Reversing the shape transition of InAs/GaAs (001) quantum dots by etching-induced lateral In segregation

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The shape evolution of epitaxially grown InAs/GaAs(001) quantum dots after the controlled removal of material by an *in situ* etching gas is investigated by atomic force and scanning tunneling microscopy. The presence of {137} facets on the surface of partially etched quantum dots and the appearance of small two-dimensional islands for long etching times indicate the reversal of the shape transition that occurs during growth. This reversibility impressively confirms that both the growth process and the etching process are dominated by thermodynamic factors. We find that the evolution of the quantum dots is not determined by direct etching but is mainly caused by the etching of the wetting layer and the subsequent diffusion of In atoms from the quantum dots onto the bare GaAs, thus rewetting the substrate.

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I. INTRODUCTION

Because of their potential applications in optoelectronics and quantum computation,[1] self-assembled semiconductor quantum dots (QDs) grown by lattice mismatched heteroepitaxy have been studied extensively over the last years. In order to design QDs with specific properties, it is necessary to achieve control over their size, density, shape and homogeneity. This requires a detailed understanding of both the growth processes and possible postgrowth modification. InAs/GaAs(001) is the most frequently used QD material system as it is interesting for optoelectronic applications. Its growth mode is of the Stranski-Krastanow type, where the formation of three-dimensional (3D) islands proceeds after the completion of a two-dimensional (2D) wetting layer (WL). The shape of the 3D islands changes as their size increases. For InAs QDs grown on GaAs(001) the early stage of the 3D growth exhibits small flat platelets that at first transform into shallow pyramidal islands and subsequently into bigger islands of a higher aspect ratio when a critical size is reached.[2–7] While the small islands (called pyramids) consist of flat {137} facets, the bigger islands (domes) have additional steeper facets of {101} and {111} type. This growth transition raises the question whether a symmetric backward transition occurs if material is removed from the fully developed QDs, as has been recently observed for SiGe islands on Si(001).[8]

A controlled removal of material can be either achieved by In desorption[9] or by AsBr$_3$ *in situ* etching.[10] The former possibility brings the disadvantage that high substrate temperatures are required for In desorption. In contrast to that, AsBr$_3$ *in situ* etching provides etching control on the atomic scale without the need for high temperatures. For planar structures, it occurs in a layer-by-layer fashion and the etching rate can be controlled by the flow of supplied etching gas.[10] Thus, it represents a flexible method for the controlled removal of material. The integration of *in situ* etching into the growth process has been used to fabricate a large variety of novel nanostructures, e.g., nanoholes,[11] or GaAs/AlGaAs QDs.[12] For this purpose, etching rates of about 0.2 monolayers/s (ML/s) are used, which lead to etching conditions typically far from thermodynamic equilibrium.

In our study we apply AsBr$_3$ *in situ* etching at low rates to systematically change the size and shape of InAs/GaAs(001) QDs. At the etching rate used here (∼0.04 ML/s), which is comparable to the In deposition rate during growth, our system is closer to thermodynamic equilibrium. Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) allow us to gain detailed insight into the shape evolution of the islands. Thus, our study provides information on the etching mechanism and the rearrangement of the atoms on the surface. We find that the island size decreases much faster than expected for a direct removal of InGaAs and that the island shape changes during etching. We ascribe these observations to In migration away from the islands as the WL is being etched. The main driving force for this "lateral segregation" is the tendency of InAs to wet the GaAs substrate because of its lower surface energy.

