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Enhanced phonon-assisted absorption in single InAs/GaAs quantum dots

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Exciton-longitudinal optic-phonon coupling in InAs/GaAs quantum dots is investigated by means of single-dot spectroscopy. Photoluminescence spectra in the excitonic ground-state region exhibit a series of new emission lines which we ascribe to single exciton recombination perturbed by charged defects close to the dot. Compared to unperturbed excitonic recombination, the resulting dipole in these complexes leads to enhanced coupling to LO phonons in photoluminescence excitation spectra. Evidence for resonant enhancement of phonon-assisted processes in absorption is also presented.

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The coupling of excitons to longitudinal optical (LO) phonons in polar semiconductors arises from the polarization of the lattice by the difference in the electron and hole (e, h) charge distributions in the exciton (the dipole moment of the exciton). Such coupling has been analyzed theoretically for bulk,[1] quantum well,[2] and quantum dot (QD) structures.[3,4] Since the coupling is determined by the excitonic charge distribution, it is highly sensitive to the form of the electron and hole wave functions. Indeed if the electron and hole charge distributions are identical as might be expected in a strongly confining QD,[3] then LO phonon features would not be observable. However, recent studies of large ensembles of weakly polar InAs/GaAs self-assembled QD's have reported Huang-Rhys parameters (S) (the ratio of the intensity of the first LO phonon satellite to the zero phonon line) of significant magnitude, e.g., 0.03 in Ref. 5, 0.01–0.5 in Ref. 6, and 0.5 in Ref. 7. Several processes have been invoked to explain these S values: separation of the electron and hole charge distributions as a result of asymmetric shape[5–7](similar to the model for quantum wells of Ref. 2), the presence of piezoelectric fields,[5] and the breakdown of the adiabatic approximation usually employed to treat exciton-LO phonon coupling,[8] where coupling of excitonic wave functions by the phonon displacement is assumed to be negligible. Extrinsic effects such as the presence of charged point defects[4] may also lead to polarization of the charge distributions and enhanced LO phonon coupling.

Single-dot spectroscopy is a direct experimental technique to investigate the electronic properties of QD's which would otherwise be obscured by strong inhomogeneous broadening. In the present paper we employ such techniques to investigate the coupling between excitons and LO phonons in single self-assembled InAs/GaAs QD's. Microphotoluminescence (μPL) and μPL excitation (μPLE) are used to probe the importance of exciton-LO-phonon coupling features in absorption (PLE) and emission spectra. The single exciton transition (X) which dominates the PL for above gap excitation is found to exhibit LO features in absorption, but not in emission. This unexpected observation is attributed to the occurrence of resonant mixing in absorption between the ground state plus one 1LO phonon state with nearby excited state transitions (breakdown of the adiabatic approximation). Surprisingly, for excitation below the wetting layer, several additional single exciton lines are observed which eventually dominate for low-energy excitation. The new lines exhibit strongly enhanced phonon coupling relative to X, and are attributed to single exciton transitions perturbed by charged defects.

The self-assembled dots were grown on a [100] GaAs substrate by molecular-beam epitaxy using the Stranski-Krastanow growth mode. After deposition of a GaAs buffer, the layer sequence was: 1350 nm $Al_{0.33}Ga_{0.66}As$ outer cladding followed by 175 nm $Al_{0.13}Ga_{0.87}As$ and 25 nm GaAs layers. The 2.4 monolayer QD layer was then deposited at 500 °C. A low InAs deposition rate ($0.01\ \mathrm{ML\,s^{-1}}$) was employed to provide a low QD density of $\sim 5\times 10^{9}\ \mathrm{cm^{-2}}$ of approximately lens shaped QD's with mean basal diameter $\sim$18 nm and height $\sim$5 nm.[9] The sample was completed with 25 nm GaAs and a second 175 nm $Al_{0.13}Ga_{0.87}As$ layer. After growth the sample was capped with Si_3N_4 and annealed for 5 min at 750 °C, to blue shift the emission from $\sim$1.1 eV as grown to above $\sim$1.25 eV where it is accessible to sensitive Si-based detectors. Following annealing, the inhomogeneously broadened excitonic ground state (GS) peak [$\sim$50 meV full width at half maximum (FWHM)] was at $\sim$1.33 eV, with the wetting layer peak at $E_{WL} = 1460 \pm 5$ meV. The sample was then fabricated into a widely spaced array of 200 nm diameter mesas using electron beam lithography and dry etching. PL was performed at $T \sim 10$ K using a μPL system containing a large aperture microscope objective to provide a sub-micron excitation spot. PL was excited using tunable radiation from a Ti:sapphire laser, collected via the same objective and dispersed using a 0.85 m double monochromator with resolution of $\sim$30 μeV, and detected using either a CCD camera or cooled Si-avalanche photodiode (APD).

