Gallium diffusion into self-assembled InAs quantum dots grown on indium phosphide substrates

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The photoluminescence spectrum of small self-assembled In(Ga)As quantum dots grown on InP substrates is composed of distinct spectral lines. These lines correspond to monolayer variations in the dots smallest dimension: their heights. We use this phenomenon in order to study the diffusion of gallium atoms into the self-assembled quantum dots. We demonstrate that substantial amounts of gallium atoms diffuse from a strained GaInP layer underneath the quantum dots into the quantum dots. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1806277]

It was recently reported that an ultrathin GaAs layer inserted between a layer of InAs self-assembled quantum dots (QDs) and a layer of quaternary GaInAsP lattice matched to InP, blueshifts the wavelength of the light emitted from the QDs.[1] The authors of Ref. 1 suggested that the deposition of a thin GaAs layer effectively reduces the size of the QDs, thus increasing the recombination energy of confined carriers in these QDs. It is proposed in Ref. 1 that the gallium atoms in the thin layer suppress the As/P exchange during growth interruption under arsenic flux and during the deposition of the InAs layer, itself. In addition, the authors of Ref. 1 briefly mentioned the possibility that gallium atoms also diffuse into the QDs, thereby modifing their composition and increasing their bandgap energy. In this letter, we demonstrate that, indeed, gallium atoms are incorporated into QDs grown on a thin, tensile strained layer of $Ga_xIn_{1-x}P$ inserted between the InAs QDs and the InP substrate. Thus, we conjecture that diffusion of atoms during the growth must be taken into account and can be utilized in studies and engineering of strained self-assembled QDs, in these and other similar material systems.

Under certain growth conditions, InAs QDs grown on InP are only a few monolayers (ML) high.[2–5] In these circumstances, the photoluminescence (PL) spectrum of an ensemble of QDs is composed of distinct spectral lines. Each such spectral line is due to emission from QDs having the same, monolayer-stepped, height. It follows that the highest energy line in the spectrum is due to recombination of carriers within the wetting layer. The next one in energy is due to recombination of carriers confined within QDs, which are 1 ML thicker than the wetting layer. The third line in decreasing energy order is due to QDs, which are 2 ML thicker, and so on. This unique feature of the QD ensemble's PL spectrum provides an unambiguous determination of the height distribution of the QDs. In this letter, we show that this feature can be efficiently used as means for probing the composition of the QDs.

The samples studied in this work were grown by a compact metalorganic molecular-beam epitaxy system at 510 °C.[6] Trimethylindium, triethylgallium, arsine, and phosphine served as group III and V sources, respectively. The samples consisted of a 200-nm-thick InP buffer layer, followed by a $Ga_xIn_{1-x}P$ layer, a single layer of 2.4 ML InAs QDs and a 50-nm-thick InP cap layer. The gallium content in the $Ga_xIn_{1-x}P$ layer was varied from $x=0$ to $x=0.3$. The $Ga_xIn_{1-x}P$ layer thickness was 10 nm for $x \leqslant 0.26$, and 5 nm for $x=0.3$. These thicknesses are well below the critical thickness for strain relaxation,[7] ensuring that the $Ga_xIn_{1-x}P$ layers are fully strained. The growth was interrupted for 40 s prior to and after the deposition of the QD layer.

Cross-sectional transmission electron microscopy (XTEM) was used to measure the size and density of the QDs. The XTEM samples were prepared by chemical thinning using a Br-methanol solution. The XTEM images were taken by a Phillips TM420 electron microscope operating at 120 kv. A typical TEM picture of two-stacked layers of InAs QDs on InP grown under the same conditions just described is shown in Fig. 1. Although a [200] dark-field condition was used to image the QDs in the figure, the presence of strain contrast around the QDs indicates a strong bending of the surrounding lattice planes induced by the mismatch. The thickness of the wetting layers is estimated as 0.6 nm; namely, slightly less than 2 ML. The height of the dot shown in the figure is about 2.5 nm, roughly 8 ML. The lateral

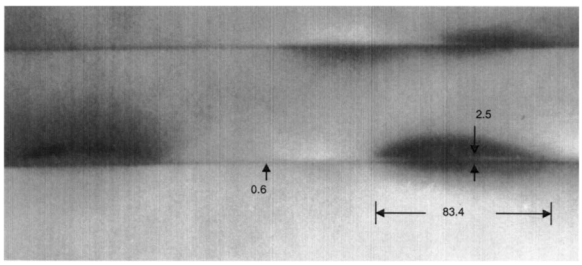

FIG. 1. TEM image of a double stack of InAs QDs grown on InP. Indicated dimensions are in nanometers.

