Phonons and radiative recombination in self-assembled quantum dots

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The radiative recombination of photocarriers has been studied in various self-assembled $In_xGa_{1-x}As/GaAs$ and $Al_xIn_{1-x}As/Al_yGa_{1-y}As$ quantum dot samples, prepared with the spontaneous island formation during molecular-beam epitaxy. Depending on the relative values of the interlevel spacings and the phonon energies, some structures display strong enhancement of the photoluminescence for excitation energies permitting resonant phonon relaxations, or strong level filling and emission from the excited states with saturation of the ground states at higher excitation intensities.

Semiconductor quantum dot (QD) structures obtained with spontaneous island formation feature strong zero-dimensional confinement (0D) of the carriers in high-quality, defect-free material.[1–10] These self-assembled QD's are formed directly by Stranski-Krastanow growth with molecular-beam epitaxy (MBE) of highly strained $In_xGa_{1-x}As/GaAs$ or $Al_xIn_{1-x}As/Al_yGa_{1-y}As$, giving QD's typically $\sim$20 nm in diameter with uniformity better than $\pm$10%, and emission in the near infrared or visible red, respectively. Although these QD's approach the ideal model of a 0D system in several aspects (high confining potential with small confining volume and high material quality), the photoluminescence (PL) spectra of most of the structures investigated do not display significant radiative emission from the excited states, or other aspects of the restricted phonon-carrier scattering rates predicted for low-dimensional systems.[11–13] The mechanism(s) leading to the efficient relaxation of the carriers to the ground states in these experimental systems might be connected to the presence of the underlying quantum well coupled to the QD's (the so-called wetting layer), the complicated strain distribution in the vicinity of the QD's, or to more fundamental mechanisms such as multiphonon relaxations or Auger-like processes.[14] In this paper, we present results of PL excited with nearly resonant energies which demonstrate how some of the self-assembled QD structures display strong enhancement in the ground-state radiative recombination for excitation energies permitting resonant phonon relaxations. Finally, we show that in the case of smaller interlevel spacings (QD diameter $\sim$36.5 nm), the PL results obtained with different excitation intensities display strong level filling resulting in emission from the excited states and saturation of the ground states with increasing excitation intensities.

The dot layer is pseudomorphically grown by MBE on a (100) GaAs substrate, and the QD's are formed by the coherent (i.e., dislocation-free) relaxation into islands of a few monolayers of low band-gap material (here $In_xGa_{1-x}As$ or $Al_xIn_{1-x}As$) between the larger band-gap semiconductor (here GaAs or $Al_xGa_{1-x}As$, respectively) for the buffer and cap layers. Transmission electron microscopy (TEM) and/or atomic force microscopy have been used to investigate the details of the islands' morphology,[1–10,15,16] and to obtain information on the QD diameter, thickness, and density, as well as the wetting layer thickness in some cases.

The first sample has $\sim$200 $Al_{0.45}In_{0.55}As$ dots per μm^2, 18$\pm$2 nm in diameter, 3.2 nm thick, clad with $Al_{0.35}Ga_{0.65}As$, and emits in the visible red at $\sim$1.88 eV. The full width at half maximum of the overall QD emission is $\sim$46 meV due to the inhomogeneous Gaussian broadening of the ground states associated with the narrow size/composition/strain distributions, but the single-dot emission line was found to be smaller than[17] $\sim$0.2 meV by measuring the PL emitted from ensembles with a small number of QD's.[6,8] Moreover, these sharp emission lines are found to be robust to increasing temperatures, displaying temperature-independent linewidths much narrower than the available thermal energy up to the onset of thermionic emission. No thermal broadening of the ground-state emissions and no significant radiative recombination from thermally populated excited states are observed,[17] in accordance with strong confinements with discrete 0D density of states.