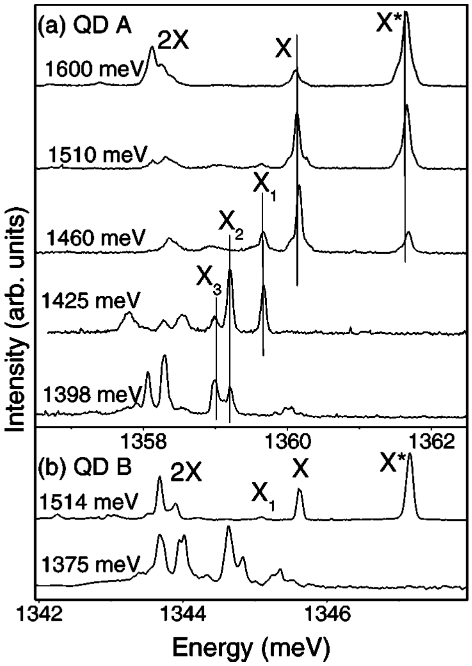

FIG. 1. (a) PL spectra from the ground state of QD A for different excitation energies above and below the wetting layer band edge (~1460 meV). (b) PL spectra of QD B for $E_{\rm exc}=1380$ and 1514 meV for comparison with (a). The energy scale has been shifted by +15 meV.

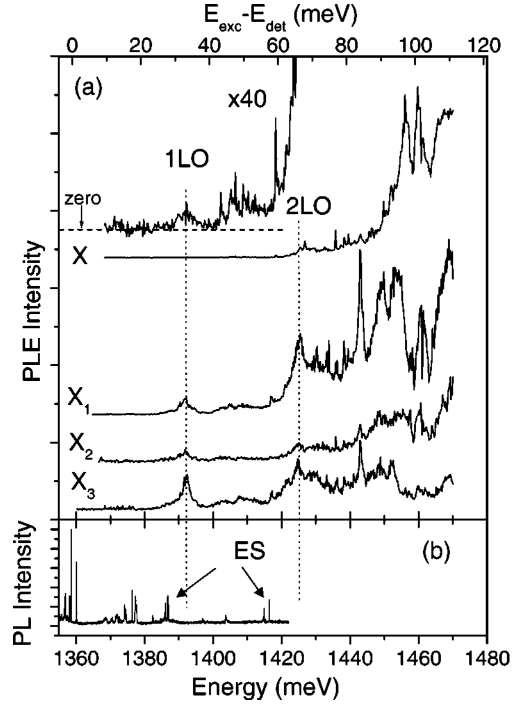

FIG. 2. (a) PLE spectra for detection at the energies of the X and X_n lines observed in PL for QD A in Fig. 1. (b) High-power PL spectrum showing the emission from excited states (ES) of QD A.

Several mesas containing one optically active dot were investigated, all of which show very similar behavior. We present results here for two representative dots. The PL spectrum in the *s*-shell, excitonic ground-state (GS) region for the first dot (dot A) is presented in Fig. 1(a) as a function of laser excitation energy ($E_{\rm exc}$). When carriers are created in the GaAs layer surrounding the dot ($E_{\rm exc}>1510$ meV), the spectrum consists of three lines separated by less than 2 meV (the excitation power ($P_{\rm exc}$) is such that the dot is occupied by approximately one electron-hole pair on average). A detailed study[10] of their power dependence shows that the central peak arises from recombination of a single electron-hole pair (X). The lower energy peak (2X), 2 meV below X, arises from biexcitonic recombination, as confirmed by its quadratic dependence on $P_{\rm exc}$. The peak X*, 1.5 meV above X, arises from a charged exciton where an electron-hole pair recombines in the presence of an additional carrier (probably a hole) in the dot.[10] As $E_{\rm exc}$ is reduced below the WL band edge ($\hbar\omega_{\rm WL}\sim1460$ meV) X* disappears, since the preferential capture of one component of a photocreated electron-hole pair can no longer occur.

