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Effects of interdiffusion on the luminescence of InGaAs/GaAs quantum dots

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Large energy shifts in the luminescence emission from strained InGaAs quantum dots are observed as a result of postgrowth annealing and also when raising the upper cladding layer growth temperatures. These blueshifts occur concurrently with narrowing (from 61 to 24 meV) of the full width at half-maxima for the emission from the quantum dot ensemble. These energy shifts can be explained by interdiffusion or intermixing of the interfaces rather than strain effects due to variations in capping layer thickness. Temperature behavior of the luminescence in annealed and nonannealed samples indicates a change in the shape and depth of the quantum dot confining potential. Quenching of the wetting layer luminescence after interdiffusion is also observed. © *1996 American Institute of Physics.* [S0003-6951(96)00139-8]

Blueshifts in quantum wells (QW) can be induced by intermixing[1] assisted by dielectric capping,[2,3] impurity diffusion,[4] ion implantation,[5] and simple thermal treatments.[6] Interdiffusion of heterointerfaces is expected to play a major role in structures of reduced dimensionality where the area of the interface is increased due to island formation, and where the overall dimensions are small (15–50 nm diam). Blueshifts in luminescence could be adjusted *in situ* (in the growth chamber, during or after growth) offering a range of tunability that might be desirable to incorporate into devices.

Achieving narrower luminescence lines for a large ensemble of quantum dots (QDs) is a major goal for both future device applications and fundamental studies of the physics of zero-dimensional (0D) structures. Size uniformity correlates with inhomogeneous broadening of the photoluminescence (PL) emission.[7] It has been predicted[8] that the 0D laser properties of low current threshold and higher quantum efficiencies can only be of benefit if size uniformity is achieved.

The presence of a so called ''wetting layer'' [effectively a very thin quantum well (1–4 ML) connecting the islands], is an inevitable result of the Stranski–Krastanow[9] growth mode upon reaching a strain-defined critical thickness. This wetting layer has been shown to have its own distinct luminescence emission,[10] often appearing as a shoulder on the brighter PL emission peak for the quantum dot ensemble. Its presence might be responsible for some nonideal 0D behavior reported in these structures[10,11] as well as constituting a technical barrier in the development of 0D lasers.

Results presented here show that blueshifts in the PL emission from a large number of quantum dots can be obtained reproducibly. These blueshifts occur as a result of thermally induced interdiffusion and are concurrent with narrowing of the full width at half-maxima (FWHM) of the PL emission from the QDs. Furthermore, quenching of the wetting layer luminescence is observed, suggesting the possibility of using interdiffusion to achieve more nearly ideal three-dimensional confinement in semiconductor quantum dots.

These structures were grown by metalorganic chemical vapor deposition using a horizontal reactor cell operating at 76 Torr. A specially designed laminar flow cell allows large areas of uniform growth. Partial pressures for $(CH_3)_3Ga$ and $(CH_3)_3In$ were 5.36×10^{-6} and 5.18×10^{-6}, respectively. AsH_3 was used for the group V source and the V/III ratio was 351. The hydrogen flow rate was 17.5 standard liters per minute. The flow of $(CH_3)_3In$ was monitored and controlled by an EPISON ultrasonic sensor.

After growth of a GaAs buffer layer at 650 °C on semi-insulating (100) GaAs substrates, quantum dots in the form of nanometer size InGaAs islands, were grown by depositing 4.5 ML (nominally) of $In_{0.49}Ga_{0.51}As$ at 550 °C. The temperature was raised to the chosen GaAs upper cladding growth temperature while growing the GaAs capping layer, or the GaAs capping layer was grown at the same growth temperature as the islands. Except in one case, the capping layer thicknesses were nominally 100 nm and a similar layer containing InGaAs islands was grown on the surface. The surface was kept in an inert atmosphere and scanning probe microscopy (Nanoscope III with etched SiN tips) was used to verify island formation and obtain structural information on average size and areal density.

Post-growth annealing was done in argon using a rapid thermal annealer at temperatures of 850–950 °C for 30 s. Low-temperature (12 K) photoluminescence spectra were obtained using the 488 nm line of an argon ion laser and dispersed using a 75 cm spectrometer. The signal was collected using a Si detector and lock-in techniques.

Plan-view transmission electron microscopy (TEM) specimens were prepared by chemical etching from the sub-

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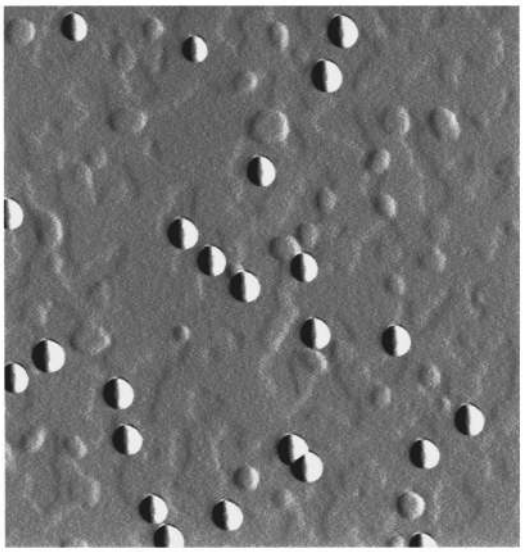

