Rapid carrier relaxation by phonon emission in $In_{0.6}Ga_{0.4}As/GaAs$ quantum dots

S. Marcinkevičius and A. Gaarder
Department of Physics-Optics, Royal Institute of Technology, 10044 Stockholm, Sweden

R. Leon
Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109
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Carrier transfer into quantum dots has been investigated by time-resolved photoluminescence spectroscopy in a set of $In_{0.6}Ga_{0.4}As/GaAs$ quantum dot structures with gradually changing interband transition and intraband level energies. Quantum dot energy levels were tuned by thermal compositional disordering of the interface. Time-resolved photoluminescence for low photoexcited carrier densities show efficient electron relaxation by LO phonon emission for samples in which the electron energy level separation is close to the LO phonon energy. Slower carrier transfer in samples with abrupt quantum dot/barrier interfaces is also found, the latter is attributed to strain-induced or compositional potential barriers at the quantum dot interface.

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Effects of carrier transfer in semiconductor quantum dot (QD) structures are being studied with increasing effort due to their importance in QD-based device operation. Contrary to bulk semiconductors or quantum well structures, carrier relaxation by optical phonon emission in QDs is often considered an unlikely process. The discrete nature of energy levels and weak dispersion of LO phonons[1,2] limits phonon-assisted relaxation to the case when energy spacings between QD levels are within a few meV of the LO phonon energy. Recent calculations performed by Li *et al.*[3] showed that the strict selection rules for carrier relaxation by LO phonon emission are relaxed due to anharmonic decay of LO phonons into bulk acoustic phonons. Therefore, efficient relaxation of carriers by phonon scattering could occur with a rather large detuning of the interlevel distance from the energy of an LO phonon.[3]

Difficulties growing QD ensembles with varying but well defined electronic structure has thus far prevented thorough experimental verification of the efficiency of interlevel carrier relaxation by optical phonon emission and its dependence on the interlevel energy separation. Efficient carrier relaxation by LO phonon emission has been reported for InAs/GaAs quantum dots by means of photoluminescence (PL) excitation spectroscopy and attributed to relaxed selection rules due to variation of shape and size of the QDs.[4] Efficient carrier relaxation has also been observed for single InGaAs/GaAs QDs, which was explained by fast carrier relaxation through the band tail states of the wetting layer (WL) and subsequent emission of localized phonons.[5] It should be noted that in the mentioned works, the QD state separation was not resonant with the LO phonon energies, and interpretation of the experimental results required additional features of the QDs such as inhomogeneous broadening, nonradiative recombination or band tail states.

Here we perform a direct experimental test of the efficiency of carrier relaxation by LO phonon emission by studying time-resolved photoluminescence in a set of InGaAs QD samples in which the interlevel energy separations are tuned in the vicinity of GaAs and InAs LO phonon energies. By studying samples with well-resolved level structure and small inhomogeneous broadening we find direct evidence for faster carrier relaxation when the interlevel distances satisfy resonant conditions. For higher photoexcited carrier densities, we observe that another efficient carrier relaxation mechanism, namely, carrier-carrier scattering, takes a dominant role in the relaxation process.

The QD samples were grown by metalorganic chemical vapor deposition on semi-insulating GaAs (100) substrates. The nominal quantum dot ternary composition was $In_{0.6}Ga_{0.4}As$. The quantum dots were capped with 100 nm of GaAs. Details of the growth procedure can be found elsewhere.[6] The structures contained QDs of (25 ± 5) nm average diameter at a low concentration of $4\times10^8\,cm^{-2}$. The islands were lens-shaped, with height/diameter ratio $\sim$1:6. The several ns-long carrier lifetimes in the QDs (Ref. 7) indicate excellent crystalline quality of the samples. Changes in confining potential and interlevel energy separation were obtained by post-growth rapid thermal annealing in a N_2 ambient for 30 s at temperatures between 700 and 900 °C. It should be noted that intermixing effects are minimal at 700 °C annealing, therefore, the optical properties of the 700 °C sample are nearly the same as of the as-grown structures.