A larger number of QD's ($\sim 10^6$) of that sample has

been studied with nearly resonant excitation energies to probe the energy level selectively,[4] and to investigate the role of phonons in the relaxation of the carriers. Such PL spectra obtained with different excitation energies (E_{ex}) in a near backscattering geometry are displayed in Fig. 1. The spectra are displayed with the horizontal axis in energy away from the peak ($E_{PL}-E_{peak}$) in (a), and in meV away from the excitation energy ($E_{ex}-E_{PL}$) in (b), with offsets on the vertical axis for clarity. The arrows on top of the spectra of Fig. 1(b) indicate the position of the peak of the QD distribution (1.88 eV). The remarkable feature is the resonances in the PL spectra at fixed energies away from the excitation as clearly seen in Fig. 1(b). The dominant features at 35 and 48 meV match closely the known[18] values of the GaAs-like and the AlAs-like longitudinal optical (LO) phonons in the $Al_{0.35}Ga_{0.65}As$ cladding material, respectively. Similarly, a recent resonant Raman study[19] on phonons in AlInAs allows the identification of the slightly weaker modes observed at 46 and 30 meV, which can be identified with the AlAs-like and InAs-like modes in the QD material. Other less pronounced resonances are clearly present at lower energies, indicating contributions from other phonon modes in the barrier and/or the QD materials.[20] Because the resonances are much broader than the spectral width of the exciting beam and because the strength of the resonances is very much dependent on the excitation energy (and not observed outside the spectral region of QD's emission), these peaks are not attributed to simple inelastic scattering of the laser line (i.e., Raman lines), but rather to enhanced PL at the phonon energies. This is also confirmed by measuring the decay time of the signal, which was found to be unambiguously longer than the excitation pulse for all the energies of the PL spectra.[17] This enhancement of the PL for excitation energies permitting resonant phonon relaxations appears to become more pronounced for certain QD's at different excitation energies. This is seen by observing how the strength of the resonances changes with the excitation energy and therefore choosing which QD's are probed with an excess of a given phonon energy. For example, it is remarkable to see that although the bottom curves of Fig. 1 were obtained by exciting close to the peak of the emission of the QD's, virtually no enhancement is observed for the various phonon energies, whereas the resonances for the 35- and 48-meV phonons appear to have their maximum enhancement for the spectra obtained with $E_{ex}\sim 1.927$ and 1.943 eV, respectively. This phenomenon is best explained assuming that the interlevel spacing (between the ground and the first excited states, for example) varies significantly for the different QD's, and that a strong PL enhancement is then observed when the excess excitation energy, a phonon energy, and the interlevel spacing are matched. Time-resolved PL, performed under such resonant conditions, where enhanced time-integrated PL signals are observed, demonstrated faster dynamics. This suggests that the interlevel spacing can play a deterministic role for the case of phonon or multiphonon relaxation of the carriers in such nanostructures, enhancing the probabilities of carrier relaxation when the interlevel spacing and the excess photocarrier energy are matched with the energy of a phonon (or a combination of phonons). It is not clear which excitation-relaxation mechanism is dominant to give rise to the PL signal from nonresonantly excited QD's giving the underlaying background of the ~46-meV broad emission peak for all excitation energies. It is likely to be linked to be multiphonon relaxation processes, hot exciton absorption, and/or to the presence of the wetting layer and the fact that for this sample the difference between the QD peak and the barrier energy is only ~120 meV (structures with deeper potential appear to be more energy selective, see Ref. 4 or Figs. 2 and 3 below). Also, the extremely narrow single-dot emission linewidth precludes the observation of the PL reemitted at the same energy from QD's directly excited in their ground states with continuous excitation [i.e., scattered laser light prevents measurements very close to $E_{ex}-E_{PL}=0$ in Fig. 1(b)].

