Exciton relaxation dynamics in quantum dots with strong confinement

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We report on the investigation of exciton relaxation, as traced by time-resolved photoluminescence, in nanoscale InP islands embedded in an $In_{0.48}Ga_{0.52}P$ matrix. Excitons are generated in excited, high-energy states. Depending on excitation energy, up to three LO-phonon replicas into lower-energy exciton states are observed. The rise of all phonon replicas, which we attribute to the LO-phonon emission time, is faster than 10 ps, our time resolution. Their $1/e$ decay times, which we attribute to acoustical-phonon scattering times, vary between 20 and 50 ps with decreasing energy of the excited exciton states. The exciton ground state is populated by acoustical phonon emission in several tens of picoseconds. [S0163-1829(96)50448-0]

Excitons in semiconductor quantum dots (QD's) with dimensions of the order of the exciton Bohr radius exhibit discrete, δ-like density of states due to the three-dimensional (3D) confinement. Various measurements on different systems have provided evidence for this discretization of energy in QD's. As examples, we refer to photoluminescence (PL) experiments with high spatial resolution[1–4] or on single dots.[5,6] Discrete density of states should lead to better device performances, e.g., lower threshold, higher gain, and a lower temperature dependence of the threshold current in QD lasers,[7] but also to problems, e.g., strongly hindered relaxation into the ground state, the laser level.[8] Presently relaxation in QD's is, not only for these, but also for the understanding of fundamental electronic properties of low dimensional systems, a very active research field. Different experiments either supported the theoretically claimed slow relaxation[3] or were interpreted as proof for a much faster relaxation.[9,10]

We report here, to our knowledge for the first time, on time-resolved PL experiments at low excitation density (in average less than one exciton per dot) in QD's with strong confinement.

The QD's consist of InP grown by the Stranski-Krastanov process between two 200 nm thick $In_xGa_{1-x}P$ layers lattice-matched to the GaAs substrate. The details of the samples are described in Ref. 11. We have chosen specifically the sample with a nominal deposition of 7.5 ML for our experiments since photoreflectance experiments have shown that it exhibits at least two confined electronic levels, e_1 and e_2, in the QD.[12] We excited either into states of excitons associated with the $e1$ level, i.e., with photon energies between the e_1hh_1 and e_2hh_2 $1s$-exciton states using a mode-locked Ti-:sapphire laser (80 MHz, pulsewidth 2 ps) or into excited exciton states close to the e_2hh_2 $1s$-exciton level using a Pyridine 1 dye-laser (80 MHz, pulsewidth 5 ps). The denotation hh_1 stands for the heavy-hole ground-state level. The sample is mounted on the cold finger of a cryostat and kept at about 10 K. The PL is dispersed by a 0.32 m spectrometer and temporally resolved by a streak camera with 2D read-out system. Spectral and temporal resolution are typically 0.6 nm and 10 ps, respectively, for the Ti:sapphire and the dye laser.

Depending on excitation energy, one, two, or three LO-phonon replicas with respect to the laser photon energy are observed. A typical spectrum, 4 ± 5 ps after excitation, with two phonon replicas labeled $P1$ and $P2$ is shown in Fig. 1(a). The assignment of $P1$ and $P2$ as phonon replicas is clearly proved by the fact that these lines move in parallel to the laser photon energy at distances of 44 ± 2 meV and 92 ± 2 meV (see Fig. 2). A third phonon line $P3$ appears at higher excitation energies at a distance of 138 ± 2 meV. The average LO-phonon energy of 46 meV lies between the InP (43.3 meV) (Ref. 13) and $In_{0.48}Ga_{0.52}P$ (47.1 meV) (Ref. 14) LO-phonon energies. The spectra, as shown in Fig. 1(a), are deconvoluted by the following procedure in order to receive

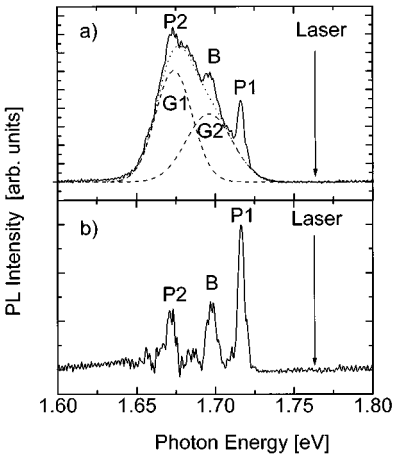

FIG. 1. Part (a) shows the photoluminescence (PL) intensity (solid line) 4 ± 5 ps after the laser maximum (laser photon energy $=1.763$ eV). The ground-state PL can be fitted (dotted line) by the sum of two Gaussian lines, $G1$ and $G2$ (dashed lines), which still show up at long delay times. Part (b) shows the PL after subtracting the ground-state PL [dotted line in part (a)]. $P1$ and $P2$ denote the one- and two-LO-phonon replicas, line B is explained in the text.