Low temperature (80 K) time-resolved photoluminescence measurements with 3 ps temporal resolution were performed using a self mode-locking Ti:saphire laser (central wavelength 780 nm, pulse duration 80 fs, repetition frequency 95 MHz) for excitation and a synchroscan streak camera with an infrared enhanced photocathode, combined with a 0.25 m spectrometer for detection. The average excitation intensity was varied from 0.3μ W to 1 mW with neutral density filters, which corresponds to approximately 6×10^8 to 2×10^{12} electron hole pairs per square centimeter per pulse.

Rapid thermal annealing at high temperatures causes interfacial compositional disordering (intermixing) in QDs, which in turn changes interband transition energies and intersublevel spacings in the conduction and valence bands.[8] Figure 1 shows PL spectra measured at 40 ps delay after an excitation pulse for several samples at medium excitation

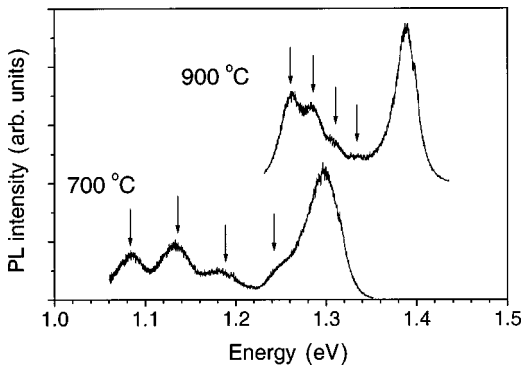

FIG. 1. Photoluminescence spectra measured shortly (40 ps) after excitation for the QD samples annealed at 700 and 900 °C. The arrows mark peaks related to transitions in the QDs.

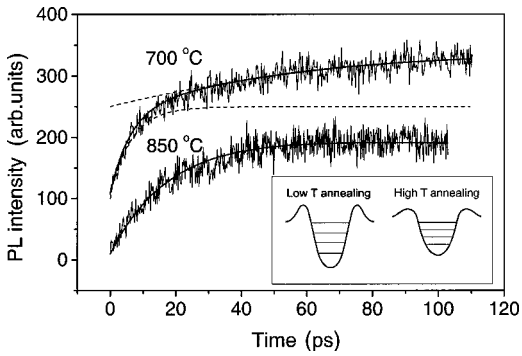

FIG. 2. Photoluminescence transients and fits for the ground state transitions for the QD samples annealed at 700 and 850 °C. Two components of the fit for the 700 °C sample are shown as broken curves. The inset shows schematic of potential profiles of the conduction band for the QDs intermixed at low and high temperatures.

intensity. The high-energy peak is due to the photoluminescence from the wetting layer, which is effectively a thin (4–5 monolayers) quantum well. The four-peak structure at lower energy originates from the QDs. These well-resolved peaks are determined by transitions between different levels in the conduction and valence bands of the QDs (Ref. 9) and indicate a small spread in QD potentials. As can be seen from the spectra, the PL peaks shift to higher energies with increasing annealing temperature, the energy separation between QD-related peaks decrease, and the inhomogeneous broadening diminishes. The same features were observed in steady-state PL spectra and were attributed to changes in QD potential profile and alloy composition by anneal-induced intermixing.[8] With increasing annealing temperature, the QD peak separation changes from 50 to 25 meV (Table I) and their inhomogeneous broadening decreases from 35 to 19 meV.[8] The intermixing-induced change in interlevel energies allows tuning them around the LO phonon energies thus allowing determination of the efficiency of LO phonon-assisted relaxation in quantum dots.

Changes in confinement potential and smoothing of the WL are the main modifications that the rapid thermal annealing inflicts on the structure of the QD samples. The integral QD and WL PL intensity is the same in the as-grown and annealed samples,[8] likewise the carrier lifetimes in the WL (~800 ps) and the QDs (2–5 ns), which indicates that the concentration of nonradiative recombination centers and defects is not much affected by annealing.