II. EXPERIMENTAL

The nanostructures were grown on a GaAs(001) substrate in a solid source molecular-beam epitaxy chamber equipped with an AsBr$_3$ etching unit. After oxide desorption a 600 nm thick GaAs buffer layer was grown at 610 °C in order to provide a smooth surface for QD growth. The substrate temperature was calibrated by observing the (2×4) to c(4×4) transition in the GaAs surface reconstruction monitored *in situ* by the characteristic reflection high energy electron diffraction pattern. Subsequently the substrate temperature was lowered to 470 °C and 1.8 ML of InAs were deposited at a growth rate of 0.008 ML/s and an As$_4$ beam equivalent pres-
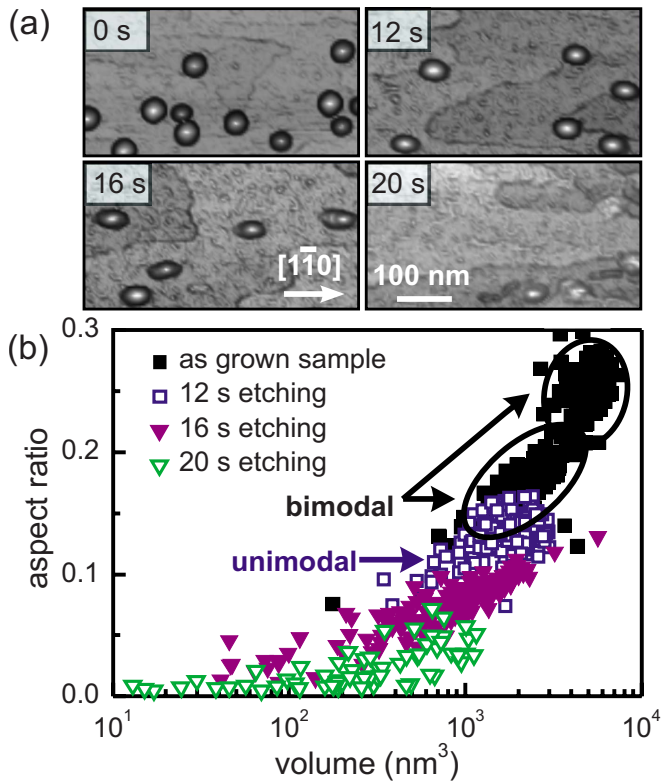
FIG. 1. (Color online) (a) AFM images of InAs/GaAs(001) islands exposed for increasing time to *in situ* AsBr$_3$ etching. The grayscale corresponds to a combination of surface height and slope to enhance small scale details. (b) Scatter plot of the islands' aspect ratio (height divided by square root of the base area) versus island volume extracted from 2×2 μm^2 AFM images for different etching times.

sure of 1.0×10^{-5} mbar. After a growth interruption of 30 s, AsBr$_3$ was introduced at a nominal etching rate of ~ 0.04 ML/s (for planar, unstrained InAs). Etching times of 0, 12, 16, and 20 s were used, followed by an immediate cooling of the samples to room temperature to freeze the surface morphology. Sample characterization was performed by both AFM measurements under ambient conditions and ultrahigh-vacuum (UHV) STM. An UHV suitcase was used in order to transfer the samples into the STM without breaking the vacuum.

III. RESULTS AND DISCUSSION

A. Backward transformation of InAs islands

Figure 1(a) shows representative AFM images of the as-grown and etched samples; the grayscale in these images corresponds to a combination of the local surface height and slope. As expected, with increasing etching time the dots become smaller until they lose their well-defined shape and only small 2D islands and small mounds remain on the surface. Scatter plots, where the aspect ratio of individual dots is plotted against their volume [see Fig. 1(b)], provide a quantitative description of the shape transformation. These plots were determined by analyzing large range AFM images
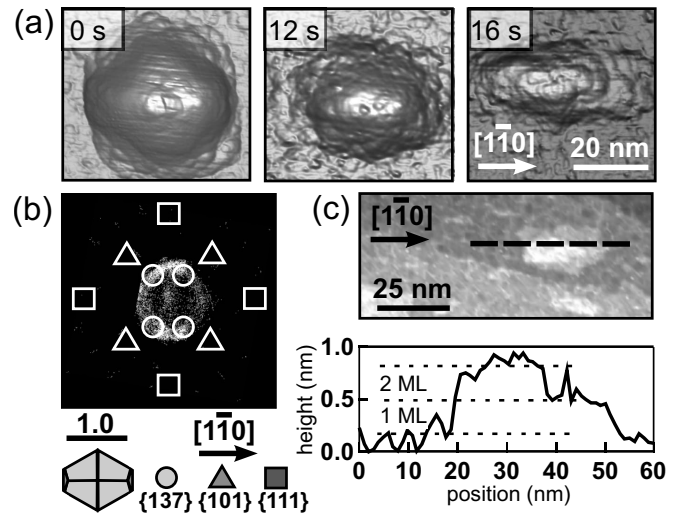

FIG. 2. (a) STM images of InAs QDs etched for different etching times. (b) Facet plot corresponding to an STM image of a 12 s etched sample. The main surface orientations are indicated. A structural model of a pyramid is also shown. (c) STM image of a 16 s etched sample. The graph shows the profile of a 2D island along the dashed line. The grayscale of the shown STM images corresponds to a combination of surface height and slope.

