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Tunable intersublevel transitions in self-forming semiconductor quantum dots

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Interfacial compositional disordering in $In_{0.6}Ga_{0.4}As/GaAs$ quantum dots has been used to tune their intersublevel energy spacings ($\Delta E_{[(i+1)-i]}$). Interdiffusion blueshifted all levels while lowering values for $\Delta E_{[(i+1)-i]}$. Rate equation simulations of photoluminescence (PL) spectra estimated relaxation lifetime ratios for intersublevel transitions. A slight trend towards increasing thermalization rates at values $\Delta E_{[(i+1)-i]} \sim$LO phonon energies was found. However, PL measurements showed strong emission from excited states for all $\Delta E_{[(i+1)-i]}$ values, which ranged from 53 to 25 meV. [S0163-1829(98)50732-1]

Issues concerning energy relaxation in zero-dimensional systems are of renewed interest since the first report of defect-free quantum dots[1] (QD's) based on coherently strained $In_{0.6}Ga_{0.4}As/GaAs$ islands. Theoretical works have postulated that due to their atomiclike density of states, efficient electron relaxation is hampered in QD's by reduced scattering rates with LO phonons.[2,3] This effect becomes important when the energies between excited subbands $\Delta E_{[(i+1)-i]}$ exceeds the thermal energy. These reduced relaxation rates were suggested as an explanation for poor luminescence efficiency in small QD's.[4] However, more recent optical measurements from self-forming QD's show that very bright luminescence can be obtained. Spectra from a reduced statistical ensemble of QD's show ultranarrow[5,6] temperature-independent[7] linewidths, consistent with a δ function density of states. Recent optoelectronic applications based on self-forming QD's show that their predicted[8] advantages are already being implemented in devices.[9,10] Still, evidence for slowed down relaxation of carriers from excited states has also been reported for these structures, and excited-state emission was observed from photoluminescence[11,12] (PL) and electroluminescence measurements.[13]

Tuning the ground-state PL emission from QD structures is important for device applications and basic studies. This has been achieved by changing the III-V band gap (composition) in the dot/barrier materials,[14] by adjusting average island dimensions for a given ternary composition,[15] and by interdiffusion of the dot/barrier interface.[16] the latter method can shift PL emission to a different spectral region (blueshifts in $In_xGa_{1-x}As/Al_xIn_{1-x}As/Al_xGa_{1-x}As$ quantum structures). Here we show that the intersublevel spacings from excited-state emission in QD's can also be tuned. The effects of interdiffusion on excited-state emission from QD's is demonstrated and analyzed. This gives a range in tunability for applications like infrared detectors and lasers based on intrasubband transitions.[17]

Here the intersublevel spacings are reduced until a match is obtained with the LO phonon energies for GaAs or InAs (36 ± 3 and 30 ± 3 meV for the GaAs-like and the InAs-like LO phonon energies, respectively[11]). Higher temperature annealings reduced $\Delta E_{[(i+1)-i]}$ to values below these LO phonon energies. Numerical simulations for the PL spectra using the rate equations estimated intrinsic carrier relaxation ratios for different values of $\Delta E_{[(i+1)-i]}$. These findings allow experimental determination of the effects of intersublevel spacings on carrier relaxation, phase filling, and phonon bottleneck in semiconductor QD's.

QD structures were grown by metalorganic chemical vapor deposition. The nominal composition was $In_{0.6}Ga_{0.4}As$. Capping layers of 100 nm were grown as in previous interdiffusion studies.[16] Details of the growth are described elsewhere.[15,16] A high arsine partial pressure and low substrate miscut angle (0.05°) gave a low concentration of uniform strained islands. A growth temperature of 550 °C formed QD's of sufficiently large dimensions for several bound states. Plan view transmission electron microscopy (TEM) (JEOL 200CX operated at 200 keV) and force microscopy (FM) gave statistical information on island sizes, shapes, uniformity, and areal densities. Thermal treatments were performed in N_2 ambient using rapid thermal annealing and proximity capping. Anneals were performed for 30 s. Low-temperature (77 K) photoluminescence spectra were obtained using the 532-nm continuous-wave output of a diode-pumped Nd:YVO_4 for excitation, and the signal was dispersed with a single grating 0.67-m monochromator, and collected using a cooled Ge detector and lock-in techniques.