After short pulse photoexcitation, carriers are primarily generated in the GaAs barrier due to its much larger thickness compared to that of the wetting layer and the dots. These carriers rapidly transfer into the WL and the QDs, hence PL from the GaAs barrier is observed only at high excitation intensities, which correspond to a partial filling of the QD and WL states. The PL dynamics from the QDs consist of a fast rise, determined by the carrier transfer into the dots, and a slow decay due to recombination. In the present work we concentrate on the PL rise times, which reflect carrier transfer from the barrier into the dots (directly or via the WL). These include transport in the barrier, and capture with subsequent relaxation in the QDs.

Figure 2 shows temporal transients for the QD ground state emission for several samples. These were measured at low excitation intensity, corresponding to only a few electron-hole pairs per dot. The carrier transfer in the 700 °C sample is faster, in addition, the PL transient for this sample exhibits a double-exponential rise in contrast with the samples annealed at higher temperatures. Figure 2 shows that the PL transient fits give both a shorter rise time (10–20 ps) component and a longer time constant (50–100 ps). The weight of the longer component continuously decreases with increasing annealing temperature. Transients measured for the samples annealed at 850 °C and higher can be successfully fitted by a single exponential. The vanishing long rise time component correlates with decreasing decay time for the WL PL: from 110 ps down to 24 ps for the samples annealed at 700 and 900 °C, respectively.

The shorter component of the PL rise transient indicates rapid transfer into the dots for the majority of carriers, the longer transient points to a sample-dependent hindrance,

TABLE I. Transition energies, interlevel spacings and low excitation intensity PL rise times for the QD samples annealed at different temperatures.

Annealing temperature °C	700	800	825	850	875	900
Transition energy of the ground transition at 80 K, eV	1.082	1.130	1.172	1.201	1.245	1.264
Average QD PL peak spacing, meV	51	45	38	34	27	26
Average electron level spacing, meV	34	30	26	23	18	17
PL rise time, ps	10.4	9.0	17.6	18.4	21.6	22.3

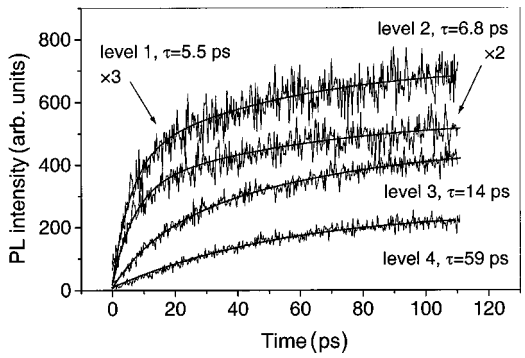

FIG. 3. PL transients for ground and excited state transitions at a medium photoexcited carrier density of 1.5 W cm^{-2} for the QD sample annealed at 700 °C.

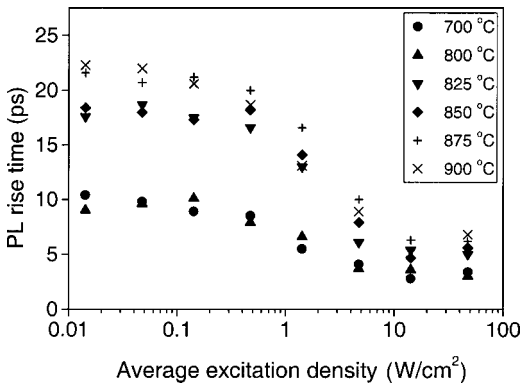

FIG. 4. PL rise times as a function of average photoexcitation density for QD samples annealed at different temperatures.

which slows down transfer for part of the carriers. For interpretation of these longer rise time components, several effects should be considered. First, it should be noted that these longer components are too long to be limited by transport of carriers generated deeper in the barriers. It has been suggested that carrier transport in the barriers proceeds by drift due to a long-range attractive potential caused by the strain field surrounding the quantum dots[4] and therefore occurs in just a few picoseconds. Even with a conservative approach of carrier transport by ambipolar diffusion, the diffusion time over a distance of 0.5 μm (the penetration depth for the exciting photons) in undoped GaAs at 80 K is about 20 ps. Thus, there has to be an additional capture barrier for the carriers to enter the dots. Such an obstacle might be strain-induced potential barriers at the barrier/QD interfaces (inset to Fig. 2), previously suggested to affect carrier capture in low density QD samples.[10,11] Due to large lattice mismatch between InGaAs and GaAs, the GaAs barrier is compressed in the direction perpendicular to the dot interface and expanded in directions parallel to the interface. Such a nonuniform strain modifies the band structure of the barrier and produces potential barriers at the interfaces.[12–14] These potential barriers are more efficient at blocking carrier transfer at low carrier densities because with increased photoexcitation intensity the mean carrier energy increases making the barriers easier to overcome. The potential barriers decrease with increased intermixing because the interfaces become more diffuse (inset to Fig. 2). This explains the diminishing weight of the long rise time component with increased anneal temperature. The majority of carriers, however, are captured into the dots while still hot (after 10 ps after the excitation the carrier temperature is ~100 K above the lattice temperature[15]) and are therefore little affected by these potential barriers, which explains their contribution to the short component of the QD PL rise time.