(2×2 μm^2). The aspect ratio was calculated by dividing the height by the square root of the area for each of the QDs. AFM tip convolution effects might slightly overestimate the exact island volumes and underestimate the aspect ratios but their relative changes should not be significantly affected. The as-grown islands are characterized by a typical bimodal size distribution,[2,13] which, however, changes to unimodal upon etching [see Fig. 1(b)]. A similar but reverse transition (unimodal to bimodal) is observed during growth.[2] In the course of etching, the QDs shrink and change their shape from high to low aspect ratio until they finally disappear. The absence of islands with high aspect ratio on the etched samples indicates that domes disappeared completely. Both observations give a first indication that a backward shape transition with respect to the growth process takes place during etching. In addition to their size reduction, the islands become elongated in the $[1\bar{1}0]$ direction [see Fig. 1(a)].

While the AFM images provide insight into the size distribution of a larger ensemble of islands, the analysis of single islands by means of STM offers the possibility to gain direct information on their shape. Figure 2(a) shows STM images of the QDs after etching times of 0, 12, and 16 s, respectively. The as-grown sample reveals the presence of domes with the typical multifaceted shape with steep {101} and {111} facets.[7] After an etching time of 12 s the steep facets disappear and the islands seem to be much flatter. In order to obtain quantitative information on the shape of the islands we make use of the so-called facet plot (FP) that represents a two-dimensional histogram of the local surface gradient.[14,15] Figure 2(b) shows the FP of an STM image of a sample that was etched for 12 s. The intensity is enhanced at four different positions close to those expected for {137} facets. No steeper facets are visible, making the FP in Fig. 2(b) very similar to the typical FP of a pyramidal island.[7]
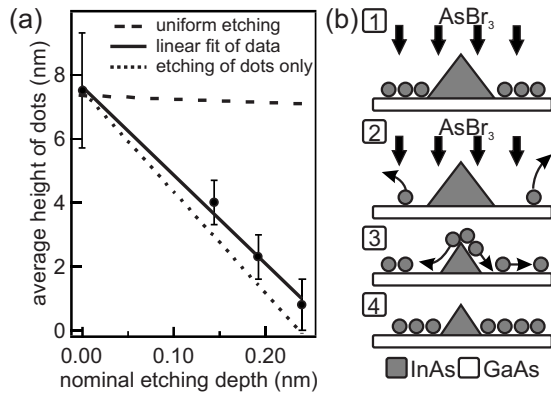
FIG. 3. (a) Evolution of QD height as a function of the nominal etching depth. The data points represent average values obtained from the analysis of several AFM images; the error bars show the corresponding standard deviation. The straight line is a linear fit to the experimental data. The dashed and dotted lines illustrate the expected height evolutions if the etching occurred layer-by-layer or from the QDs only, respectively. (b) Schematic illustration of the etching mechanism: the etching of the WL (1, 2) drives In away from the islands to rewet the surface (3) and produces the observed island size reduction (4).

These facets are not as well defined as for the pyramids that develop during growth. This could be due to a strong redistribution of material that occurs during the etching process. The reason for this material rearrangement will be explained later in detail. Figure 2(a) shows that further etching (etching time of ~16 s) results in an irregular island shape and the disappearance of the {137} facets. This is not surprising since precursors of InGaAs pyramids can also be expected to be partially unfaceted, similar to the SiGe/Si(001) case.[16] All the etched samples, particularly the 16 and 20 s ones, reveal the presence of small 2D islands only a few monolayers high [see Fig. 2(c)]. It has been reported that the 3D island growth starts from such small platelets,[17,18] which thus represent the early precursors of pyramids during the growth process. That means that the surface morphology after long etching is similar to what can be observed directly before the 2D to 3D transition during growth. Thus, the results in Fig. 2 strongly indicate that a low etching rate leads to an island shape evolution that resembles the reversal of the growth process.