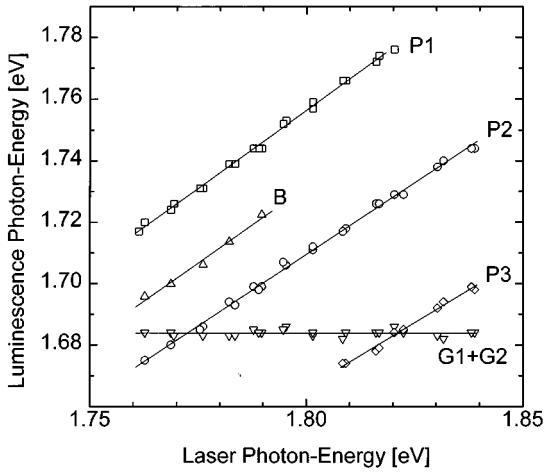

FIG. 2. Luminescence peak energies are shown as a function of the laser photon energy for the 1- (□), 2- (○), and 3-LO-phonon replica (◇), the ground-state luminescence (∇), and line B (△).

the luminescence transients of the various transitions: We subtract the luminescence due to the decay of ground-state excitons as it still shows up at long delay times. This asymmetric spectrum is well fitted by the sum (dotted line) of two Gaussian lines (dashed lines) $G1$ and $G2$ at 1.675 eV and 1.692 eV, which are caused by two types of dots with different sizes [see Fig. 1(a), details are discussed below]. After deconvolution, we obtain spectra as shown in Fig. 1(b). Then the integrals of the remaining phonon replicas $P1$ to $P3$ are plotted as a function of time to reveal the relaxation dynamics. The results are shown in Fig. 3(a), which depicts the transients of a one (□), two (△), or three (○) phonon replica for a nearly constant luminescence photon energy. The emission of a further LO phonon is not possible due to energy conservation. The excitation photon energy is, respectively, one, two, or three phonon energies higher. Clearly, the onset and the decay of the luminescence lines is almost identical in all three cases. The rise time is with 10 ps limited by our time resolution. No distinct differences were observed for excitation above or below the first excited electronic state, the $e_2\mathrm{hh}_2$ state. The decay is in the range of 40–60 ps, which is comparable to the acoustical phonon emission time in bulk materials. However, in low dimensional systems, much longer acoustical phonon emission times have been predicted.[15] Theoretically phonon scattering times <100 ps are possible if a defect level is present in the vicinity of the dot.[16] Energy conservation considerations suggest that acoustical phonon emission is the relaxation mechanism. Figure 3(b) shows the transients of the one and two phonon replicas for one specific excitation energy, which was chosen such that the decay of the second LO-phonon replica via emission of a third LO phonon is not possible. Clearly, the decay time increases from 17 ps to 58 ps with decreasing luminescence photon energy from 1.746 eV (∇) to 1.699 eV (△), respectively. The onset is once more in both cases faster than our time resolution. We plot in Fig. 3(b) the transients of the ground-state luminescence lines $G1$ and $G2$ at the same excitation energy. With the chosen excitation energy, the $G1$-dot ground states are only populated via acoustical-phonon emission, while the $G2$-dot ground states are populated via LO- and acoustical-phonon emission. Rise

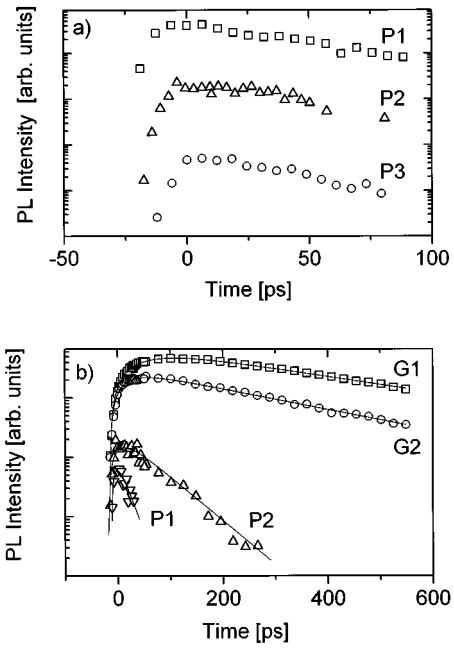

FIG. 3. Part (a) depicts the temporal variation of the photoluminescence (PL) intensity for the 1- (□), 2- (△), and 3-LO-phonon (○) replicas at a PL energy of 1.699 eV. The laser photon energies are, respectively, 1, 2, and 3 LO-phonon energies higher than the PL energy. Part (b) shows the temporal dynamics of the PL intensity for a constant laser photon energy of 1.790 eV for the 1- (∇) and 2-LO-phonon (△) replicas, as well as for the ground-state PL for the $G1$ (□) and for the $G2$ dots (○).

times of 59 ps and 30 ps and decay times of 321 ps and 247 ps are observed, respectively.