The QD levels become consecutively filled with increasing excitation intensity. For partially filled QDs, the PL rise times increase with the level number and can be considerably longer than that of the ground state. These differences are shown in Fig. 3. At low to intermediate excitation, longer PL rise times for transitions from the excited levels indicate that carrier scattering out of these levels is faster than the rate of carrier supply from the barriers or the wetting layer.[16] For increasingly higher excitation intensities, the PL rise times for the higher-level transitions continuously decrease until they become similar to the ground state PL rise time.

The ground state PL rise times for all the samples measured at different excitation intensities are summarized in Fig. 4. Only the shorter rise time components are shown for the samples with the double-exponential PL rise times. For the lowest intensities, the rise times are intensity independent and decrease in the medium and high intensity range. As can be seen from the figure, the low intensity PL rise times for the samples annealed at 700 and 800 °C are about half the values for the other samples.

Let us discuss the possible reasons for these different rise times. First, as the structure of all the samples is the same, the difference should not be due to transport in the barriers. This is confirmed by similar WL PL rise times, which account for transport in the barriers and capture into the WL and are about 7–8 ps for all the samples. Secondly, the time of eventual transport in the WL before the capture into the dots should be at least not longer in the samples annealed at high temperatures, because, as can be judged from the narrower WL PL lines[8] and shorter WL PL decay times, the width fluctuations and related scattering are reduced by the annealing process. Therefore, the differences in the PL rise times should be ascribed to the carrier capture and/or relaxation.

In the literature there is still a confusion as to whether the capture or the relaxation is a faster process. Theoretical calculations indicate that cold carrier capture strongly depends on dot sizes and is slower than the relaxation.[17] On the other hand, phonon resonances observed in the PL excitation spectra of QDs showed that carrier capture is much faster than the subsequent relaxation.[4] For the present work the important issue is which of these effects determines the difference in the PL rise times for different samples. Recent calculations have shown that the rate of phonon-assisted carrier capture is larger if the energy difference between the states in the WL and the QD is in resonance with the LO phonon energy.[17] However, estimations of the energy level structure in our quantum dots (based on the PL spectra and the band offsets for InGaAs,[18] see also discussion below) indicate that the energy levels for the samples showing the shortest PL rise times are *not in resonance* with the WL. In addition,

high carrier temperature would diminish possible differences in the capture rate. Intensity independent PL rise times for low carrier densities indicate that Auger assisted capture, which, according to the calculations of Ref. 19, is dot size dependent, is of minor importance for these photoexcited carrier densities. Therefore, we do not expect carrier capture to be very different in different samples, and the differences in the PL rise times should be attributed mainly to the relaxation process.