FIG. 1. Morphology of one of the samples used in this study before annealing or capping layer growth as imaged using scanning probe microscopy. The width of the scan is 750 nm.

strate side using $H_2SO_4:H_2O_2:H_2O=8:1:1$ after a 1 min etch in $H_2SO_4:H_2O_2:H_2O$ $(=1:8:500)$ to remove the top surface QDs. TEM specimens were investigated in a Philips EM 430 operating at 300 keV.

Results from two growth experiments are presented: in one, the same QD structure was annealed at different temperatures; in the other, the structures were grown separately but identical conditions were used except for the temperature of the 100 nm upper cladding layer. In one case, the thickness of the upper cladding was changed to eliminate possible *in lapido* strain effects[12] and both layers were grown at the same temperature as the QDs.

The preannealing average diameters and areal concentrations were 43 nm and $1\times10^{10}/\text{cm}^2$ for the QDs producing the luminescence in Fig. 2 and 33 nm to $9\times10^{9}/\text{cm}^2$ for Fig. 3. Figure 1 shows a scanning probe image of the surface morphology for one of the samples showing the nanometer size InGaAs islands. Figure 2 shows dark field plan-view TEM images of both unannealed and annealed samples with QDs.

All structures showed very bright QD luminescence. Figure 3 shows that a large blueshift can be observed with a corresponding narrowing of the peak with progressively

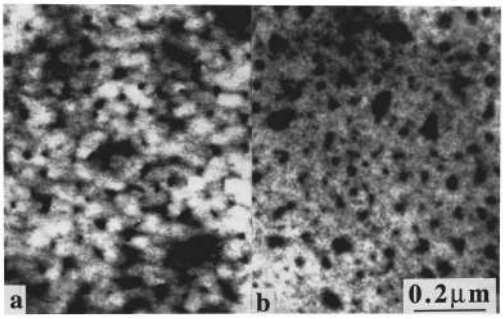

FIG. 2. Plan-view TEM 220 dark-field images taken from an (a) unannealed and (b) annealed at 950 °C quantum dot samples, showing that quantum dots are still present after annealing.

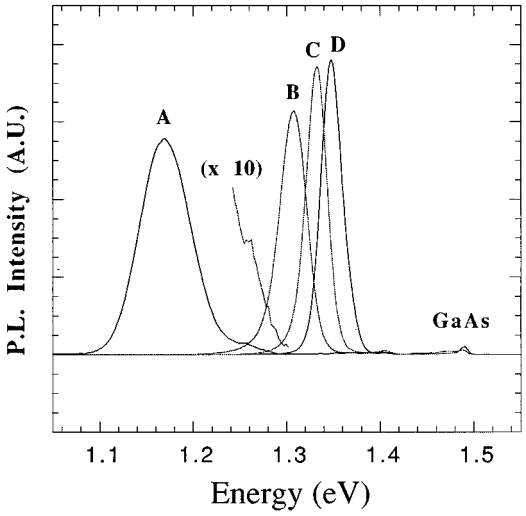

FIG. 3. Low-temperature (12 K) photoluminescence spectra showing emission from quantum dots in as-grown and annealed samples. The smaller peak at 1.5 eV is due to free and impurity bound excitonic transitions in the GaAs buffer layer and substrate. Peak A is from an InGaAs/GaAs quantum dot sample where the quantum dots were grown at 550 °C and the GaAs buffer and cladding layers were grown at 650 °C. This sample was then annealed for 30 s at 850 °C (peak B), 900 °C (peak C), and 950 °C (peak D). The maximum blueshift observed in the sample annealed at the highest temperature is 140 meV, and the FWHM for the inhomogeneously broadened peak changes from 61 to 24 meV.

higher annealing temperatures. Emission from GaAs (free and impurity related excitonic transitions) and wetting layer luminescence are also shown. Figure 4 shows PL spectra for quantum dot samples grown under identical conditions but with varying upper cladding growth temperature.

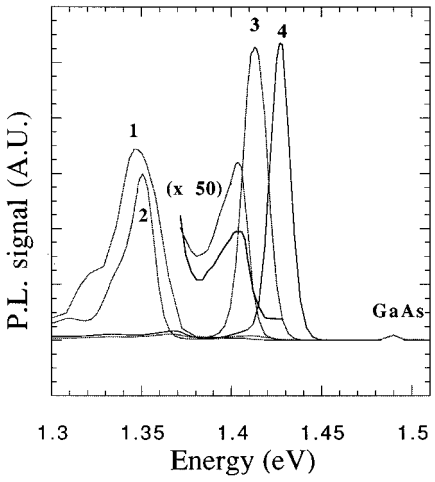

FIG. 4. Low-temperature PL for QD structures with different capping layer growth temperatures. This is equivalent to *in situ* annealing at a temperature of 675 °C for 12 min for the sample with emission peak labeled ''3'' and 800 °C for also 12 min for the peak labeled ''4.'' Peak ''1'' shows emission from a sample where the upper cladding was grown at 550 °C. Another sample also grown with an upper cladding growth temperature of 550 °C but much thinner (20 nm) produces PL emission peak ''2.'' The broader emission from peak ''1'' is due to islands with less uniformity in size. The average diameters for the islands before annealing was equivalent in all these samples. The magnified signal at higher energies for ''1'' and ''2,'' is attributed to the wetting layer. Wetting layer luminescence is not observed for samples ''3'' and ''4.''