In addition to the disappearance of X*, the PL spectrum undergoes further major modifications when $E_{\rm exc}$ is decreased further. The intensity of X decreases very rapidly for $E_{\rm exc}$ below the WL band edge, and is very weak for excitation below 1420 meV. At the same time a series of new peaks of decreasing energy (X_n) emerges on the low energy side of X. These lines gain in relative intensity and successively dominate the spectrum as $E_{\rm exc}$ is reduced. This behavior has been observed for different single dots from the same wafer. PL spectra obtained for $E_{\rm exc}=1380$ and 1514 meV for QD B are shown in Fig. 1(b) to illustrate the similarity of these modifications. The relative intensities of the lines are thus very sensitive to E_{exc} but were found to be independent of $P_{\rm exc}$, excluding contributions from higher-order exciton complexes. Furthermore, the intensity of X_1 was found to vary linearly with $P_{\rm exc}$, indicating that it (and the other X_n lines) arises from a single exciton complex.

In order to obtain more information on the X_n features, PLE experiments were performed. PLE spectra are shown in Fig. 2 for detection on X, X_1, X_2, and X_3 respectively. All spectra show two pronounced features (1LO and 2LO in Fig. 2) ~31 and 62 meV, respectively, above the detection energy. These peaks have a large width of ~3 meV compared with the ultra-narrow linewidths measured in emission, of 50−100 μeV.[11] The energies of 31 and 62 meV correspond closely to typical one and two LO-phonon energies reported in the literature for similar dots.[12,13] However, the PLE intensities for X and X_n detection exhibit very different behavior when $E_{\rm exc}$ is reduced below $\hbar\omega_{\rm WL}$ ~1460 meV. The intensity of X decreases very strongly (but not completely) for $E_{\rm exc}<\hbar\omega_{\rm WL}$ with the intensity for excitation at the phonon-related features more than 2 orders of magnitude smaller than the intensity for $E_{\rm exc}>\hbar\omega_{\rm WL}$. In strong contrast, the phonon features in PLE for X_n detection have approximately the same intensity as for $\hbar\omega_{\rm WL}$ excitation, showing that X and the X_n series couple very differently to LO phonons and that they arise from two distinct types of excitonic species.

LO-phonon features may, in principle, arise in PLE of QD's as a result of several distinct processes. We discuss these in turn, and exclude all but one as the likely origin of

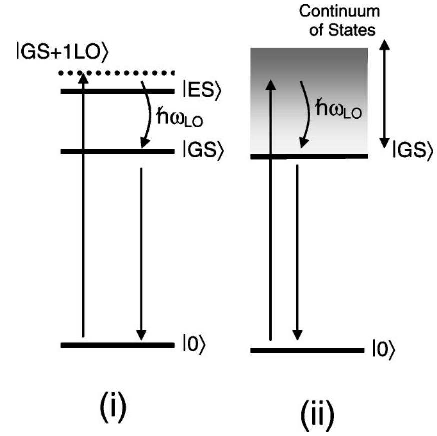

FIG. 3. Possible mechanisms to explain the presence of phonon-related features in PLE. (i) Phonon-assisted absorption. (ii) Absorption into a continuum of electronic states and fast relaxation to the GS.

the 1 and 2 LO features observed. The possible processes are summarized in Fig. 3. (i) Phonon-assisted absorption:[14] a photon is absorbed into the state $|\mathrm{GS}+n\mathrm{LO}\rangle$ ($n=1$ or 2) followed by creation of an exciton in the ground state $|\mathrm{GS}\rangle$ and the simultaneous emission of n LO phonons. (ii) Absorption into a continuum of states as postulated by Toda *et al.*[15] and fast relaxation by LO-phonon emission to the GS. Such a mechanism is similar to that observed in low quality quantum wells where only at energies $n\hbar\omega_{\mathrm{LO}}$ above the detection is relaxation sufficiently fast to lead to PL in the presence of competing nonradiative processes.[16] However, this picture is difficult to reconcile with the fully quantized energy levels in QD's.[17] (iii) Raman scattering: this process is very similar to (i) but is coherent and is expected to lead to polarization memory between the incident and emitted photons. Such polarization memory is not found for excitation at 1LO and 2LO, arguing against a Raman explanation.