Figure 1 shows the PL spectra from $In_{0.6}Ga_{0.4}As/GaAs$ QD's as a function of excitation power. Higher energy peaks become more prominent with increased excitation. Excited-state emission can be observed even at very low excitation power, with emission from the $(i+1)$ levels before the (ith) level saturates. The sample producing the spectra shown here contains a concentration of $4\times10^8/cm^2$ $In_{0.6}Ga_{0.4}As$ QD with 30-nm average diameters. The islands were not faceted

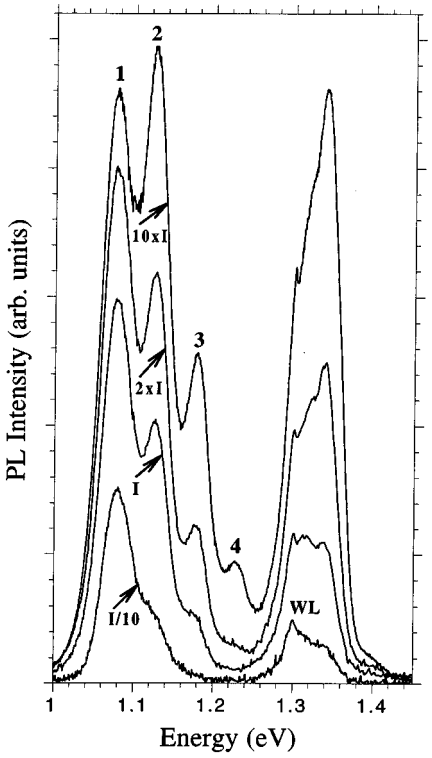

FIG. 1. PL spectra taken at different excitation powers from $In_{0.6}Ga_{0.4}As/GaAs$ QD's. The spectra show wetting layer luminescence and emission from excited states. The unit excitation power density I is approximately 5 W/cm^2. Energy levels are labeled 1, 2, 3, and 4 for the ground state, first, second, and third excited states, respectively. Relative intensities between WL luminescence and luminescence from QD states are shown.

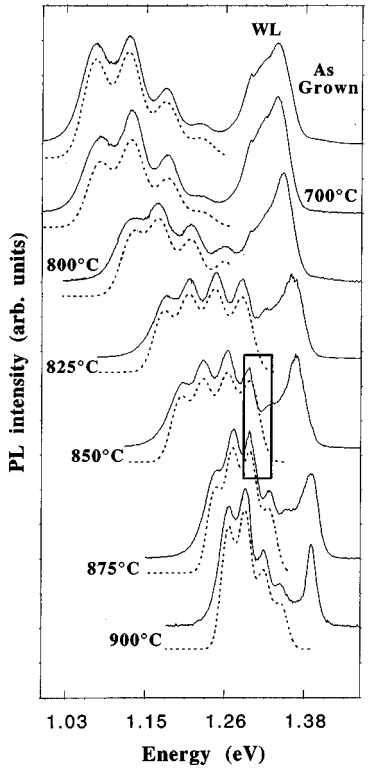

FIG. 2. Effects of compositional intermixing of the $In_{0.6}Ga_{0.4}As/GaAs$ interface on the radiative emission of QD's that show excited-states luminescence. Dashed lines show the results of simulation by solution of the rate equations. The inhomogeneous broadening, energy levels, and lifetime ratios are shown in Table I. The rectangular frame indicates sharp non-Gaussian features detailed in Fig. 4.

but of continuous curvature, like convex lenses, and the height/diameter (h/d) ratio $\sim 1/6$. A small spread in island sizes gives small inhomogeneous broadening, which allows resolving excited states. The spectra seen in Fig. 1 thus reflect the excited-states emission of a single quantum dot. Calculations based on lens shaped QD's (Ref. 18) predict four bound states. The present results are in reasonable agreement with these calculations.[19]

Figure 1 also shows wetting layer (WL) luminescence, which is expected for low QD concentrations. The WL is effectively a thin (4–5 ML) quantum well with PL emission at higher energies. The peak intensity ratio between WL/QD increases with the excitation power. The increase in intensity of the shoulder on the WL peak with excitation power is consistent with excited-state emission. We propose that this WL has some lateral quantum confinement, possibly due to the strain from neighboring QD's. QD's do not form in ordered arrays, and variations in QD concentration and position cause differences in local strain that could account for lateral confinement in the WL. Sometimes, regions in the WL that are denuded of QD but surrounded by ''strings'' of strained dots can be seen in TEM and FM imaging. Some of these structural features can be seen in published work (see, for example, Fig. 1 in Ref. 20 and Fig. 5(a) in Ref. 15). The closely spaced excited-state emission energies are consistent with the much larger lateral dimensions expected in such ''pinched'' WL structures. The first peak is sharp as expected from a QW.

