Spontaneous quantum dot formation due to strain induced phase segregation of GaInAs

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Introduction

During the last few years, spontaneously formed quantum dots (QDs) have received a lot of attention due to the inherent high crystalline quality exhibited by such structures. It has been observed that InAs quantum dots grown on InP substrates have great potential for future device applications in optics as well as electronics [1,2]. However, this materials system has been shown to be extremely sensitive to surface chemistry effects, like As/P exchange reactions [3,4] which in the extreme case could produce excess InAs enough to form QDs on a patterned surface, even without any actual InAs deposition [5].
A commonly used technique to create artificial molecules by the use of self−assembled quantum dots has been to stack them vertically [6,7]. A first layer of seed dots is grown, and dots in successive layers arrange on top of each other if the separating material between them is thin enough, due to a local expansion of the lattice constant just above the buried dots. For an overview of stacked quantum dots, see ref. [8].
Size and shape of quantum structures are important factors for their electronic and optical properties. Commonly, atomic force microscopy on freestanding or transmission electron microscopy on buried dot structures has been used to characterize the morphology of the dots. Recently, reports have been made on the use of cross−sectional scanning tunneling microscopy (XSTM) to characterize buried quantum dots in the InAs/GaAs system [9−14]. Using X−STM it is possible to obtain atomic resolution images of narrow cross−sections of quantum dot structure. This results in very detailed information about the local dot structure, defects and local variation in the stoichiometry. In the case of InAs dots in GaAs it was found that the spatial structure, and thereby the electronic structure, of the quantum dots and wetting layer is strongly dependent on the specific growth conditions.
We report on the first XSTM investigations made on InAs QDs in InP. We grew nominally five−fold dot stacks of QDs, but find that commonly six dots are observed in the stacks. The sixth dot is observed on top of the final InP barrier, where no actual InAs was deposited. The dots seem to spontaneously form by phase segregation of the ternary GaInAs that is grown on top of the InP material, and from As/P exchange reactions.

Experiments

The samples were grown by low pressure (50 mbar) MOVPE, using phosphine (PH3), arsine (AsH3), trimethyl−indium (TMI) and trimethyl−gallium (TMG) as precursors. The molar fractions were $5x10^{-4}$ for arsine, $1.5x10^{-2}$ for phosphine, with Sn−doped (n+) InP (001) serving as substrate.
A buffer of 250 nm GaInAs, which also served as a marker for the XSTM measurements, was first grown, at 600 °C, after which the first 5 nm InP was deposited. Growth was then interrupted, the temperature being ramped down to 500 °C for the deposition of dot material on a well−defined surface on which monolayer (ML) high steps were located [15]. The five dot layers were grown by deposition of either 1.5 ML, 1.2 or 0.9 ML for different samples, at a growth rate of 0.3 ML/s. The dots were subsequently annealed under arsine for 12 s. InP layers with thickness of nominally 15 nm were grown in−between these dot layers. Then 12 nm InP was grown on top of the fifth dot layer. During this step the temperature was ramped up to 600 °C for the subsequent growth of 20 nm GaInAs, which served as a marker for XSTM, and then 300 nm InP. STM measurements were carried out in a separate chamber, using a commercial Omicron STM, with a special sample holder for cleavage. All samples were cleaved in ultra high vacuum at a pressure < 1x10−10 Torr. The cleavage exposed the [110] surface plane of the crystal, and all images shown are filled state images recorded at −2V and 0.2nA.

Results and discussion

Figure 1 shows a schematic of the grown structure, together with an AFM image of freestanding InAs QDs that would correspond to the seed dot layer when 1.5 ML InAs had been deposited on the InP surface. The density of the QDs is 1.3×10^{10} cm^{-2}, which most probably is slightly lower than the corresponding density for capped dots [16].

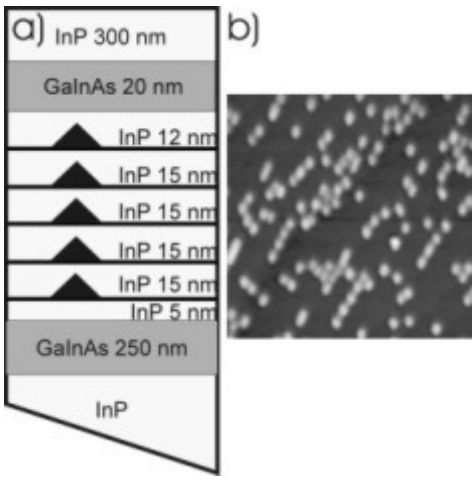

Fig. 1 a) Schematic of the grown structure and b) 1×1 μm^2 AFM image of the seed dot layer after 1.5 ML InAs deposition on InP

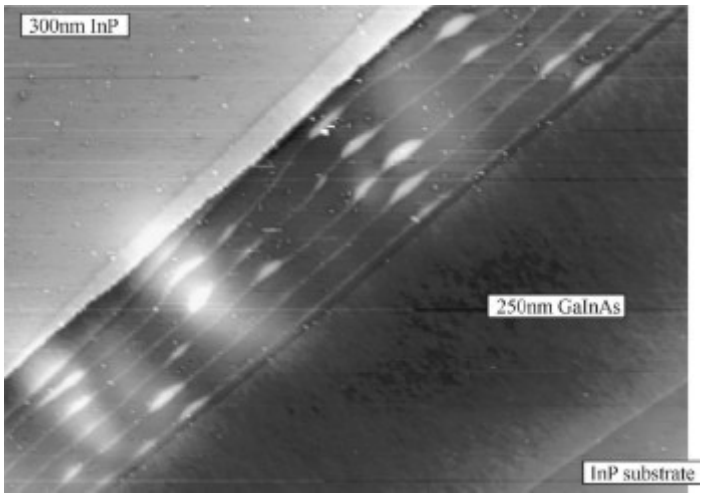

Fig. 2 Cross sectional STM image of several quantum dot stacks. Growth direction is from bottom right to top left.