We thus conclude that only mechanism (i) provides a convincing explanation for the 1 and 2 LO phonon features in PLE. It is important to note that the PLE LO phonon features lie within a few meV of the *p*-shell excited state transitions observed in Fig. 2(b), and thus the transition probability will be enhanced by resonant coupling with excited state transitions, as depicted in Fig. 3(i) (similar resonant mixing was observed recently in a different context in inter-sub-level spectroscopy of InAs QD's).[18] The large energy range (~ 3 meV) of phonon-assisted absorption around 1 and 2 LO in Fig. 2 follows naturally as a result of the distribution of phonon energies in self-assembled dots, due to the inhomogeneous strains around and within the dot, of $\sim 1-2$ meV.[12,19]

Even though clear LO phonon features are observed in PLE, the intrinsic LO-phonon coupling in the dots under investigation is very weak. This is seen by examination of the PL spectrum in the energy range 20 to 40 meV below the X, X_n lines shown in Fig. 4, for excitation at 1.46 eV in the wetting layer region. In the energy range where LO phonon features would be expected ($\sim$30–36 meV), no LO features are observed within the sensitivity of the experiment of

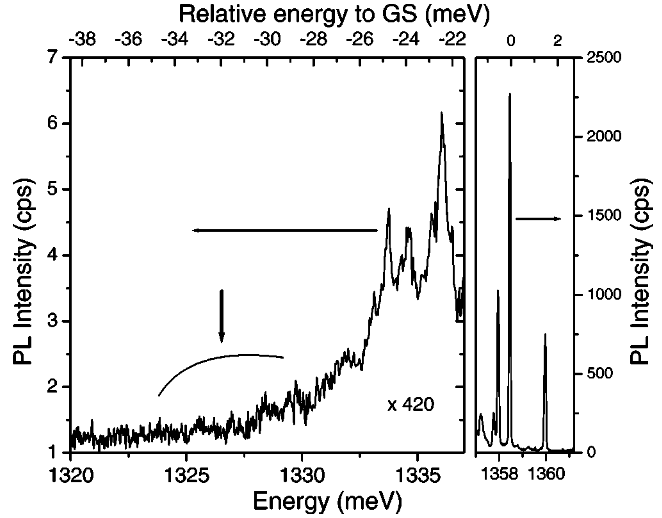

FIG. 4. PL spectrum on the low-energy side of the ground-state emission for QD A. No indication is found of LO-phonon satellite emission, expected in the energy range 30–40 meV below the ground-state emission, to within a factor of 5000 of the intensity of the zero phonon lines. The noise level in the 1320–1330 meV region is 0.0001 of the X signal.

0.0002 of the intensities in the X region.[20] On the other hand in the X PLE spectrum in Fig. 2(a), the $\hbar\omega_{\mathrm{LO}}$ feature is clearly observable, with intensity $\sim$400 times weaker than that of the WL feature. The significant intensity of the 1LO feature in absorption (PLE) but not in emission provides good evidence for the role of resonant enhancement of the phonon-assisted process in absorption by mixing with nearly resonant excited states. Such resonant mixing cannot occur in emission since there are no states below the zero phonon energy.