The main carrier relaxation channels in QDs are carrier-carrier and carrier-phonon scattering. For the same (low) photoexcitation intensity, the rate of carrier-carrier scattering should be the same for our samples because they have the same dot density. The carrier-LO phonon scattering, on the other hand, strongly depends on the level structure of the QDs. Experimentally, interlevel energy spacings for *both* conduction and valence bands in lens-shaped QDs have been studied in several recent works. Schmidt *et al.*[20] measured these energies in InAs dots using capacitance (C-V) and photoluminescence spectroscopy and found that the electron level spacing ΔE_c for their QDs was 50 meV, and the ratio between electron and hole interlevel energies $\Delta E_c/\Delta E_v$ was equal to 2. Similar results, $\Delta E_c = 49\,\mathrm{meV}$ and $\Delta E_v = 25\,\mathrm{meV}$, were obtained for InAs QDs from transmission measurements in the far and near infrared spectral regions.[21] Recently, energy level spacings in lens-shaped $In_{0.5}Ga_{0.5}As$ QDs have been studied by PL and C-V spectroscopy.[22] Again, the ratio $\Delta E_c/\Delta E_v = 2$ was found. These consistent results give us confidence to assume that the same value for the interlevel spacing ratio (electron:hole 2:1) holds for the QDs structures used in our experiments. The electron interlevel energies in the samples annealed at 700 and 800 °C are then in the range of available phonon energies (30 ± 3 and 36 ± 3 meV) for the InAs-like and GaAs-like phonon energies, respectively.[23] Table I shows the PL rise times with their corresponding interlevel energies in the conduction band. It can be seen that the PL rise times are clearly shorter when the interlevel energy in the conduction band is close to the energy of the LO phonon. This can be considered direct evidence for efficient carrier relaxation by LO phonon emission in QDs. We should also like to note that our data favors free carrier rather than exciton relaxation,[4] otherwise we would observe a decreased relaxation time for the samples annealed at 825 and 850 °C, for which the exciton interlevel energy matches that of the LO phonon.

According to calculations of electron relaxation by LO phonon emission,[3] the carrier relaxation time from the first excited state to the ground state increases with detuning from the LO phonon energy (solid plot in Fig. 5). Direct comparisons of our PL rise times with these values are complicated by inhomogeneous broadening from the QD structures, and by the fact that the PL experiments with above barrier excitation do not allow distinguishing carrier capture from relaxation. Nevertheless, assuming that the carrier transport and capture account for the major part of the shortest QD PL rise

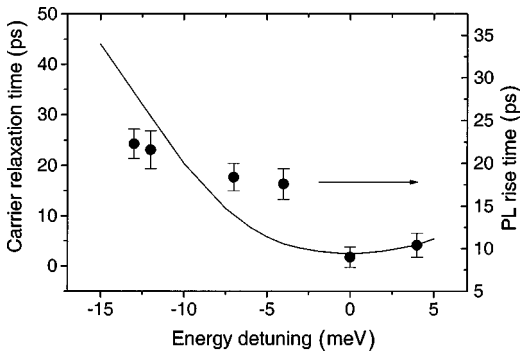

FIG. 5. Electron relaxation time from the first excited state to the ground state at 300 K as a function of detuning of interlevel spacing from the LO phonon energy after Ref. 3 (full line). Dots represent ground state PL rise times for our intermixed samples at low excitation intensity. In the latter case zero detuning is assumed for 30 meV interlevel energy separation.

time observed for the 700 and 800 °C samples (please recall the 7–8 ps WL PL rise time), our data is in qualitative agreement with calculations (see Fig. 5). For large detuning energies, reduced PL rise times with respect to calculations may be partially attributed to inhomogeneous broadening. Some of the dots would have energy spacings resonant with the phonon energies even for large detuning, and this would increase the response rate from the whole ensemble.

With increased photoexcited carrier density, the PL, rise times decrease and attain comparable values for all samples (see Fig. 4). Similar excitation intensity dependencies have been observed earlier[24–26] and attributed to an increased rate of carrier relaxation by Auger-type process,[17,27] in which a carrier in an excited level of a dot relaxes to a lower level by giving the excess energy to a carrier in the wetting layer. High relaxation efficiency by carrier-carrier scattering at high carrier densities shadows the importance of LO phonon-assisted process in this (high) photoexcitation density range.

In summary, we have investigated a series of InGaAs/GaAs quantum dots in which transition energies and level structure were tuned by means of thermal annealing. For low photoexcited carrier densities, increased rate of carrier relaxation has been observed for quantum dots with conduction band interlevel energy separation close to the LO phonon energy. We consider this observation a direct confirmation of efficient carrier relaxation in quantum dots by optical phonon emission. Effects of strain-induced potential barriers at dot/barrier interfaces on carrier transfer times has also been observed in samples with small intermixing and abrupt quantum dot/barrier boundaries.

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