Resonant spectroscopy of II-VI self-assembled quantum dots: Excited states and exciton–longitudinal optical phonon coupling

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Using resonantly excited photoluminescence (PL) along with photoluminescence excitation (PLE) spectroscopies, we study the carrier excitation processes in CdTe/ZnTe and CdSe/ZnSe self-assembled quantum dots (QD's). PLE spectra of single CdTe QD's reflect two major mechanisms for carrier excitation: The first, associated with the presence of sharp and intense lines in the spectrum, is a direct excited-state–ground-state transition. The second, associated with the appearance of up to four much broader excitation lines, is a longitudinal optical (LO) phonon-assisted absorption directly into the QD ground states. LO phonons with energies of both QD's and ZnTe barrier material are identified in the PLE spectra. Resonantly excited PL measurements for the QD ensemble as a function of excitation energy makes it possible to separate the contributions of these two mechanisms. We find that for CdTe QD's the distribution of excited states coupled to the ground states reflects the energy distribution of the QD emission, but shifted up in energy by 100 meV. This large splitting between excited and ground states in CdTe QD's suggests strong spatial confinement. In contrast, the LO phonon-assisted absorption shows significant size selectivity. In the case of CdTe dots the exciton-LO phonon coupling is strongly enhanced for smaller-sized dots which have higher emission energies. In contrast, for CdSe QD's the strength of exciton-LO phonon coupling is nearly uniform over the whole ensemble—that is, the dot energy distribution determines the intensities of LO phonon replicas. We show that for CdTe QD's after annealing, that is, after an increase in the average dot size, the exciton-LO phonon interaction reflects the dot energy distribution, as observed for CdSe QD's.

I. INTRODUCTION

Extensive spectroscopic studies of excitons in semiconductor quantum dots (QD's) show that either strong or weak longitudinal optical (LO) phonon coupling can be observed depending on the energy scales involved. This variability of exciton-LO phonon coupling is caused by the discreteness of the quasi-zero-dimensional energy levels in QD's and the ability to tune the energy levels through size or chemical composition engineering. The strong coupling regime is obtained when the energy distance between electronic levels in a QD approximately matches the LO phonon energy. In this nonadiabatic case a quasiparticle, the polaron, is formed due to the strong interaction between carriers (electron, hole, or exciton) and the phonon bath.[1–3] Experimentally, the formation of the polaron is observed as a Stokes-shifted line in the resonantly excited spectrum of QD's.[4] The energy difference between the positions of such a polaron line and the excitation laser corresponds to the polaron binding energy. As a quasiparticle, the polaron is characterized by excited states within the quantum dot which are spaced by the LO phonon energy from each other, as has been observed in photolumi-

nescence excitation (PLE) experiments on shallow QD's.[5] These polarons can be stable even at room temperature, and are characterized by very long lifetimes.[6]

On the other hand, when the ground-state–excited-state (GS-ES) energy difference becomes much larger than the LO phonon energy, the exciton-LO phonon coupling enters the weak coupling regime. Characteristic of this regime, an exciton-LO phonon complex is formed which appears as a broad emission line spaced by multiple LO phonon energies from the laser.[4] These spectral signatures of excitons coupled weakly to LO phonons have been observed for different QD material systems by means of resonantly excited PL or PLE.[7–12] In all cases, however, the intensity dependence of LO phonon replica on the excitation energy has reflected the shape of the nonresonantly excited PL spectrum. Since in most cases the nonresonant PL is associated with the ground-state energy distribution within the QD ensemble, such a result indicates, that all probed QD's interact with LO phonons with the same strength. Somewhat indirectly, the size-dependent exciton-LO phonon coupling has been reported through comparing the Huang-Rhys factors obtained for several InAs QD samples with different ground-state

energies.[12] Nevertheless, no clear evidence of size influence on exciton-LO phonon coupling in a single QD ensemble has been reported so far. This paucity of experimental evidence is explained by the theoretical studies,[13] which indicate that in order to observe size-dependent exciton-LO phonon coupling, extremely small QD sizes are required. Indeed, in the case of QD's with sizes comparable or smaller than the exciton Bohr radius, the change of the exciton wave function due to confinement should result in a change of a dipole moment of the exciton. This, in turn, would change the interaction between the QD-confined exciton and the LO phonon.