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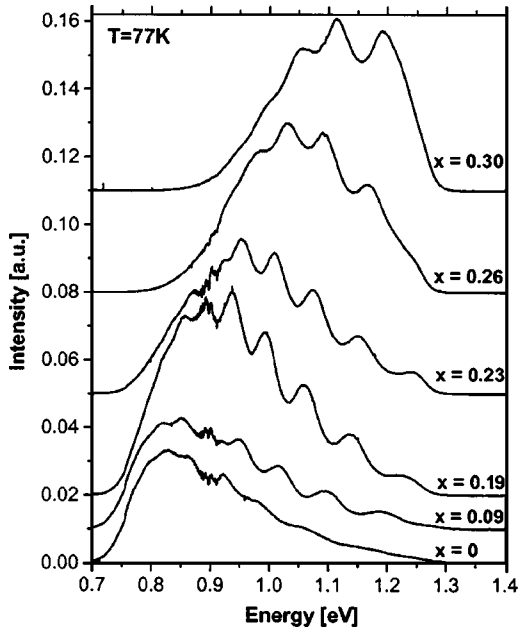

FIG. 2. 77 K PL spectra of nominally 2.4 ML InAs QDs layer on a $Ga_xIn_{1-x}P$ layer for gallium content ranging from $x=0$ to $x=0.3$.

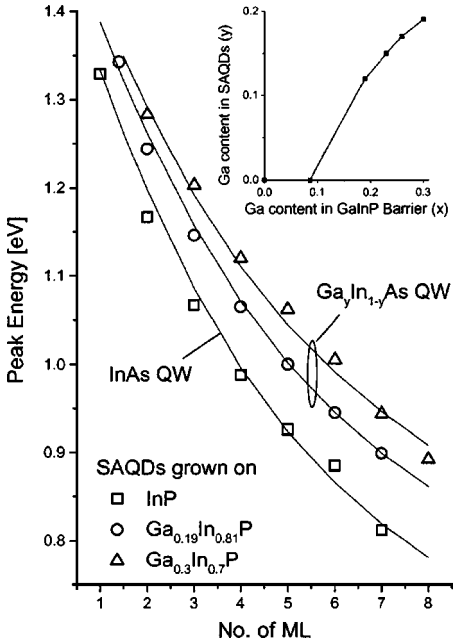

FIG. 3. Measured (symbols) and calculated (lines) QD PL emission energies at $T=1.8$ K. The inset shows the fitted gallium content in the QDs (y) as a function of the gallium content in the GaInP layer (x).

dimension of the QD is about 84 nm. The density of the QDs is estimated to be 5×10^9 cm^{-2} as measured by atomic force microscopy of uncapped samples, and by TEM for capped QDs.

The 77 K PL spectra of the samples are shown in Fig. 2. As can be seen in the figure, each spectrum is composed of a series of distinct spectral lines, as is the case for InAs QDs grown directly on InP.[2–5] The spectra are clearly shifting to the blue with the increase in the Ga content of the strained $Ga_xIn_{1-x}P$ layer. The blueshift is observed for both the entire spectrum and for the individual lines. The blueshift of the entire spectrum is due to a variation in the dot height distribution.[1] The density of the smaller dots increases, therefore, the entire spectrum shifts to the blue. We now follow the blueshift of the various lines as the Ga concentration in the GaInP strained layer is increased. Evidently, the multiline PL spectrum of the QDs grown on GaInP is also due to monolayer differences in the average height of the QDs. Hence, the number of monolayers in the various subsets of the QDs is exactly known. With this information at hand, their composition can be determined by fitting the PL lines spectral position to our model, using the composition as the only fitting parameter.

We note here that peaks in the PL spectrum of QDs are frequently attributed to emission due to recombination of electron–hole pairs from higher energy states of confined carriers in the QDs. Since the spectra reported here do not vary for four orders of magnitude variations in the exciting laser intensity, we safely rule out this interpretation.