We now develop a relaxation scenario which is able to explain the experimental findings: The dots probably exhibit irregular shapes and size distributions leading to an inhomogeneous distribution of ground and excited exciton states. Various transitions become optically allowed, the selection rule $\Delta(n-m)=0$ for an $e_n\mathrm{hh}_m$ transition is no longer strictly valid, and radiative decay of excited exciton states $e_1\mathrm{hh}_m$ is observed. Additionally, other excited exciton states with angular momentum of $J=1,2\ldots$ are possible.[5] In some dots the energetic distances between different excited states or between an excited and a ground state are equal to one or multiples of the LO-phonon energy. Therefore, LO-phonon emission is possible in these specific cases, whereas acoustical phonons are required for relaxation in all other cases. Specific excited states, which are preferentially populated by optical-phonon emission, show up as luminescence, as LO-phonon replicas. The emission of acoustical phonons is not detectable as phonon replicas, because the acoustical phonon energy can vary widely in contrast to the LO-phonon energy. However, the decay of a LO-phonon replica, from which only the emission of an acoustical phonon is possible, will show the temporal behavior of the acoustical-phonon emission process. The luminescence transients at a certain photon energy then reveal an average of processes, where the averaging occurs over different excited states in different dots but with the same exciton energy.

We come to the following interpretation.

(i) The fast rise and decay times of the LO-phonon repli-

cas clearly prove the ''hot-exciton-luminescence'' picture as suggested in Ref. 17, where the electron and the hole are in a correlated state and do not relax separately.[18] This attribution is supported by the polarization properties: The emission is unpolarized, clearly contradicting an interpretation as resonant Raman scattering. The LO phonons are emitted instantaneously (within our time resolution) if their energy (or the sum of their energies) fits into the energy difference between two exciton states in specific QD's. Once an excited exciton state is reached from which no further LO-phonon emission is possible, the relaxation continues via emission of acoustical phonons, making the relaxation process slow of the order of several tens of picoseconds (Fig. 3).

(ii) Acoustical-phonon emission is faster for the higher energy states since more final states are then present.

(iii) The ground state is filled up in 59 ps, a similar time constant as the decay of the phonon replica at lower energy. We attribute this time constant also to the emission process of an acoustical phonon.

(iv) The decay times of $G1$ and $G2$ correspond to the intrinsic lifetime of the excitonic ground state.[19]

Phonon replicas with respect to the exciting laser photon energy were recently reported[1,20] and interpreted as hot-exciton luminescence.[17] In contrast, time-resolved PL experiments on single QD's were also recently published,[21] revealing Coulomb scattering as an important relaxation mechanism, and no influence of phonon scattering was observed. One reason for these different results is certainly that the investigastions were performed with different systems under different experimental conditions. For instance, the experiments in Ref. 21 were conducted at high exciton densities (i.e., with more than one exciton per dot) and in a system with closely spaced energy levels due to a comparatively weak confinement, whereas the experiments in Ref. 17 were made at lower densities in a QD system with stronger confinement.

A very fast transient with rise and decay times faster than our time resolution is observed additionally to the phonon replicas at a distance of 68 meV to the excitation energy and a spectral width of 8 meV (see line B in Fig. 1 and in Fig. 2). The origin of this line is not clear. Its energetical distance to the excitation energy is close to the energy difference of 75 meV between the $e_1\mathrm{hh}_1$ ground-state exciton and the $e_2\mathrm{hh}_2$ $1s$ exciton.[12] The very fast transient indicates that it could be related to the decay of the two-exciton state into one exciton and a photon.[22]

Finally, we discuss the origin of the two Gaussian distributions contributing to the exciton ground-state luminescence. A splitting into two groups of dot sizes was seen in atomic force microscope images of nonovergrown InP islands after deposition of 3 ML of InP.[23] Corresponding cw PL measurements also showed a splitting into two distinct peaks. The different groups of quantum dot sizes can be a result of the different times during growth at which dot formation starts and of the dynamics of the growth process. A dot that starts to grow at an earlier time depletes the InP in the surrounding area. As a consequence, the neighboring dot formation starts later and smaller dots grow there. The formation of two distinct dot types results.[23] Images of 7.5 ML samples were not able to resolve the dot sizes due to the close packing of the dots. Nevertheless, the two distributions in the case of the 7.5 monolayer sample could be the origin for the two Gaussian lines. This assignment is supported by the intensity ratio $G1/G2=0.4$, which corresponds to the density distribution of the QD's with two different sizes in the 3 ML samples.

In conclusion, we have shown that excitonic relaxation in QD's is fast (faster than 10 ps) if LO phonons are emitted. Relaxation is slower, however (several tens of ps), if only acoustical phonons can be emitted. Clearly our experiment and its interpretation suffer from two deficiencies. First, we are not able to probe the relaxation in isolated, single QD's. Second, we do not know the shape of the dots. The latter, however, is necessary in order to calculate the ground and excited exciton states, the phonon scattering times between them, and their relative radiative oscillator strengths. Nevertheless, our experiments show that, as predicted, at low exciton densities with one exciton per dot, relaxation between excitonic states is only fast if the transition can occur with emission of one or multiple LO phonons. A phonon bottleneck actually slows down relaxation if only emission of acoustical phonons is possible.

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