Figure 2 shows an XSTM image of five−dot stacks of InAs dots. The growth direction is from lower right corner to upper left corner. From evaluating a number of dots we find that the dots have baseline widths of 25−30 nm and a height of 5−6 nm in good agreement with previous TEM and AFM measurements. In these quantum dot stacks, the dots are not always perfectly aligned vertically on top of each other. We believe that this is due to dots that have nucleated nearby the forming stack, causing a shift of the strain energy minima at the surface from the centre of the visible seed dots. From figure 2 it is evident that some stacks are stable, whereas some are eliminated and simply end during growth, this has been observed before for InAs/GaAs QDs [11]. The elimination of columns has been previously described as occurring because the overlap in the strain fields from adjacent columns produces a minimum in strain energy on the top surface between nearby columns [7]. It is also visible that the dots increase in

size for each new layer. Materials competition will contribute to the extinction of some columns.

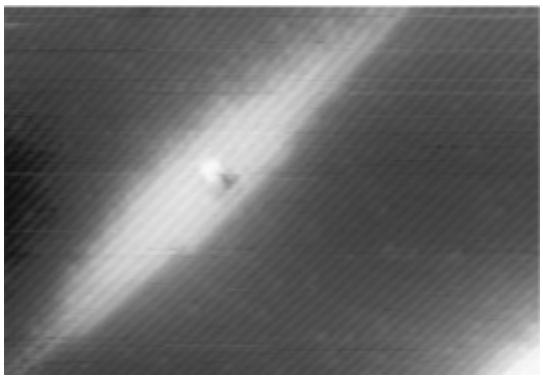

Fig. 3 High−resolution XSTM image showing atomic resolution of the group V rows on one InAs dot in a stack.

On figure 3 the atomic rows of the group V elements, i.e., the As and P atoms are resolved on one of the dots. Besides from a single large defect induced after the cleavage, there are no slight depressions visible in the bright quantum dots, which indicates a pure InAs stoichiometry [17]. This is interesting as the As/P exchange reactions are severe and could lead to P incorporation into the QDs, $InAs_x P_{1-x}$. A very interesting observation is shown in figure 4, where a XSTM image shows two adjacent quantum dot stacks. There are not only the five intentionally grown dots in the stack, but a sixth dot is formed in the stack on top of the final 12 nm InP barrier, directly on the InP/GaInAs interface.

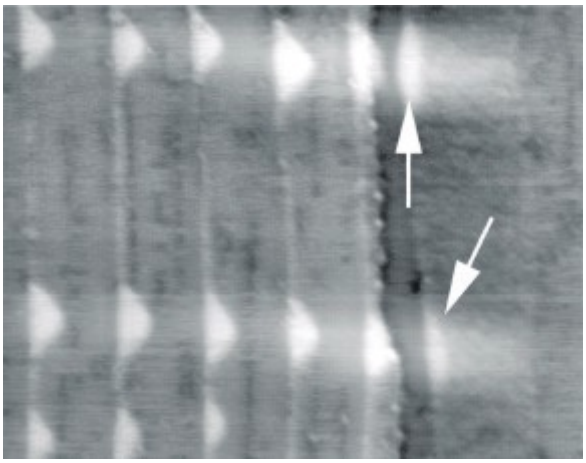

Fig. 4 Cross−sectional STM image of two adjacent six−fold QD stacks. Arrows indicate the spontaneously formed dots.

We can see two possible mechanisms that contribute to the nucleation of this additional dot layer. i) In has a longer diffusion length in comparison to Ga on the growing surface [18]. During growth of the ternary GaInAs, In diffuses towards the tensile strained areas with a locally lowered chemical potential, for the InAs species, just above the buried stacks. This leads to a phase segregation of the GaInAs, resulting in accumulation of InAs just above the stacks. ii) As/P exchange reactions have been shown to be more aggressive at strained regions [19], and thus more material for dot formation should be available above the stacks, as compared to areas with less strain. We speculate that this effect could also be a reason for the ML thick fluctuation in the InP layer thickness just beneath a formed dot, seen in high resolution images of the dots (figure 3), as one extra ML of InP may be consumed and converted into InAs. Another possibility is, of course, non−complete planarization of the InP surface during the 15 nm InP growth.
In figure 4, one can also observe throughout the 20 nm thick GaInAs layer light−colored or dark−colored features

corresponding to indium−rich or gallium−rich regions, respectively, deriving from GaInAs phase segregation. In enriches in the GaInAs vertically above the QD stacks, in contrast to earlier observations of phase separated InAlAs induced by buried QDs, which then led to anti−correlated stacking of InAs dots [20].

Summary

We have presented the first XSTM results of stacked InAs/InP QDs, enabling us to study the structure in atomic resolution. We found that, when capping a structure of QDs embedded within InP barriers with GaInAs, strain induced phase separation of the GaInAs caused the formation of an additional, spontaneously formed, non−intended QD layer. To which extent As/P exchange reactions contribute to dot material is unclear. These results are important for the understanding and design of structures for electrical and optical purposes within this materials system.

Acknowledgements

This work was carried out within the Nanometer Consortium in Lund and was supported by grants from the Swedish Science Council (VR), Crafoordska Stiftelsen, and the Swedish Foundation for Strategic Research (SSF).

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