The spectral positions of the various PL lines were calculated by an eight-band $k\cdot P$ model, which takes lattice mismatch strain into account.[8] In the calculations, bulk parameters from Ref. 8 were used. The lateral dimensions of the QDs are much larger than their heights, as can be clearly seen in the TEM image. For these dimensions, we found out that an infinite one-dimensional layer with thickness equal to that of the QD height can be safely used for the PL calculations. In Fig. 3, the calculated and measured 1.8 K QD PL peak energies are compared. An excellent agreement is obtained for the InAs QDs grown on InP. Our one-dimensional model thus coincides with the experimental data without any fitting parameters, for this known composition case. This precise agreement between experiment and theory supports the monolayer height fluctuation interpretation of the PL spectrum put forward in Refs. 2–5. It also rules out As/P partial exchange during growth or As/P interdiffusion, resulting in the formation of InAsP dots. Intermixing of As and P atoms may, evidently, lead to an exchange of an entire monolayer of As by P (or vice versa). This, however, just results in a decrease (or increase) by 1 ML in a particular QD height.

The PL peak positions of the QDs grown on $Ga_xIn_{1-x}P$ layers with higher ($x>0.1$) gallium contents are blueshifted compared to those of QDs grown directly on InP layers. We attribute this blueshift to diffusion of gallium atoms into the QDs. A change in the number of monolayers associated with each spectral line can be safely ruled out, since the lines that correspond to 2–8-ML-high QDs are clearly resolved in all the spectra. We have also verified by the simulation that the presence of the strained GaInP layer underneath the QDs alone does not significantly vary the energies of confined carriers within the QDs, and therefore does not explain the blueshift of the peak positions.

Having established that the blueshift of the individual line position is a fingerprint of Ga incorporation into the dots, the Ga concentration in the QDs was obtained by fitting the calculated peak position to the experimental data. The fitted values are presented in the inset to Fig. 3 as a function of the gallium content in the underlying $Ga_xIn_{1-x}P$ layer. Our results thus indicate that considerable amount of gallium atoms diffuse into the QDs during the growth. A possible driving force for the diffusion of gallium from the underlying layer into the QDs is that strain in both the underlying layer and the QDs layer is reduced by this process. This is also the case in the experiment reported in Ref. 1. Similar phenomenon of interdiffusion between QDs and their surrounding

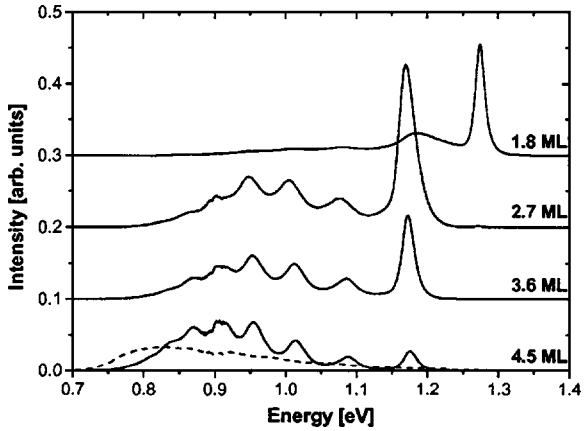

FIG. 4. 77 K PL spectra of nominally 1.8 to 4.5 ML $Ga_{0.18}In_{0.82}As$ QD layer on InP. Also shown, as a dashed line, is the 77 K PL spectrum of nominally 2.4 ML InAs QD layer on InP.

host material was also reported for InAs/GaAs QDs, where QD gallium concentrations as high as 50% were observed.[9]

To further demonstrate that the observed blueshift is due to gallium incorporation into the QDs, we have grown $Ga_{0.18}In_{0.82}As$ dots directly on InP. The spectral positions of the peaks in the PL spectrum from this sample are shown in Fig. 4. They agree well with our model calculation for this sample, for which the Ga concentration within the QDs is accurately known.

In conclusion, we have demonstrated that gallium atom diffuse from an underlying $Ga_xIn_{1-x}P$ layer into InAs QDs during crystal growth. This effect is responsible for the experimentally observed blueshift in the photoluminescence from these dots, as quantitatively accounted for by our model.

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