The LO phonon features in the $X_{1,2,3}$ PLE spectra are much more prominent still with 0.1–1 of the intensity of the $\hbar\omega_{\mathrm{WL}}$ features. In the introduction it was explained that the strength of exciton-LO phonon coupling is determined by the dipole moment of the one exciton state of the system. As discussed elsewhere in the context of phonon coupling[5,7,6] and in studies of the Stark effect,[9] shape asymmetries, compositional nonuniformities and piezoelectric fields all act to reduce the *e*,*h* overlap and hence enhance the dipole moment. In order to explain the enhanced phonon coupling of the X_n lines relative to X (which will experience the shape, compositional, and piezoelectric field effects) we propose that the X_n lines arise from exciton recombination perturbed by charged defects in/around the dot, which lead to polarization of the *e*, *h* charge distributions, to an enhanced dipole, and hence to enhanced LO phonon coupling. The presence of charged defects also explains the (Stark) shifts of the X_n lines to lower energy below X. For example, a single point charge 200 Å from the dot, an electric field at the dot of 2.5 kV/cm is expected, and will lead to energy shifts in the range 0.2–1 meV below X, consistent with the experimental observations. We suggest that the presence of several distinct X_n lines arises from time varying occupation of different defects, each individual defect when occupied giving rise to an individual X_n line. Such defects are likely to be neutralized at the much higher exciton densities in the surrounding matrix for above gap excitation, but for below gap excitation where carrier creation in the GaAs is very weak, charge fluctuations in the occupancies of the defects are likely to be important.[21] Such a multiplicity of X lines has not been reported before in single InAs QD studies (see, e.g., Refs. 15 and 14), although in many cases significantly lower spectral resolution was employed than here. We speculate that the formation of the perturbing defects may result from the annealing process commonly employed to upshift the spectral energies to $\sim$1.3 eV into the range of sensitive detectors. This conclusion is supported by recent results we have obtained from InGaAs dots which emit in the 1.3 eV region without the need for the annealing step required for the InAs dots. These samples were processed into mesas for micro-PL studies using the same etching techniques as for the InAs dots, but did not exhibit any perturbed X_n excitonic recombination.

In conclusion, exciton-LO phonon coupling in InAs/GaAs quantum dots has been probed using single dot spectroscopy. Its strength is found to be intrinsically weak as measured in emission. However, in absorption, resonant mixing with excited states leads to enhancement of phonon-assisted processes. Further enhancement is observed for excitonic recombination perturbed by charged defects, which give rise to several new lines at energies below the main exciton line which dominates the spectrum for above gap excitation.

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[1] J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).
[2] K. J. Nash, M. S. Skolnick, P. A. Claxton, and J. S. Roberts, Phys. Rev. B **39**, 5558 (1989).
[3] S. Schmitt-Rink, D. A. B. Miller, and D. S. Chemla, Phys. Rev. B **35**, 8113 (1987).
[4] S. Nomura and T. Kobayashi, Phys. Rev. B **45**, 1305 (1992).
[5] R. Heitz *et al.*, Phys. Rev. Lett. **83**, 4654 (1999).
[6] M. Bissiri *et al.*, Phys. Rev. B **62**, 4642 (2000).
[7] A. García-Cristóbal *et al.*, Phys. Status Solidi B **215**, 331 (1999).
[8] V. M. Fomin *et al.*, Phys. Rev. B **57**, 2415 (1998).
[9] P. W. Fry *et al.*, Phys. Rev. Lett. **84**, 733 (2000).
[10] J. J. Finley *et al.*, Phys. Rev. B **63**, 073307 (2001).
[11] In addition to the broad 1LO and 2LO features, sharp lines in PLE are also seen in Fig. 2(a) due to pure excitonic absorption transitions.
[12] R. Heitz *et al.*, Phys. Rev. B **56**, 10 435 (1997).
[13] M. J. Steer *et al.*, Phys. Rev. B **53**, 17 738 (1996).
[14] F. Findeis, A. Zrenner, G. Böhm, and G. Abstreiter, Phys. Rev. B **61**, R10 579 (2000).
[15] Y. Toda, O. Moriwaki, M. Nishioka, and Y. Arakawa, Phys. Rev. Lett. **82**, 4114 (1999).
[16] A. Chomette *et al.*, Semicond. Sci. Technol. **3**, 351 (1988).
[17] Even in the absence of a continuum, the selection of specific spectral energies by phonons can occur for large ensembles. In this case the phonon picks out those dots where the excited-ground state splitting is close to $n\hbar\omega_{LO}$, as discussed in Refs. 12 and 13. In single dot spectroscopy such processes cannot occur.
[18] S. Hameau *et al.*, Phys. Rev. Lett. **83**, 4152 (1999).
[19] J.-M. Gérard, in *Confined Electrons and Photons, New Physics and Applications*, edited by E. Burstein and C. Weisbuch (Plenum, New York, 1995), p. 357.
[20] The spectral features $\sim$20 meV below the X lines may arise from shake-up processes involving excitation of an additional carrier(s) to an excited state. The energy of $\sim$20 meV corresponds reasonably well to the energy between the ground state X lines and the excited state transitions at $\sim$1380 meV in Fig. 2(b).
[21] H. D. Robinson and B. B. Goldberg, Phys. Rev. B **61**, R5086 (2000).