In the majority of experiments reported so far, dots with sizes larger than the exciton Bohr radius have been studied. For instance, the typical size of II-VI CdSe QD's, where the exciton Bohr radius is equal to 3 nm, ranges from slightly larger than this value[14] to even 15 nm in a diameter.[15] In these cases then, the leakage of the exciton wave function into the barriers is not expected to change significantly for QD size distributions within an ensemble. Consequently, for large QD's no size dependence of the exciton-LO phonon coupling is observed.

In this work we analyze resonant PL and PLE measurements for two II-VI semiconductor self-assembled QD systems. Self-assembled CdTe/ZnTe QD's are characterized by sizes between 2 and 4 nm in diameter, which are significantly smaller than the exciton Bohr radius in bulk CdTe (10 nm). On the other hand, self-assembled CdSe/ZnSe QD's with sizes between 8 and 10 nm are significantly larger than the Bohr radius. The results reported here show that the excitons confined to both CdTe and CdSe QD's, while strongly confining electrons and holes, are in the weak exciton-LO phonon coupling regime, because the GS-ES energy splittings are substantially larger ($\sim$100 meV) than frequencies of LO phonons in these materials ($\sim$28 meV, on average). From resonantly excited PL of CdSe QD's we find only weak dependence of the exciton-LO phonon coupling on the QD emission energy. In contrast, in the case of smaller CdTe QD's the exciton-LO phonon coupling is strongly enhanced for QD's emitting at higher energies, i.e., those with smaller sizes. However, by increasing the effective average CdTe QD size *in the same sample* by rapid thermal annealing, we find that the exciton-LO phonon coupling becomes much less sensitive to the emission energy, similar to what is observed in the CdSe QD case. The increase of the coupling for smaller QD's has been ascribed to changes in the wave function of the exciton confined in a QD.

II. SAMPLES AND EXPERIMENTAL DETAILS

The CdTe/ZnTe and CdSe/ZnSe QD samples were grown by molecular beam epitaxy on GaAs substrates. Self-assembled CdSe (CdTe) QD's were formed by depositing 2.6 (4) monolayers on a ZnSe (ZnTe) surface. A 50-nm-thick ZnSe (ZnTe) capping layer covered the dot layer. Further details of the sample growth and their optical characterization can be found elsewhere.[16,17] It is important to note that the sample set chosen enables us to study QD's with consid-

erably different lateral sizes. Namely, CdTe QD's are very small, and, as estimated by transmission electron microscopy and magnetophotoluminescence measurements, their lateral size is of the order of 2–4 nm in diameter.[18] On the other hand, the average lateral size of CdSe QD's studied here is larger and it approaches 8–10 nm in diameter. In order to extend the available sizes of CdTe QD's we annealed the sample containing CdTe QD's.[19] The annealing that results in Zn interdiffusion into the QD's was performed in argon atmosphere at $T=470\,°C$ for 15 s. From the diamagnetic shift values obtained by single dot spectroscopy in a magnetic field we estimate the average Bohr radius of the excitons in annealed CdTe QD's enlarges almost a factor of 2 to approximately 8–10 nm.[20] We note that for both II-VI QD structures studied here, no spectral evidence (PL or PLE) of a uniform wetting layer is observed, in contrast to the III-V semiconductor QD's.[21,22]

Optical spectroscopy measurements were performed in a continuous-flow helium cryostat with sample temperatures of 6 K. Photoluminescence excitation (PLE) measurements of single CdTe QD's were carried out through an aperture in an opaque metal mask. The emission was excited by an Ar ion pumped dye laser (Rhodamine 590) focused to a spot diameter of 1.7 μm using a microscope objective. The QD emission was dispersed by a DILOR *XY* triple spectrometer working in a subtractive mode and was detected by an LN$_2$-cooled CCD detector. Multichannel detection used in this experiment allows the study of a number of QD's simultaneously. The excitation spectrum for a single QD can be easily obtained by analyzing the intensity of the particular emission line as a function of laser energy.[23] PLE spectra were normalized to the laser power. In the case of single dot PLE experiments, the spectral resolution is that of the dye laser, which was about 100 μeV. In order to obtain information about exciton-LO phonon coupling in our QD's, we performed resonantly excited PL measurements on CdSe QD's and on both as-grown and annealed CdTe QD's. In this case the emission was excited resonantly by a tunable dye laser using Rhodamine 590 and Coumarine 6 days. The spectral resolution for PL measurements was 70 μeV.