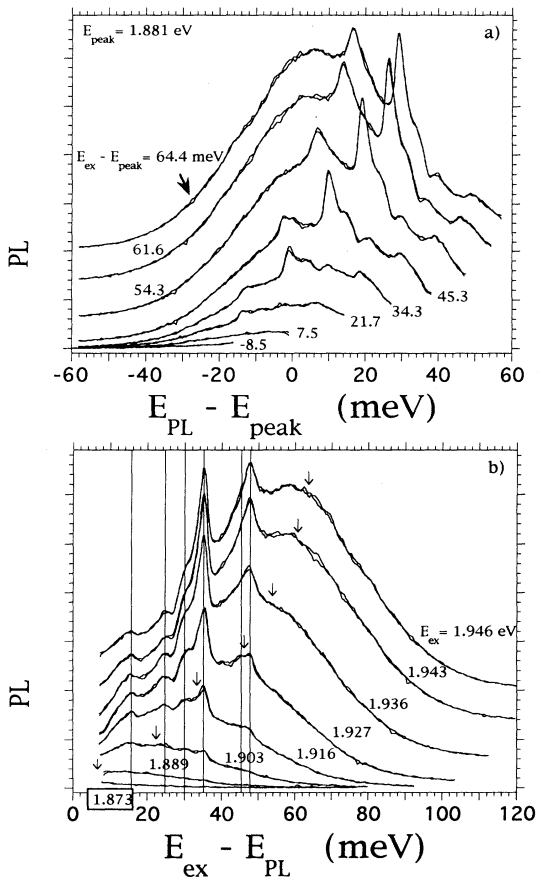

FIG. 1. PL spectra obtained at $T=5$ K with different excitation energies (E_{ex}) with $\sim 10^6$ $Al_{0.45}In_{0.55}As/Al_{0.35}Ga_{0.65}As$ QD's, 18 nm in diameter. The spectra are displayed in energy away from the peak ($E_{PL}-E_{peak}$) in (a), and in meV away from E_{ex} ($E-E_{ex}$) in (b). Strong enhancements of the PL are observed for excitation energies permitting resonant phonon relaxations. In (b), the arrows indicate the peak of the QD's emission.

The spectra of the selective excitation of the PL reported in Ref. 4 for the slightly larger (25-nm diameter measured by TEM) $In_{0.5}Ga_{0.5}As/GaAs$ QD's displayed no

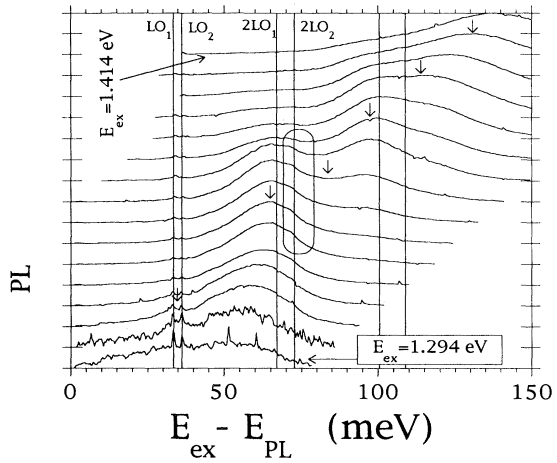

FIG. 2. Selective excitation of the PL as in Fig. 1, but obtained on $In_{0.67}Ga_{0.33}As/GaAs$ QD's, 15 nm in diameter. The sharp Raman doublet would correspond to a ~60% In composition. PL enhancements are also observed at multiple times the phonon energies (see inside the oval for example).

"phonon signature" but only indications of the energy selectivity associated with the slightly varying interlevel spacing in the discrete QD levels.[21] Other examples of spectra obtained with different excitation energies are shown in Fig. 2 for $In_{0.67}Ga_{0.33}As/GaAs$ QD's 15 nm in diameter, and in Fig. 3 for $In_{0.5}Ga_{0.5}As/GaAs$ QD's 13 nm in diameter, with their QD emission peaking in the infrared at 1.276 and 1.282 eV, respectively at $T \sim 5$ K. For some excitation energies, the selectivity splits the spectra of Fig. 2 in at least three peaks, and in addition, Raman peaks are observed. The resolution-limited doublet at 36.3 and 33.5 meV can be associated to the inelastic scattering of the laser line with the GaAs LO and GaAs-like LO phonon in the InGaAs, respectively.

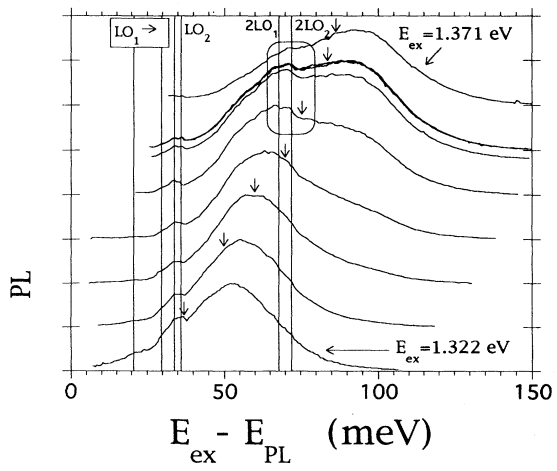

FIG. 3. Selective excitation of the PL as in Figs. 1 and 2, but obtained on $In_{0.5}Ga_{0.5}As/GaAs$ QD's, 13 nm in diameter. The sharp Raman doublet would correspond to a ~50% In composition. PL enhancements are also observed at multiple times the phonon energies (see inside the oval for example).

