STEM imaging of InP/AlGaInP quantum dots

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Abstract. InP quantum dot structures embedded between ternary AlInP, ternary GaInP or quaternary AlGaInP have been grown by metal organic vapour phase epitaxy on GaAs(001) at temperatures of 640 ºC or 730 ºC under different growth conditions and were investigated by scanning transmission electron microscopy (STEM). We found quantum dots higher than 2nm only for samples grown at 640 ºC and the sample grown at 730ºC with the lowest growth rate and additional growth interrupts. For the higher growth temperature and high growth rates quantum dot sizes evolve differently: the dots either stay much smaller and remain embedded into the wetting layer, essentially forming quantum wells with lateral compositional variations, or occasionally they can form agglomerates of super-size islands that protrude to the surface. This demonstrates that quantum dot formation is favoured by slow growth, while fast kinetics promotes flat layer growth.

1. Introduction
InP quantum dots (QDs) embedded between (Al)GaInP lattice matched to GaAs substrates emit around 700-800nm wavelength. This is potentially useful for applications as laser diodes (LD) [1] or semiconductor saturable absorber mirrors (SESAMs) [2]. Therefore, it is very important to control both the microstructure and the chemical composition of such QDs. In this study four samples with different growth temperatures, different growth rates and growth interrupts have been compared.

2. Experimental
InP QDs were grown by metal organic vapour phase epitaxy (MOVPE) on GaAs (001) substrates. Table 1 presents the nominal structures of the QD layers and growth conditions. Electron transparent <110> cross-sectional specimens were prepared by standard methods, gluing together stacks of material, then cutting, grinding, polishing and finally Ar⁺ ion milling them until perforation.

| sample number MR | 2629 | 2620 | 2725 | 2727 |
|------------------|------|------|------|------|
| growth temperature (ºC) | 640 | 730 | 730 | 730 |
| growth rate (nm/sec) | 0.38 | 0.76 | 0.76 | 0.38 |
| growth interrupt | 20sec | none | none | 10sec |
| upper barrier | GaInP | GaInP | AlInP | AlInP |
| InP QD thickness (nm) | 1.50 | 0.70 | 0.76 | 0.76 |
| lower barrier | GaInP | AlGaInP | AlInP | AlInP |
| repeat sequence | ×6 | ×5 | ×5 | ×5 |

Table 1. Structural details and growth conditions
We applied bright-field (BF) and annular dark-field (ADF) STEM in a JEOL 2010F field-emission transmission electron microscope equipped with a scan unit, providing an electron beam ~0.25nm in size at ~10mrad semi-angle of beam convergence and 0.5mm spherical aberration constant. The intensity in ADF imaging is approximately proportional to the square of the average atomic number (‘Z-contrast’) if the inner collection angle is very large and the specimen uniformly flat.

3. Results
BF and ADF STEM imaging have been used to study the density and the size of the QDs. Example images are shown below, with the growth direction pointing from bottom left to top right.

Figures 1a and 1b show stacks of quantum dots in sample MR2629 where the QDs in the lower two or three layers have a well-defined dot geometry while the upper ones appear flatter and laterally diffuse. The GaInP barriers are relatively narrow, so QDs in successive layers are pushed upwards. Their In content appears maximum in the upper halves of the nominally pure InP QDs, indicating some intermixing at least with the lower barriers. Also, in some areas, such as in Figure 1c, cation ordering on alternating \{111\} lattice planes is visible, pointing to the onset of spinodal decomposition in the ternary GaInP alloy [3] of the barrier.

Figure 1. MR2629: overview at 250kX magnification in BF (a) and ADF (b) mode; ADF lattice images of QDs at 1.2MX magnification (c).

Figure 2 shows that the quaternary AlGaInP/InP/GaInP structures (MR2620) are almost planar, and a well-defined In-rich layer ~2.5nm wide with lateral compositional variations is formed above the lower barriers. These may be considered QDs that are still embedded in the wetting layer formed typically during strained layer epitaxy.