III. EXPERIMENTAL RESULTS

A. Photoluminescence excitation of a single CdTe quantum dot

In Fig. 1 we present typical PLE spectra obtained for two single CdTe QD's collected through an aperture with a diameter of 0.8 μm. The linewidths of these single dot PL emissions are around 100 μeV, typical for II–VI semiconductor QD's.[24] We have chosen two QD's to emphasize two distinct spectral features observed in the PLE spectrum. A typical PLE spectrum of a single CdTe QD taken over the whole range of the excitation energy is presented in Ref. 25. The broad excitation peak observed for QD1 [Fig. 1(a)] at a relative energy of 22 meV above the detection energy is attributed to LO-phonon-assisted absorption into the QD ground state, as schematically shown in the inset of Fig. 1(a). Similar LO phonon-related absorption lines have been recently found for single InAs QD's. (Ref. 26) and single CdSe
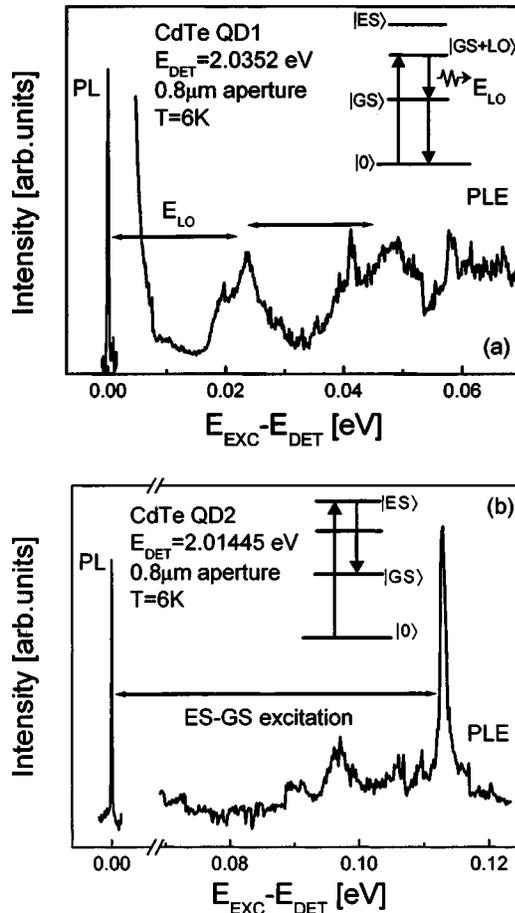
FIG. 1. PLE spectra of two single CdTe QDs taken at $T=6$ K on 0.8 μm aperture. Both (a) LO phonon-assisted absorption and (b) excited-state (ES) ground-state (GS) excitation are shown. The actual emission energies of these two QD's are also given. The insets illustrate the respective energy diagrams of these excitation processes.

QD's.[27] Typically we observe up to three such resonances. The shape of these resonances can be deconvoluted into at least three Gaussian lines, yielding direct evidence that LO phonons with different energies participate in this process.[7,10] In particular, the characteristic energies for bulk CdTe and ZnTe LO phonons are 21 and 24 meV, which agree with energy spacing observed for the resonance in Fig. 1(a). The presence of ZnTe LO-phonon assisted absorption line suggests that the wave function of the exciton confined in a QD is leaking out into the ZnTe barriers. We also observe a tail at energies less than 10 meV from the QD1 detection energy. This tail may originate from absorption mediated by acoustic phonons,[27] but the possibility that at least part of this intensity is related to the stray laser light cannot be excluded.

Apart from excitations related to LO phonon-assisted processes we also observe a number of very intense and relatively sharp (with a linewidth of less than 2 meV) excitation lines on a nearly background-free PLE spectrum, as shown for QD2 in Fig. 1(b). From the measurements of tens of single CdTe QD's we find these lines predominantly in the range of 80–140 meV above the QD detection energy. The energy difference between these strong resonances and the

detection energy varies from dot to dot revealing the influence of both size and chemical composition/strain inhomogeneities in the QD ensemble. We tentatively assign them to the direct excited-state (ES) ground-state (GS) excitations [see inset to Fig. 1(b)]. It seems that on average the ES energy for CdTe QD's is significantly larger than, for instance, that observed for InAs (Ref. 26) or CdSe QD's.[27] Since the ES-GS splitting is associated with the strength of spatial confinement, we may conclude that excitons in these CdTe QD's are very strongly confined. This finding agrees with a small lateral QD size ($\sim$2–4 nm in a diameter) estimated from previous magneto-PL spectroscopy results.[18]

A detailed analysis of single CdTe QD's PLE results will be presented elsewhere. For the purpose of this paper we point out the presence of two dominant excitation mechanisms in CdTe QD's: direct ES-GS excitation (at around 100 meV) and LO phonon-assisted absorption.