The simultaneous observation of WL and QD luminescence allows comparing the effects of interdiffusion on these structures. Figure 2 shows the results of thermally induced intermixing on the sample producing the spectra shown in Fig. 1. When excitation power was varied, spectra for all annealed samples showed similar behavior as seen in Fig. 1.

Figure 2 shows that all PL peaks blueshift, and the inhomogeneous broadening diminishes. Furthermore, the intersublevel spacings become narrower with increased diffusion lengths. All spectra in Fig. 2 have been simulated using solutions to the rate equations[13] calculated for four discrete levels:

$$P(E)=\sum_{n=1}^{4}(f_i N_i/\tau_r)\exp[-(E-E_i)^2/2\Gamma^2],$$

where the filling ratio f_{i-1} of the $(i-1)$ level is proportional to the electronic relaxation rate in the ith level. ($N_i=2\times i$) was used for level degeneracies and τ_r is the carrier recombination lifetime. Different values for τ_{0i} were needed to achieve acceptable fits to the experimental spectra. Diffusion lengths reported in Table I were established from measurements and calculations of diffusivity values in quantum wells of the same ternary composition:[16] $D(T)=[0.19]\exp[-(3.4\text{ eV})/\text{kT}]$. Emission energies for each excited-state peak are plotted as a function of diffusion lengths and anneal temperatures in Fig. 3.

TABLE I. Values obtained for intrinsic relaxation times from simulations shown in Figs. 2 and 4. Sample annealing temperatures are in degrees C. Ratios for relaxation rates τ_{0i} are indicated with respect to the as-grown sample values. Intersublevel spacings are in meV. Values for G (the generation rate in electron-hole pairs per ns) ranged from 5 to 13. Γ is the inhomogeneous broadening factor in meV and L is the diffusion length in angstroms.

	As grown	800	825	850	875	900
τ_{02}	1.0	0.18	0.18	0.18	0.18	0.36
τ_{03}	1.0	0.81	0.74	0.64	0.49	0.95
τ_{04}	1.0	4.0	5.0	4.0	2.1	4.4
ΔE_{1-2}	49.0	39.0	37.0	33.2	26.0	25.0
ΔE_{2-3}	53.0	46.0	38.0	34.8	26.0	27.0
ΔE_{3-4}	51.0	49.0	40.0	34.0	28.0	25.0
Γ	34.6	32.2	28.3	26.1	20.5	19.0
L	0.0	2.5	3.8	5.7	8.4	12.2

The wetting layer is treated here as an infinite reservoir of carriers. The reported observation of a very large increase in QD luminescence when the excitation energy exceeds the WL energy confirms that electron-hole pairs are generated in the WL and provide a reservoir of carriers for the dots.[21] Also, WL/QD emission ratios increase with excitation power, further justifying this assumption in the model.

The ratios for relaxation rates (τ_{0i}) reported in Table I are based on $\tau_r = 0.5$ ns. Calculations were also performed with values of 0.8 and 3 ns for τ_r. Measured values for τ_r in $In_{0.6}Ga_{0.4}As/GaAs$ and $In_xAl_{1-x}As/Al_xGa_{1-x}As$ QD range from 0.4 to 1 ns.[12,20] Changing the assumed value of τ_r shifts calculated values for τ_{0i} but the trends shown in Table I are maintained. These indicate an increase in thermalization rates for τ_{02} and τ_{03} when $\Delta E_{[(i+1)-i]} \sim$ LO phonon energies. τ_{02} and τ_{03} increase again as $\Delta E_{[(i+1)-i]}$ decreases below the LO phonon energies (900 °C anneal). The exception to this trend is τ_{04} where there is an apparent decrease in thermalization rates. The possibility of interaction with WL states should probably be considered for this fourth QD level.

Two observations can be made regarding the values of the inhomogeneous broadening Γ shown in Table I. The most obvious one is the progressive reduction in Γ with increased intermixing. A similar observation was made from the ground state PL emission from intermixed $In_{0.6}Ga_{0.4}As/GaAs$ QD of different dimensions.[16] Recent PL measurements from interdiffused $In_xAl_{1-x}As/Al_xGa_{1-x}As$ and $In_xGa_{1-x}As/Al_xGa_{1-x}As$ QD's show this behavior to be general but strongly dependent on the dot/barrier III-V composition.[22] A narrower inhomogeneous broadening occurs as the confining potential in a Gaussian distribution of QD sizes is made shallower by interdiffusion, since QD size inhomogeneities will produce broader PL spectra with a deeper confinement. Here we demonstrate that this effect is also observed for excited-states emission.