Figure 2. MR2620: overview at 200kX in BF (a) and ADF (b); lattice image at 1.2MX in ADF (c).
Figure 3. MR2725: ADF images at 80kX (a, c) and 600kX magnification (b).

Figure 3 presents the QDs formed in MR2725, which are mostly very small and difficult to resolve (cf. Figure 3a). Only occasionally do they form proper QDs under 10nm in height (Figure 3b) or agglomerate into very large islands that protrude to the surface (cf. Figure 3c). Sample MR2727 shown in Figure 4, however, exhibits a rather broad and continuous size distribution of QDs.

Figure 4. MR2727: ADF images in overview at 80kX (a) and at 500kX magnification (b, c).

4. Discussion
From the ADF STEM images acquired from individual sample regions 10-20µm in total length we produce a table comparing the samples qualitatively.

| sample code | height of individual QDs |
|-------------|--------------------------|
|             | S <2nm | M 2-5nm | L 5-10nm | XL 10-15nm | XXL >50nm |
| MR2629      | -     | -       | 14       | 96         | -         |
| MR2620      | 180   | -       | -        | -          | -         |
| MR2725      | 1210  | 3       | 2        | -          | 65        |
| MR2727      | 1107  | 56      | 34       | 13         | -         |

Table 2. Comparison of the height of the InP QD in the various samples studied

According to the STEM images, all samples produce InP QDs stacked along the growth direction (only in MR2727 the stacking is slightly oblique). For the lowest growth temperature and growth rate, InP QDs 5-15nm in height are formed between GaInP. Those QDs formed first are very pronounced while the upper QDs grown later are flatter and have been pushed upwards by the underlying ones.

When the growth temperature is increased to 730°C and the growth rate is doubled, the InP layers generally become more planar and it is difficult to observe obvious QDs. An In-rich layer is formed between AlGaInP and GaInP barriers, with intensity fluctuations indicating the onset of formation of
QDs embedded within wetting layer. In order to improve the contrast in the ADF images and study the formation of InP QDs in more detail, the barrier materials around the QDs have been changed to ternary AlInP, retaining the same growth temperature of 730ºC, while the growth rate for one sample was kept at 0.76nm/sec and for another one it was halved and a 10sec growth interrupt was applied as well. The size and density of the QDs in these samples have been investigated further.

MR2725, which grew fast and without interrupts, yielded many small QDs near to each other, while larger QDs as shown in Figure 3b and 3b only appeared once over ~10µm field of view. Sample MR2727, with reduced growth rate and growth interrupts, has QDs of many different sizes, with heights ranging from ~2nm to 13nm and widths from 17 to 56nm. Figure 5 presents histograms after investigating ~100 QDs. Neglecting contrast reduction due to finite collection angles [4] we can in this system approximate a compositional map of In, the heaviest element, by calculating the square root of the ADF image intensity. The heights and widths of the QDs have been measured as full widths at half maximum (FWHM) of intensity line profiles across the square root of the ADF image intensity map.

![Figure 5. Sample MR2727: height distribution (a) and width distribution (b) of ~100 QDs resolved.](image)

Figure 6 shows a histogram of the distances between adjacent QD stacks acquired from images taken at magnifications of 60kX or 80kX. With reduced growth rate plus growth interrupt the average distance between two nearby QDs is nearly doubled and the standard deviation increased. Moreover, the sample grown slower and with growth interrupt shows a bimodal distribution of the QD spacing, indicating slow growth leads to QD formation while rapid growth inhibits their formation kinetically.

![Figure 6. Histogram of the distances between adjacent QD stacks with AlInP barriers.](image)

5. Conclusion
InP QDs can be produced by using MOVPE at relatively low growth temperature of 640ºC or, at higher growth temperature of 730 ºC, if slow growth rates are used and growth interrupts are applied. Rapid growth favours epitaxy of quantum wells and suppresses the QD formation.

References
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