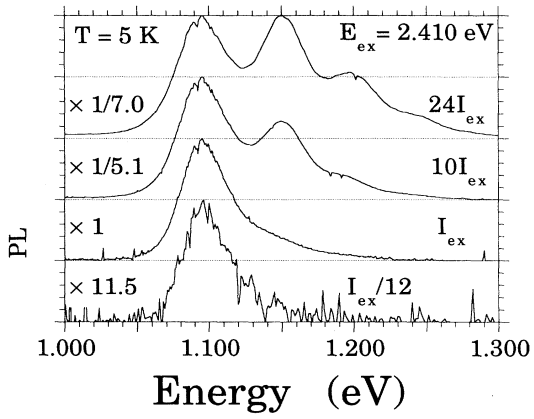

FIG. 4. PL spectra obtained at $T = 5$ K with different excitation intensities (I_{ex}) with $In_{0.5}Ga_{0.5}As/GaAs$ QD's, 36.5 nm in diameter, displaying strong level filling and emission from the excited states and saturation of the ground states with increasing excitation intensities. $I_{ex} \sim 10$ W/cm^{-2}.

From the energy of the latter phonon, the indium composition in the QD can be estimated to be 60%, close to the nominal value of 67% deposited. By drawing lines at the expected position of 2 and 3 times the above phonon energies, one can distinguish a small enhancement in the PL as the peak of the QD emission (marked by the arrows) passes through these energies, for example, see in the oval in the middle of Fig. 2 and Fig. 3 at $2LO_2$. The enhancements of the PL for excitation energies permitting resonant phonon relaxations appear to be more pronounced for the sample of Fig. 3, suggesting that there is a closer match between the phonon energy and the interlevel spacing as discussed above. We observe again that the indium composition extracted from the phonon energies is close to the nominal value deposited.[22]

Finally we present the results obtained with an $In_{0.5}Ga_{0.5}As/GaAs$ QD sample, which gives exceptionally[23] strong emission at energies higher than the single inhomogeneously broadened QD peak observed at the lowest excitation intensities. The TEM results show ~100 QD's per μm^2, with a good diameter uniformity of 36.5 ± 3 nm. Thus, for that sample, a smaller interlevel spacing is to be expected as a consequence of the larger diameter. Figure 4 shows the PL spectra obtained with nonresonant excitation ($E_{ex} = 2.410$ eV) at $T = 5$ K with different excitation intensities (I_{ex}). At low excitation, a single peak ~38 meV wide is observed, originating from the ground-state emission of the QD's. But as the excitation intensity is increased, up to 3 or 4 additional higher-energy peaks are replicating the emission of the ground states. A clear saturation of the ground-state transitions with relatively low excitation intensities is also observed. For example, at ~240 W/cm^{-2} the second peak in Fig. 4 has an amplitude equal to that of the lowest-energy peak. This intensity-dependent behavior with side peaks having line shapes very similar to the lowest-energy peak suggests that the QD's are emitting through excited-state transitions (about ~50 meV apart[24]) for higher excitations, with saturation of the ground-state transitions.

Such behavior is expected for a system combining small density of states, and having intersublevel decay times comparable to the ground-state excitonic recombination times. Further experiments are needed to measure the ground-state excitonic recombination time and the excited-state decay times to determine the intersublevel relaxation times for different excitation intensities, and thus establish if this sample exhibits restricted phonon scattering rates as suggested for a 0D system with low-dimensionality-induced slowed relaxations.

In conclusion, PL spectra excited quasiresonantly showed that some of the self-assembled QD structures display strong enhancement of the photoluminescence for excitation energies permitting resonant phonon relaxations. This PL enhancement appears to be correlated with a resonance between the interlevel spacing and the phonon energies. The importance of the interlevel spacing in the relaxation of carriers in self-assembled QD's has been further demonstrated with a QD sample having a smaller interlevel spacing displaying strong level filling, and emission from the excited states with saturation of the ground states for increasing excitation intensities.

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[21]The selectivity is broadened due to the large number of QD's probed and several QD's having the same ground-state energies can have different excited states.

[22]Another sample (not shown) having a higher indium composition gave phonon frequency higher than expected. This could be related to the strain-induced shift of the phonon modes, or to indium reevaporation during the deposition.

[23]The singularity of this sample might be linked to the fact that it was taken from a wafer obtained by sweeping the coverage of the QD material deposited, as described in Ref. 15.

[24]Preliminary calculations indicate that the ~50-meV peak spacing would be associated to radiative transitions that would be observed for electrons and holes with the same quantum numbers.