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Transformation of Self-Assembled InAs/InP Quantum Dots into Quantum Rings without Capping

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ABSTRACT

Transformation of self-assembled InAs quantum dots (QDs) on InP(100) into quantum rings (QRs) is studied. In contrast to the typical approach to III–V semiconductor QR growth, the QDs are not capped to form rings. Atomic force micrographs reveal a drastic change from InAs QDs into rings after a growth interruption in tertiarybutylphosphine ambient. Strain energy relief in the InAs QD is discussed and a mechanism for dot-to-ring transformation by As/P exhange reactions is proposed.

Ring-shaped semiconductor nanostructures, that is, quantum rings (QRs) or nanorings, have gathered growing attention in recent years. These structures have many interesting electronic properties[1] and have been shown experimentally to confine carriers into ringlike quantum states.[2] QRs also provide a means to study quantum effects involving magnetic flux.[3]

Most of the experimental work in this field has been done on In(Ga)As/GaAs QRs. By capping self-organized InAs quantum dots (QDs) by a thin GaAs layer followed by a growth interruption, we find that a dot shape change into ring takes place.[4] Although the detailed mechanism of this transformation is still unknown, two models have been proposed. According to a thermodynamic model,[5] the material redistribution is due to a change in the InAs dot surface energy caused by the GaAs capping layer. A kinetic model,[4] however, explains ring formation by the different surface diffusion rates of Ga and In atoms. In addition to these models, a study has shown that strain relaxation of the dot has to be taken into account to explain the formation of SiGe/Si QRs.[6] Other QR material systems also differ from the above growth considerations because CdTe/ZnTe[7] and GaSb/GaAs[8] QRs have reportedly been achieved by direct deposition.

In a recent paper[9] in which InAs/InP QRs were fabricated by partially capping InAs QDs by InP, the experimental data was reported to disagree with the kinetic model. The difference in group III surface mobilities cannot explain the ring formation because, in contrast to InAs/GaAs QRs, both compounds here share the same group III atom. Instead, group V exchange reactions have been shown to be major contributors to the formation[10,11] and shape[12] of InAs nanostructures on InP.

In this paper, quantum rings are fabricated by annealing as-grown InAs QDs in a phosphorus ambient. Unlike the typical method, no capping of dots is utilized to achieve the dramatic change in the QD morphology. We also study the effect of temperature on the InAs/InP dot-to-ring transformation. The formation mechanism of QRs is discussed in terms of As/P exchange and the strain of the QD/QR system. The advantage of this QR fabrication process is that it separates the capping step from the ring formation. Thus, the capping of the rings can be studied separately. Moreover, it may allow the use of alternative capping materials, such as ternary or quarternary compounds in the design of InP-based QR structures.

The samples were fabricated by metal-organic vapor phase epitaxy (MOVPE) under atmospheric pressure. Hydrogen was used as a carrier gas while utilizing trimethylindium (TMI), tertiarybutylphosphine (TBP), and tertiarybutylarsine (TBA) as precursors. The epitaxial layers were grown on semi-insulating InP(001) wafers. Prior to deposition, the substrates were annealed for 5 min at 650 °C after which a 100-nm InP buffer layer was grown at 640 °C. The temperature was subsequently decreased to 560 °C where 0.6−1.0 monolayers (MLs) of InAs were deposited at a growth rate of 0.8 ML/s. The self-organized growth of coherent InAs/InP QDs by MOVPE is described in more detail elsewhere.[11] Following the deposition of InAs QDs, a 10-s flush in TBA was performed after which the group V

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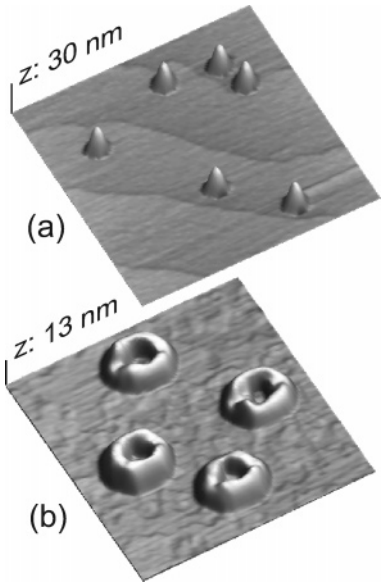

Figure 1. Atomic force micrographs of InAs QD samples (a) flushed with TBA during cooldown and (b) annealed in TBP for 9 s at 560 °C. The lateral scale of the images is 1.4 × 1.4 μm^2. Note the different vertical scales.

precursor flow was switched to TBP. The temperature and duration of the anneal in TBP were varied. A reference uncapped QD sample was also grown where TBA was not switched to TBP. The surface morphology of all of the samples was imaged ex situ by contact-mode atomic force microscopy (AFM).