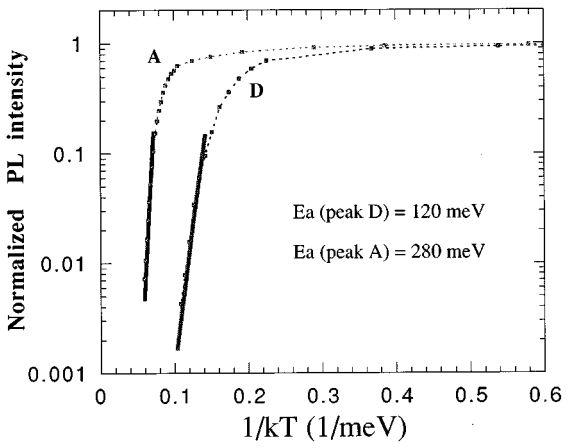

FIG. 5. Normalized PL intensity as a function of $1/k_BT$ for the unannealed and annealed samples with PL emissions labeled ''A'' and ''D'' in Fig. 3.

The normalized PL signal as a function of temperature for the unannealed sample in Fig. 1 (peak A) and for the sample after annealing at 950 °C (peak D) are displayed in Fig. 5, showing that the temperature dependence of the luminescence changes significantly after annealing.

The observed blueshifts in Fig. 3 indicate a trend with higher temperature annealing. These shifts are a remarkable change, given the short annealing times involved in the experiment. Initial enhancement of interdiffusion and non-Fickian behavior in strained systems[6] is most likely at play. Interdiffusion in systems where strain is as large as in the samples studied in this work (3.5%) has not been systematically studied for quantum wells. It is expected, however, that the transient component of the diffusivity and deviation from Fick's law would be of even greater importance than in the strained systems studied by S. W. Ryu *et al.*,[6] where $In_{0.2}Ga_{0.8}As$ was used (~1.4% lattice mismatch). The large strain present in $In_{0.49}Ga_{0.51}As$ QDs might result in a greater transient component of the diffusion causing a large effect even for short annealing times.

Narrower FWHM with higher annealing temperatures could be explained by a homogenization of sizes for the individual InGaAs islands. Narrower FWHM luminescence peak for QD ensembles has been correlated with narrower size distribution.[7] These changes could also be partly accounted for by a smaller expected variation in emission in dots of different sizes with a shallower confining potential. Plan-view TEM of annealed and unannealed quantum dot samples shows that the annealing process does not destroy the QDs, but a weaker strain contrast results from the thermal treatment. This observation is consistent with interdiffusion of the InGaAs/GaAs interface. A more detailed TEM study of the effect of intermixing on QD size, QD size variations, and changes in QD shape is in progress.[13]

The fact that blueshifts are obtained upon increasing the cladding layer growth temperature indicates that the observed shifts in emission energies are due to interdiffusion rather than strain effects from the capping layer. This result might have the implication that most of the recent PL studies of self-organized QD emission arise from quantum dot samples that do not have abrupt or square confining potentials. The fact that the PL did not shift for caps grown at the same temperature as the dots when the cap thickness was changed from 20 to 100 nm indicates that strain effects are unimportant beyond capping layer thickness above the reach of the strain field (around 20–30 nm above QDs).

To first order, the quenching of the luminescence as a function of temperature can be modeled by thermal emission of the carriers out of the quantum dots. Previous measurements including quantum dot systems with different confining potentials show similar behavior.[14] An Arrhenius plot of log normalized luminescence intensity shows a thermally activated nonradiative recombination mechanism; the slopes of the straight portions of Fig. 5 give an activation energy related to the depth of the quantum dot confining potential.[15,16] The lower temperature quenching in the annealed samples as well as the lower activation energy extracted from the slope in the Arrhenius plot (280–120 meV change) can be interpreted as a change both in the depth and in the shape of the confining potential caused by interdiffusion during annealing.

In summary, large blueshifts result from thermal annealing of strained InGaAs/GaAs quantum dots. The FWHM from the quantum dot ensemble PL also becomes narrower, and wetting layer luminescence indistinct. Similar blueshifts are obtained with high upper cladding growth temperatures, indicating that most samples are already blueshifted, and that interdiffusion rather than strain effects are responsible for these shifts.

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