in the first and second excited state have been measured in the CdS sample investigated so far. The results are shown in Fig. 4. At 300 K and low excitation intensities of 500 kW/cm^2 corresponding to about one electron-hole pair per dot, the dephasing time has been determined to be $T_2 =$ 280 fs. This is one of the largest values reported up to now for the dephasing time in CdS QD's at room temperature and has been ascribed to the low excitation densities used in the measurements and the high interface quality of the sample. For excitation intensities well above 1 MW/cm^2, a significant increase in the wings of the detuning curves can be seen, much more pronounced as in the temperature-depending measurements. The excitation densities used in the experiments correspond to densities well above the corresponding Mott density in the bulk and the interaction between the excited electrons and holes is no more negligible. The excitation of a few more electron-hole pairs inside one dot is accompanied by an increase of the interparticle scattering overwhelming finally all other dephasing channels. The characteristic time constant for this scattering mechanism is 30 fs, derived from the limit at highest excitation densities. Notice that the T_2 time is now, strictly speaking, only a phenomenological parameter, since the underlying model does not involve many-particle interaction. However, the clear increase of the diffracted signal for the larger detuning values $\Delta\omega$ if increasing the intensity, indicates unambiguously the discussed behavior. The very fast dephasing at high excitation is a clear hint that many-particle interaction becomes an efficient channel of phase loss. QD's of larger sizes show,

therefore, similar behavior as known from the bulk material at comparable excitation densities.[19]

In the inset of Fig. 4 the dephasing times as a function of excitation intensity are shown both for the transition from the first and from the second excited hole level to the lowest electron level. We get from these measurements first hints that the dephasing process is not very different if starting from the first or from the second excited state.

Summarizing, whereas in CdSe QD's smaller than the Bohr radius the dephasing can be explained by interaction of electron-hole pairs with phonons, lifetime phase loss due to fast trapping of electrons or holes at a localized surface state, and elastic scattering at imperfections at the QD's boundary;[5] one more important scattering mechanism appears if going to larger sizes. When exciting more than one electron-hole pair per dot, which can easily be attained by excitation densities usually applied in experiments of nonlinear optics, the interparticle interaction is the dominant scattering process. While scattering between the different type of carriers (electrons, holes, and excitons) has been widely investigated in two-dimensional structures, only little is known for QD's. The experiments presented here can be considered as a first step towards the understanding of many-particle interaction in zero-dimensionally confined systems.

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