B. Resonantly excited photoluminescence of quantum dots

The PLE data presented above shows that there are two dominant excitation processes in these structures: direct excitation into the QD ground states through LO phonon-assisted absorption or excitation into excited states followed by relaxation to ground states. This suggests that both excitation processes should be observed when resonantly exciting the QD ensemble. Indeed, as we shall show next, comparison of resonant PL's of large QD ensembles with single-dot PLEs makes it possible to draw more general conclusions about the importance of both QD excitation processes.

In Fig. 2(a) we show resonantly excited PL spectra measured through a 1.5 μm diameter aperture for CdTe QD's at $T=6$ K. The spectra are shifted vertically for clarity and compared with nonresonantly excited QD PL [shaded area in Fig. 2(a)]. The broadening of the nonresonantly excited PL spectrum reveals variation of both size and chemical composition within the QD ensemble. Solid triangles mark the laser energy for each spectrum. Depending on the excitation energy, the resonantly excited PL emission is composed of up to four clearly separated lines superimposed on a broad background. The energy spacing between these lines is roughly equal to 22 meV, which matches the energy spacing between detection energy and LO phonon absorption line observed in the PLE spectrum. Moreover, the shape of the first LO phonon replica is very similar to the absorption line observed in Fig. 1(a) in the PLE experiments. We attribute these lines to the recombination of QD's excited directly into their ground states through LO phonon-assisted absorption. As one can see, the intensity of the LO phonons replicas depends strongly on the excitation energy. For instance, in the case of spectrum (2) in Fig. 2(a), the highest emission intensity is associated with the third LO phonon replica, while spectrum number (4) in Fig. 2(a) is dominated by the first LO phonon emission. Moreover, the spectral features related to LO phonon enhanced PL become broader for the second and following replicas compared to the first replica. This broadening may be attributed to acoustic phonon scattering, which could be as efficient as higher order LO phonon relaxation processes.[9]
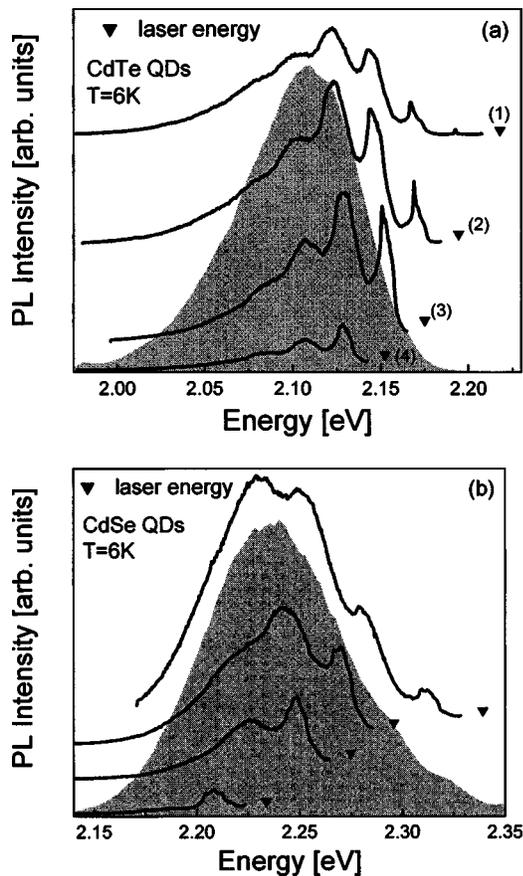
FIG. 2. Resonantly excited PL spectra obtained for (a) CdTe QD's and (b) CdSe QD's at different laser energies (marked by the solid points). The spectra are shifted vertically. Also the nonresonantly excited PL emissions are shown.

FIG. 3. Typical fits (black solid line) of the experimentally obtained PL spectra (solid points). The contribution of both excited state-ground state excitation (dashed line) and LO phonon-assisted absorption (grey lines) is shown for (a) CdTe QD's and (b) CdSe QD's.