Figure 1a shows the AFM image of the reference InAs QD sample. Islands with an average height of 28 nm, a base diameter of 110 nm, and an areal density of 1.8×10^8 cm^{-2} are observed. For the sample shown in Figure 1b, the procedure following the InAs QD growth was different: the sample was annealed for 9 s in TBP at 560 °C after which the temperature was ramped down. The AFM image clearly shows ring-shaped structures (QRs) 8−10 nm in height, with an areal density of 7.2×10^7 cm^{-2}. Pronounced differences between the QD and the QR morphology are seen in the AFM cross section profiles in Figure 2. It should be acknowledged that because of the finite curvature of the AFM tip, the lateral size of the features is somewhat exaggerated. The QR (solid line) has a distinct center hole and the inner and outer diameters are 90 and 330 nm, respectively. Comparing to the width of the reference QD (dotted line), it can be noted that most of the QR material has moved outward from the initial dot location. Based on the AFM data, the volumes of the QD and QR are estimated to be of the same magnitude.

To understand the transformation of the InAs QD morphology during the TBP anneal, the elastic strain relaxation in the island is considered first. It has been shown that the chemical potential of partially relaxed, coherent InAs/GaAs islands causes Ga adatom migration away from the QD top surface.[13] Similarly, the top of the InAs/InP QD is an energetically unfavorable site for InP growth. Thus, if In adatoms are released from the InAs QD under P overpressure, then they would migrate outward along the surface of the

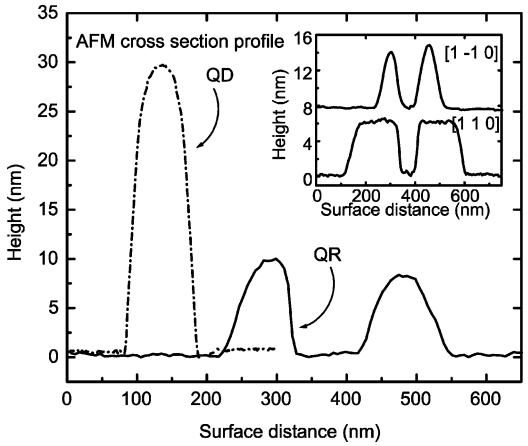

Figure 2. AFM cross section profiles, taken along the [1 −1 0] direction, of an InAs QD (dotted line) and a QR (solid line) formed at 560 °C. The inset shows corresponding profiles of a QR formed at 540 °C, taken along the [1 −1 0] and the [1 1 0] direction. The curves are offset for clarity.

island.[12] This diffusion, together with As/P exchange, may be the driving force behind the mass redistribution from QD to QR.

QD strain distribution was considered recently to explain the formation of SiGe/Si QRs,[6] as already mentioned. In that case, Si from partial capping layer deposition diffuses outward from the top of the Ge QD. Simultaneously through surface segregation and diffusion, Ge atoms are released from the QD. They mix and alloy with Si on the QD side surface where the lateral lattice constant matches SiGe with varying composition. In another paper,[12] strain-driven In migration off partially capped InAs/InP QDs was shown to result in a modification of the QD morphology, even holes. Both of these reports verify the significance of strain-controlled surface diffusion effects.

Returning to the experimental data, AFM images showing the effects of temperature and duration of the TBP annealing to the formation of rings are seen in Figure 3a−d. The QR sample annealed for 9 s at 560 °C is shown again in Figure 3a. The base of each ring has a hexagonal shape that resembles the base shape and orientation of faceted InAs[14] and InP[15] islands. For the sample in Figure 3b, the annealing step was skipped and the temperature was ramped straight down from 560 °C after TBA was switched to TBP. Instead of rings, hexagonally shaped islands are seen. Thus, the formation of QRs in a is due to the 9-s anneal in TBP, not the TBA flush or the ramp-down of temperature in TBP. For the next sample in Figure 3c, a 9-s TBP anneal was performed at 540 °C. Hexagonally shaped islands, elongated in the [1 1 0] direction, are observed. Increasing the annealing time to 54 s leads to rings, shown in Figure 3d. As opposed to QRs in Figure 3a, the rings formed at 540 °C are notably elongated in the [1 1 0] direction, also illustrated by the AFM cross section profiles in the inset of Figure 2. By comparing Figures 3 a−d, the rate of material redistribution in the dot-to-ring transformation is noted to decrease as the temperature decreases. With decreasing temperature, both As/P exchange[16] and In surface migration slow down, which might explain the observed trend.