The same values for Γ were used for simulation of the four excited states peaks, giving good fits to most of the

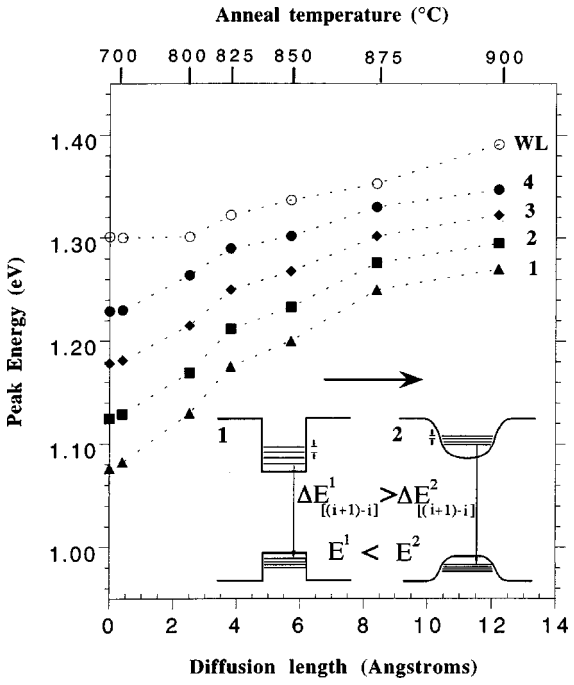

FIG. 3. Energy position of each level as a function of diffusion length and anneal temperature. The diagram shows a one-dimensional representation of the changes in confining potential indicating the blueshifts and decreasing values for $\Delta E_{[(i+1)-i]}$.

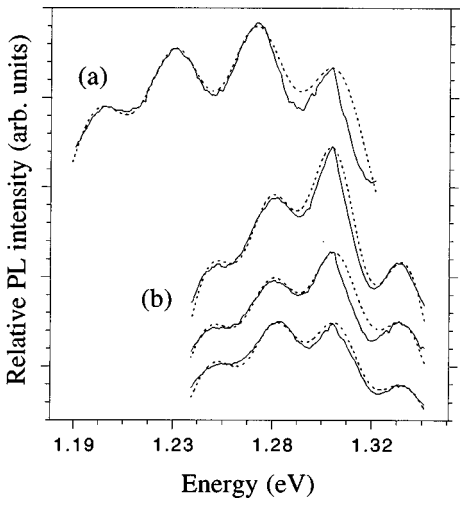

FIG. 4. PL spectral details and simulations of a QD sample annealed at (a) 850 °C and (b) 875 °C. In (b), three separately measured spectra indicate the reproducibility of the non-Gaussian sharp features.

curves. One exception is the third and fourth levels in the curve after 850 °C anneals and the third level after 875 °C anneals. This is indicated in the boxed section in Fig. 2 and presented in more detail in Fig. 4. Figure 4 shows the experimental spectra and simulation for (a) the sample annealed at 830 °C, and (b) 3 different spectra taken at slightly different excitation powers for the sample annealed at 875 °C. A couple of the peaks are consistently narrower than the Gaussian envelope that fits the other peaks. The origin of these sharper features could be explained by examining the behavior of QD's in large statistical ensembles. Inhomogeneous broadening is a direct consequence of small size fluctuations in QD's. Since narrower peaks for certain excited transitions are simultaneously observed with broader Gaussian peaks, it is possible that QD's of selected sizes are experiencing faster relaxation times for certain transitions and thus not contributing to the ensemble's radiative emission. This would select part of the QD population out, where very fast relaxation occurs. This deviation from Gaussian behavior might be reflecting changes in relaxation rates due to closely matched $\Delta E_{[(i+1)-i]}$ and LO phonon energies.

Changes in lifetimes are expected in quantum wells with shallower confining potentials.[23,24] Lower radiative lifetimes have been measured as a result of intermixing and previous temperature-dependent measurements confirm the effects of shallower potentials in QD's.[16] These effects should be considered with changes in the carrier relaxation mechanism in examining the data presented in Table I.

While some subtle effects seen from these experiments and simulations could be attributed to changes in carrier relaxation from matching $\Delta E_{[(i+1)-i]}$ and LO phonon energies, strong peaks from excited-state emission are present at different values of $\Delta E_{[(i+1)-i]}$. This makes this finding very promising for device applications based on QD intraband transitions.

To conclude, we have shown the effects of intermixing on the radiative emission from QD structures with excited-state luminescence. All peaks blueshifted and narrowed. The intersublevel spacings $\Delta E_{[(i+1)-i]}$ were reduced and could be tuned continuously for values of $\Delta E_{[(i+1)-i]}$ greater, similar, and lower than the LO phonon energies in InAs and GaAs.

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