We also performed resonant PL measurements for the larger-sized CdSe QD's in order to study the impact of QD size on the excitation processes. From the PLE results reported for single CdSe QD's with similar sizes as CdSe QD's discussed here,[26] in these structures both LO phonon-assisted absorption and direct ES-GS excitations are present. In Fig. 2(b) we show an example of PL spectra of CdSe QD's taken for different excitation energies (as marked with solid triangles). The shaded area represents the nonresonantly excited PL emission. As can be seen, resonantly excited PL spectra of CdSe QD's look qualitatively similar to the results found for CdTe QD's. All of the spectra consist of LO phonon assisted absorption lines and the broad background luminescence.

In order to determine the excitation energy dependence of the intensity of each component of the spectra we fit the data similar to that displayed in Figs. 2(a) and 2(b) with a series of Gaussian line shapes. Extrapolating the results of single QD PLE over the whole ensemble, we assume that only the two aforementioned excitation processes determine the shape and the intensity of the resonant PL spectrum. We neglect, for instance, the effect of acoustic phonon-assisted hopping between QD's with different energies. Since all measurements were carried out at low temperature, this process should not substantially influence our analysis. In addition,

the low excitation power used in these experiments allows us to rule out the possibility of Auger-type excitations. We also assume that for each particular excitation energy the ES-GS excitation process leads to a random QD occupation determined by the energy distribution of the ground states within the entire QD ensemble. As a consequence, we keep the energy and the linewidth of the background luminescence identical to the nonresonantly excited PL emission for all fits. Typical results of the fitting for CdTe QD's and CdSe QD's are presented in Figs. 3(a) and 3(b), respectively. As can be seen, the fitted (solid lines) and the measured (points) spectra agree reasonably well. By performing this fitting for all spectra, we are able to obtain the intensity of both the ES-GS transition and LO phonon-assisted absorption as a function of the excitation energy.

In Fig. 4 we plot the intensity of the first LO phonon replica as a function of the QD emission energy for CdSe QD's and both as-grown and annealed CdTe QD's. The QD emission energy corresponds to the energy position where the first LO phonon replica is observed. For the QD systems studied in this work, this energy shift is equal to 22 and 27 meV for the CdTe QD's and CdSe QD's, respectively. The energy dependence of the intensity of the first LO-phonon enhanced PL (solid points) is plotted along with the
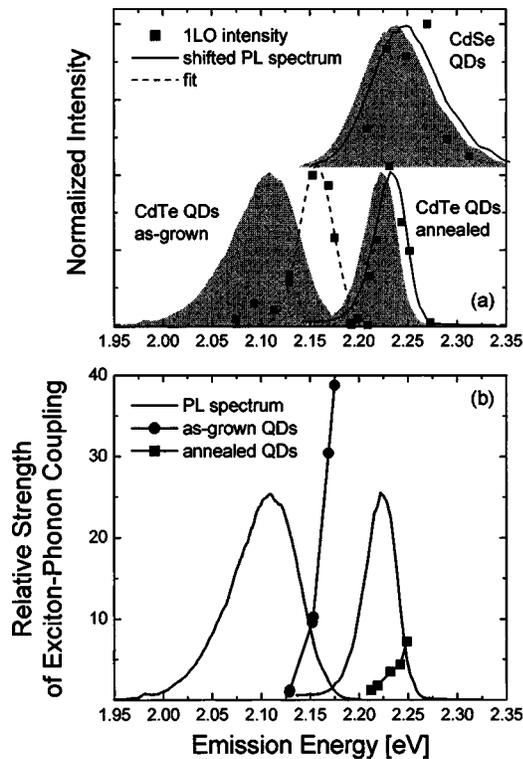
FIG. 4. (a) The intensity of the first LO phonon replica obtained for as-grown CdTe QD's, annealed CdTe QD's and CdSe QD's as function of the emission energy. The shaded areas represent the nonresonantly excited PL spectra. Solid lines are the nonresonant PL spectra shifted by 10 meV towards higher energies, while the dashed line is the least square fit to the data. (b) Relative change of the exciton-LO phonon coupling obtained for as-grown and annealed CdTe QD's by dividing the intensity of the first LO phonon replica by the intensity of the nonresonantly excited PL spectrum taken at the same energy.

nonresonantly excited PL (shaded areas) measured for each sample. The solid lines are the nonresonant spectra shifted by 10 meV towards higher energies in order to obtain agreement with the results, while the dashed line is the least square fit to the data. The behavior of the second and third LO phonon replicas, as far as the emission energy dependence is concerned, is similar to the one obtained for the first LO replica. However, the higher order replicas have somewhat broader linewidths probably due to scattering from acoustic phonons. We shall therefore concentrate here only on the emission originating from absorption with one LO phonon involved. In addition, we find that the integrated intensity of the LO phonon replica increases with the number of phonons involved in the excitation process.[25] Qualitatively similar behavior has been recently reported by Steer *et al.*[11] We interpret this increase as a result of higher density of states due to the presence of excited states in the studied sample.