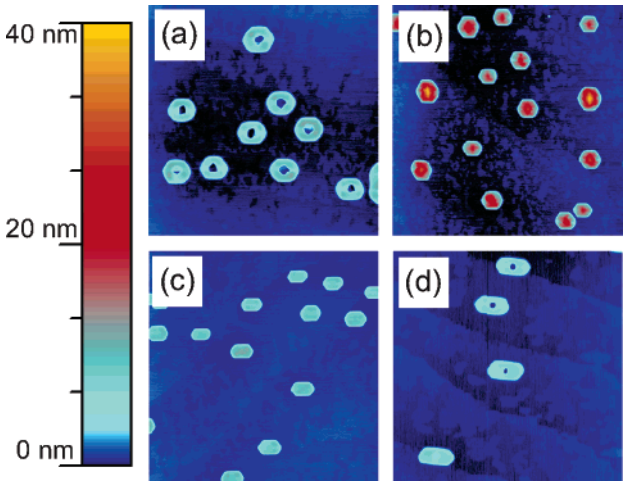

Figure 3. Atomic force micrographs ($3 \times 3\ \mu m^2$) of samples with varying TBP annealing procedures following a 10-s TBA flush of InAs QDs. The samples were annealed for (a) 9 s at 560 °C, (c) 9 s at 540 °C, and (d) 54 s at 540 °C. In b, the temperature was ramped straight down from 560 °C in a TBP ambient.

Revisiting the formation mechanism of the QR and considering the role of As/P exchange, some interesting observations are made. It is assumed that As released from the InAs QD and wetting layer is reincorporated to some extent in the QR. This is supported by the finding that residual As atoms remain on an MOVPE-grown In(Ga)As surface for several seconds even at 620 °C.[17] Therefore, the QR is most likely ternary $InAs_yP_{1-y}$. To determine the exact composition of an uncapped QR, however, one would need a detailed TEM study. Furthermore, it has been reported that under arsenic overpressure, In atoms tend to migrate from a strained InP surface toward the apex of InAs islands.[18] Thus, if both As and P exist at the periphery of the dissolving InAs QD, a balance between In(P) migration away from and In-(As) migration toward the island might in part explain the formation of the ring structure. As the ring grows, it offers further incorporation sites for new In atoms released from the remaining QD.

A schematic diagram of the proposed QR formation process is shown in Figure 4: When TBA is switched to TBP, As/P exchange releases In atoms from the InAs lattice (a). The In adatoms migrate toward the base of the InAs island where the lateral lattice constant is closer to InP (b) and are reincorporated at an energetically more favorable site. Material redistribution continues (c) until the initial InAs island has vanished.

It should be emphasized again that in this work QRs are fabricated uncapped. Thus, in our case, the thermodynamic model, which assumes that the QR is formed as the surface energy of the QD with respect to a partial capping layer is minimized, would not offer a plausible explanation. The mass transportation and strain minimization associated with QR formation is most likely a complex process with both kinetic and thermodynamic characteristics. Here the dot-to-ring transformation seems to be dominated by kinetic effects, however.

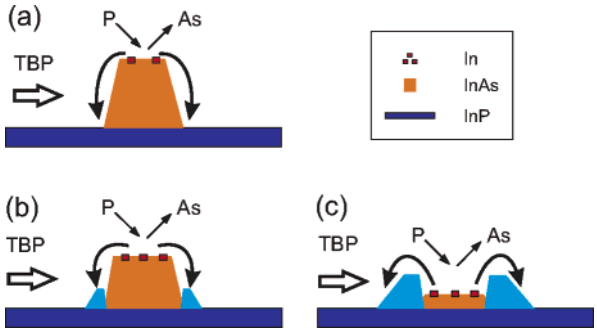

Figure 4. Schematic diagram of the dot-to-ring transformation of an InAs/InP QD. (a) In atoms are released by As/P exchange and migrate outward from the InAs island. (b) In atoms are reincorporated at the interface of the QD and the flat surface. (c) Material redistribution continues until the initial InAs island has disappeared.

In summary, quantum rings with distinct cross section profiles were fabricated by annealing as-grown InAs quantum dots in TBP. At 560 °C, the dot-to-ring transformation took place in 9 s but at 540 °C the process had already slowed notably. The formation of rings was discussed in terms of As/P exchange and migration of thus-released In atoms away from the partially relaxed island apex. Because of group V exchange reactions, the uncapped rings were assumed to consist of $InAs_yP_{1-y}$. The presented transformation process adds a degree of freedom to the design of QR structures as the capping of the rings can be executed separately from the ring formation.

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