B. Indirect material removal by lateral In diffusion

For a more detailed understanding of how the material removal occurs, we compare the size evolution of the dots with the nominal amount of etched material. Since the volume of the dots, as determined by the AFM images, is not very accurate because of the tip convolution, we revert to the much more reliable measurement of the height of the islands. For this reason we measured the evolution of the average height as a function of the nominal amount of etched InAs by analyzing several AFM images for each etching time [Fig. 3(a)]. After 20 s the average island height is less than 1 nm, which means that the islands have almost disappeared. Although one would clearly expect that the QDs' height decreases with the etching time, the measured height reduction

is much larger than what would be derived if the material was etched uniformly all over the surface [dashed line in Fig. 3(a)]. For example after etching for 20 s at a rate of 0.04 ML/s the total amount of material removed is 0.8 ML. If this was taken uniformly from the whole surface, the height of the QDs should have reduced by less than 1 ML, while the actual measured height reduction is almost 7 nm (~20 ML). Thus, the experimental data cannot be explained by a uniform, layer-by-layer removal of the material. On the other hand, the measured height reduction fits better to a scenario where the whole amount of material is taken exclusively from the QDs, even if these occupy approximately only 10% of the surface (QD density ~75 μm^{-2}). In fact, by assuming a simplified cone shaped geometry for the islands this model would result in a height reduction of ~8 nm after 20 s, which is quite close to what is observed [dotted line in Fig. 3(a)].

In order to identify the origin of this drastic height decrease, we consider the relevant mechanisms which might take place during the etching process. The etching step goes along with an additional growth interruption that might result in In desorption and intermixing. Since we use a low substrate temperature and the etching times are comparatively short, the amount of desorbed In is more than an order of magnitude smaller than the material removed during etching.[19,20] Moreover, the short etching times also prevent strong intermixing.[21]

Thus desorption and intermixing cannot be considered to play a key role during etching and we must focus on the reaction of AsBr$_3$ with Ga and In surface atoms and on their subsequent desorption. Different factors have to be taken into account in the interaction between the etching gas and the substrate. First, the etching is slightly material- and strain-selective [the etching rate of pure InAs is approximately 1.3 times as high as the one for GaAs (Ref. 10) and strain-enhanced etching was argued in Ref. 11], but this cannot properly explain the above mentioned massive size reduction of the dots. Second, considering that the WL is very thin compared to the dots (about 1 ML after dot formation) we would expect the WL to be removed almost completely after 20 s etching. However, STM images of the planar surface far away from the QDs are still characterized by a typical In-rich $3 \times n$ reconstruction and also photoluminescence (PL) measurements still show the characteristic peak of the WL even after 20 s etching (data not shown). Furthermore, the PL peak ascribed to the QDs disappeared prior to the disappearance of the WL peak. Thus, we conclude that the progressive removal of material from the WL is accompanied by In migration from the QDs onto the bare substrate to compensate for the In depletion [see Fig. 3(b)]. Because of the lower surface energy of InAs with respect to GaAs, this latter process lowers the free energy of the system and, as a consequence, the dots start to shrink. Since the etching occurs at a low rate, i.e., sufficiently close to thermodynamic equilibrium, the shape transition of the QDs is reversed. A similar process, i.e., wetting of the GaAs surface by InAs provided by islands, has been discussed also by Wang *et al.*[22] in the case of islands which are annealed after partial capping with GaAs. With this approach, which is used to adjust the height of dots after their growth,[23,24] the lack of a WL of the

partially covered islands leads to their dissolution in favor of the formation of a new WL. This means that the WL cannot be removed by *in situ* etching in presence of QDs, even if its thickness is much smaller than the QD height.

Finally, the strong material redistribution described above might also be the reason for the observed elongation of the islands (due to anisotropic diffusion of In atoms), the increase in their base in the $[1\bar{1}0]$ direction and an enhanced alloying. In fact, once In atoms have left the QDs' top, they might redeposit together with Ga at the base of the islands.[25] We note that our findings could also be used as an alternative explanation for similar experiments performed at higher AsBr$_3$ etching rates.[11]

IV. CONCLUSIONS

In summary, using *in situ* etching we have investigated the evolution of InAs/GaAs(001) QDs grown by molecular-beam epitaxy. By means of scanning probe techniques we were able to observe indications of a backward transition of the growth process. The study of the islands' height evolution demonstrates that the net effect of the etching is a migration of In away from the QDs in order to maintain an In-rich wetting layer onto the GaAs substrate. This shows that the removal of the wetting layer is the driving force for the reverse shape transition of self-assembled QDs.

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