The results shown in Fig. 4(a) demonstrate quite different dependence of LO phonon intensity on the emission energy depending on the QD sample. In the case of the larger CdSe QD's the maximum of the intensity of the first LO phonon replica as well as its linewidth are very similar to those of the

nonresonant PL emission. The small shift (10 meV) of the maximum of the first LO phonon replica enhancement with respect to the nonresonantly excited emission could be ascribed to the possible energy dependence of the exciton-LO phonon coupling. However, since the determination of the LO phonon intensity is not very accurate, it can also originate from the experimental error. In contrast, for the as-grown CdTe QD's the highest intensity of the first LO phonon replica is observed at the energy shifted (by ~50 meV) towards higher energies with respect to the maximum of the nonresonant QD emission. Moreover, the linewidth of the LO phonon intensity dependence is narrower (~30 meV) than the inhomogeneous broadening of the CdTe QD PL (~70 meV). Interestingly, the same sample after annealing shows a behavior that is very similar to the one obtained for CdSe QD's. Since annealing effectively increases the average size of CdTe QD's (presumably through Zn interdiffusion),[19] this result strongly suggests that exciton–LO phonon coupling in II-VI QD's depends sensitively on the emission energy of QD's, and therefore presumably on the QD size.

It is important to note that the data in Fig. 4(a), which shows the energy dependence of the enhancement of the first LO phonon intensity, is a combination of two effects: the change in the exciton-LO phonon coupling, as well as the ground-state energy distribution of the QD's. However, we can approximate the energy distribution of the QD ensembles through the non resonantly excited PL emission spectra shown as shaded regions in Fig. 4(a). Therefore, the relative change in the exciton-LO phonon coupling can be separated through direct division of the emission intensity of the first LO phonon replica by the intensity of the nonresonant PL emission taken at the same energy. The result of this procedure is displayed in Fig. 4(b), where we present the relative enhancement of the exciton-LO phonon interaction obtained for the as-grown CdTe QD's and the annealed CdTe QD's. We would like to emphasize that this is only a very qualitative way of showing the strong dependence of the exciton-LO phonon interaction on the QD emission energy. Nonetheless, as one can see, the relative enhancement of the exciton-LO phonon interaction is by more than order of magnitude larger in the case of the as-grown (small size, broad size distribution) QD's than of the annealed (large size, smaller size distribution) QD's.

The approach used in Fig. 4(a) to measure emission energy dependence of the LO phonon-assisted absorption process in QD's, can also be used to obtain the excitation energy dependence of the intensity of the emission which we associate with a direct ES-GS excitation in QD's. In Fig. 5 we plot the intensity of the background emission obtained for CdTe QD's and CeSe QD's at $T = 6$ K. The results are compared with the nonresonant PL line shapes (shaded areas in Fig. 5). In the case of CdTe QD's we find that the maximum enhancement of the ES-GS-related emission occurs for the laser energy approximately 100 meV above the maximum energy of the nonresonant PL. This energy agrees with the typical ES-GS splittings found in PLE spectra of single CdTe QD's. In addition, the shape of the excitation energy dependence reflects the shape of the shifted nonresonant PL spectrum (solid line in Fig. 5). Importantly, we do not see, in
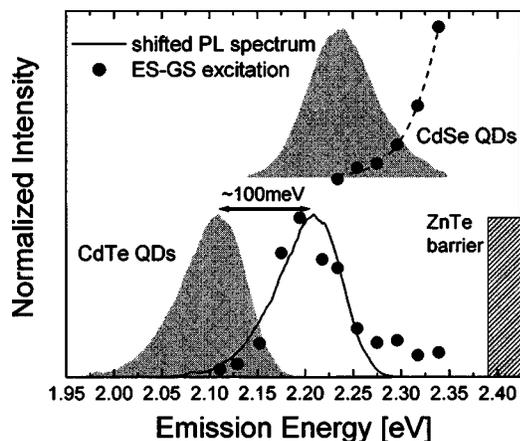
FIG. 5. The intensity of the ES-GS excitation obtained for as-grown CdTe QD's and CdSe QD's as a function of the excitation energy. The shaded areas represent the nonresonantly excited PL spectra. The solid line is the nonresonant PL spectrum shifted by 100 meV towards higher energies, while the dashed line is the least square fit to the data. The ZnTe barrier energy is also shown.

agreement with PLE data, any indication of two-dimensional wetting layer for this sample. In fact, the intensity of ES-GS transition decreases rapidly after 100 meV. On the other hand, for CdSe QD's we observe a monotonous increase of the intensity ascribed to ES-GS excitation, even for the energies above 100 meV from the nonresonant PL spectrum (see Fig. 5). Possible explanations of this behavior are discussed later in the paper.

IV. DISCUSSION

The results of resonant PL spectroscopy together with single-dot PLE measurements allow us to construct a consistent picture of excitation mechanisms in II-VI self-assembled QD's. In particular, we find two major processes that determine the optical properties of these structures. The first is associated with QD-confined exciton coupling to LO phonons while the other is related to direct transitions from excited to the ground state of the QD.

The ES-GS excitation process manifests itself by the presence of very sharp lines in the single dot PLE spectrum. The energy distance between these lines and the ground-state QD energy varies from dot to dot, simply due to fluctuations of QD parameters (such as size or chemical composition) within an ensemble. The most important factor which determines the value of GS-ES splitting, however, is the spatial confinement of excitons. For the very small CdTe QD's (the lateral size $\sim 2-4$ nm) the majority of ES-GS excitations are observed ~ 100 meV above the QD ground state.[25] Interestingly, the linewidth of these resonances yields the lifetime of this transition in the picosecond range, which means that this excitation process is very effective.

The analysis of the resonant PL data is consistent with our interpretation of the PLE results. For CdTe QD's a background emission is observed, whose intensity depends strongly on the excitation energy. The energy dependence of this emission reflects to a good approximation the energy

distribution of QD's within the ensemble. We conclude that the excited states in CdTe QD's have a similar energy distribution to the energy distribution of the QD ground states, as has also been measured for other QD systems.[11,12,28] Moreover, the energy difference between the maximum of the ES-GS transition and the nonresonant PL emission of ~ 100 meV corresponds well to the average energy spacing between excited and ground states obtained from PLE measurements.

Another explanation of the spectral features identified here as direct ES-GS transitions could be associated with the excitation of CdTe QD's through a two-dimensional wetting layer. However, both power-dependent PL and PLE measurements show no evidence for such a continuum of states. Furthermore, if the background emission observed in resonant PL were originating from the WL, then the linewidth of its excitation energy dependence would be much narrower. As has been shown in previous studies,[29] the PL linewidth of CdTe/ZnTe quantum wells does not exceed 40 meV. Furthermore, if these excitations were related to the two-dimensional wetting layer, it would feature the two-dimensional continuum density of states.[7] In contrast, the excitation energy dependence of the intensity of the ES-GS emission shows a well-resolved peak, so that the presence of a wetting layer can be ruled out.

In the case of CdSe QD's the intensity associated with ES-GS excitation shows a continuous increase with increasing excitation energy up to more than 100 meV above the maximum of nonresonantly excited PL. At this point we cannot exclude the presence of the wetting layer in this sample, but power-dependent PL measurements certainly do not support the existence of such a wetting layer. Moreover, the fact that we do not observe any other spectral lines below 100 meV would indicate that the enhancement of the background emission intensity originate, as in CdTe QD's, from the ES-GS transition.

All of these observations indicate then that both sharp lines in micro-PLE spectra and the background emission in resonantly excited PL experiments are related to direct relaxation from an excited state down to the QD ground state. In both CdTe QD's and CdSe QD's the energy difference between ES's and GS's is significantly larger than the LO phonon energies characteristic for these materials. This justifies the assumption of a weak regime of the exciton-LO phonon coupling in these QD's.

Although the excitation energy dependence of the ES-GS excitation is qualitatively similar for both CdTe and CdSe QD's, the LO phonon-assisted processes show some important differences. In the case of the larger CdSe QD's, the maximum of the first LO phonon intensity dependence on the PL energy corresponds approximately to the maximum energy of non resonantly excited PL emission [see Fig. 4(a)]. The linewidths of both these curves are also very similar. We argue that the LO phonon scattering strength in CdSe QD's is nearly independent of the QD size, and thus the intensity of the LO-phonon replica reflects only the ground-state energy distribution within the QD ensemble. The behavior found for exciton-LO phonon coupling in CdSe QD's is similar to the direct ES-GS relaxation processes discussed earlier. We conclude that for CdSe QD's the size range and the size distri-

bution in the CdSe QD's ensemble is too narrow to induce any significant changes in the overlap between electron and hole wave function.

The observed behavior of the exciton-LO phonon coupling in CdSe QD's agrees, at least qualitatively, with the results of calculations by Melnikov and Beall Fowler.[13] performed for CdSe/ZnSe QD's as a function of the QD size. We recall that the average size of the CdSe QD's studied here is around 8–10 nm in diameter. The findings presented in Ref. 13 predict, in this case, a monotonic increase of the coupling strength for QD's with decreasing QD size, exactly the same behavior as we observe experimentally [see Fig. 4(b)]. However, we estimate the relative increase of the coupling to be approximately four times larger than found in Ref. 13. This discrepancy could be related to some limitations of the model, which assumes a spherical shape and uniform chemical composition of the QD's. Clearly, the QD's studied in this work are more lens shaped[14] and the chemical composition is one of the parameters that vary randomly over the ensemble. We note, however, that the theory presented in Ref. 13 could possibly be verified by studying very small CdSe QD's (with sizes below 5 nm in a diameter). Indeed for such small QD's it is expected that a well-defined maximum in the exciton-LO phonon strength should be observed, which is due to strong leakage of exciton wave function from the QD into the barriers.

A situation where changing the overlap between electron and hole confined to QD's changes the strength of the exciton-LO phonon coupling, is in fact observed for the CdTe QD's, which are considerably smaller than CdSe QD's. As shown in Fig. 4(a), the CdTe QD's data feature a completely different dependence of the intensity of the first LO phonon replica on the excitation energy. Namely, the experimental results show that excitons in a narrow energy distribution of QD's couple much more strongly to LO phonons. First of all, the linewidth of the excitation energy dependence of the first LO phonon replica is much narrower than the QD energy distribution as a whole (revealed by nonresonant PL emission). Secondly, we observe a large energy separation between the nonresonant PL maximum and that of the first LO phonon enhancement. Since the intensity of the LO phonon replica depends on both exciton-LO phonon coupling and the density of states, it is necessary to deconvolute the dependence found for the first LO replica for CdTe QD's with the nonresonant spectrum. After the deconvolution we obtain the QD emission energy dependence of the LO phonon coupling, as shown in Fig. 4(b). We find a strong increase of the LO phonon coupling for the dots with higher

emission energies, probably reflecting their smaller size. Strong evidence that the effect observed for the as-grown CdTe QD's is related to size sensitivity of the exciton LO phonon coupling comes from the results obtained for the annealed CdTe QD sample. As shown previously,[19,20] annealing of CdTe QD's leads to an increase of the effective average QD size through Zn interdiffusion, and simultaneously improves the homogeneity of the ensemble. In such a case, one would expect that the exciton-LO phonon coupling would approach the situation observed for CdSe QD's. Specifically, since the dots are larger and the size distribution is smaller, the experimentally measured intensity of the LO phonon replica would be determined mainly by the ground state energy distribution. The result presented in Fig. 4 for the CdTe QD's annealed at $T=470\,°C$ confirms this expectation.

V. CONCLUSIONS

By using single-dot PLE together with resonant PL spectroscopy, we identify two major carrier excitation mechanisms in CdTe QD's and CdSe QD's. The first one is direct excitation into the QD excited states followed by relaxation to the ground state and is predominantly governed by the ground-state energy distribution within the QD ensemble. The second one is associated with direct excitation into the QD ground states through LO phonon-assisted absorption. By analyzing PL spectra obtained under resonant excitation, we show that the strength of exciton-LO phonon coupling increases significantly for QD's with lateral sizes smaller than the exciton Bohr radius, e.g., as-grown CdTe QD's. In contrast, for larger QD's (CdSe QD's) the strength of the exciton-LO phonon coupling is largely independent of the QD emission energy, and thus the intensities of LO phonon replicas are determined by the ground-state energy distribution of the ensemble. For CdTe QD's with an increased average size obtained by rapid thermal annealing, we again find no dependence of the exciton-LO phonon coupling on the excitation energy. These results show that in the regime of weak exciton-LO phonon coupling the strength of this interaction may strongly increase for small QD's, in agreement with recent theoretical considerations.

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