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Three-dimensional isocompositional profiles of buried SiGe/Si(001) islands

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The authors investigate the composition profile of SiGe islands *after capping with Si* to form quantum dots, using a two step etching procedure and atomic force microscopy. Initially, the Si capping layers are removed by etching selectively Si over Ge and then the composition of the disclosed islands is addressed by selectively etching Ge over Si. For samples grown at 580 °C the authors show that even when overgrowth leads to a flat Si surface and the islands undergo strong morphological changes, a Ge-rich core region is still preserved in the dot. At high growth and overgrowth temperatures (740 °C), the experiments show that the newly formed base of the buried islands is more Si rich than their top. Furthermore, the authors find that for the growth conditions used, no lateral motion takes place during capping. © *2007 American Institute of Physics*.

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The composition of SiGe islands has attracted much interest in the past years because it determines, together with their size and shape, their electronic structure. For most applications, these nanostructures must be capped, i.e., epitaxially embedded in a host matrix, so it is essential to understand the composition profile of buried islands after capping. Various methods have been used to address the composition of freestanding islands.[1–4] On the other hand, much less studies have investigated the stoichiometry of buried islands. Photoluminescence together with linear deformation potential theory was used to estimate the average composition in capped islands and island stacks.[5] Vertical composition profiles through the middle of embedded SiGe islands have been measured by transmission electron microscopy and x-ray scattering techniques.[6,7] Despite such efforts, a full three-dimensional (3D) composition profile of embedded islands has not been revealed, yet.

It has been shown that a combination of atomic force microscopy (AFM) and selective wet chemical etching can provide 3D isocompositional profiles of freestanding SiGe islands.[8] While this method has the ability to produce 3D isocompositional profiles and to establish relative compositional changes between different samples it cannot provide full 3D composition profiles. Many studies have been performed since then using the same technique for freestanding islands.[4,9–12] Recently, Li *et al.*[13] investigated the island composition at the initial stages of overgrowth using the same method.

In the case of freestanding pyramids and domes, this method revealed that the lateral compositional profile exhibits a fourfold or cylindrical symmetry. This picture, however, breaks down during *in situ* annealing.[10,14] Indeed, during postgrowth annealing an asymmetric compositional profile develops while the islands move laterally on the surface. Very recently, Capellini *et al.*[15] reported that overgrowth also leads to a lateral motion of SiGe islands and promotes ordering.

Here, we extend the technique of selective wet chemical etching and AFM to extract information about the 3D composition of *buried* SiGe islands. We show that for low overgrowth temperatures (up to 450 °C) there is no change in the compositional profile of the islands. For higher overgrowth temperatures (580 °C) where the shape of the QD undergoes strong morphological changes, the intermixing does not lead to a complete dilution of the original dots. There is still a Ge-rich core, as in the case of the dots capped at low temperature. Experiments performed on samples grown and overgrown at high temperatures (740 °C) prove that the newly formed base of the buried islands is more Si rich than their top.

The samples used in this study were grown by solid source molecular beam epitaxy (MBE). After deoxidation and Si-buffer growth, 5.9 ML of Ge were deposited at a rate of 0.04 ML/s while the substrate temperature was kept at 580 °C. After the formation of 3D islands, 20 nm of Si were deposited at a rate of 0.7 ML/s at 300, 450, and 580 °C. A second set of islands was grown by deposition of 10 ML of Ge at a temperature of 740 °C. This sample was overgrown at the growth temperature with 30 nm of Si. Some samples were etched in a 2*M* potassium hydroxide (KOH), a 31% hydrogen peroxide (H_2O_2), and a 1:1 volume 31% hydrogen peroxide/28% ammonium hydroxide (H_2O_2/NH_4OH) solution. The samples were characterized *ex situ* by means of AFM in tapping mode.

In order to investigate the buried islands, the Si cap was removed by using a solution which etches selectively Si over Ge. We chose as etchant a 2*M* potassium hydroxide (KOH) solution. The experiments were performed at room temperature in order to have slow etch rates, which allow a better control over the experiment. The calibration of the used 2*M* KOH solution was done by etching virtual substrates of different compositions which were grown by low energy plasma enhanced chemical vapor deposition.[17] All samples were initially dipped into a 50% HF solution to remove the native oxide from the surface. Figure 1 displays the obtained

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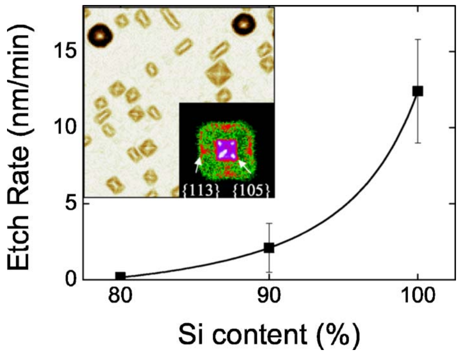

FIG. 1. (Color online) Etch rate diagram of the $2M$ KOH solution at room temperature. The inset displays a 500×500 nm^2 AFM image of buried islands which were previously capped at 300 °C. The facet plot analysis (Ref. 16) indicates that traces of the facets can be still distinguished.

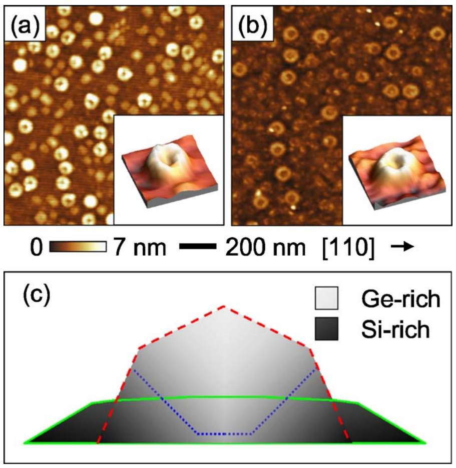

FIG. 2. (Color online) [(a) and (b)] AFM images showing the buried islands after they have been additionally etched for 10 min in a 31% H_2O_2 solution. (a) was capped at 450 °C and (b) at 580 °C. Insets are 3D views of etched dome islands. (c) Schematic illustration of the morphology and composition of the disclosed islands. The dashed (red) line corresponds to an island overgrown at low temperature (300–450 °C), similar to a freestanding island. The solid (green) line shows the morphology of an island capped at 580 °C, as subsequently disclosed. The dotted (blue) line represents the Ge-rich region that is removed by subsequent Ge-selective etching.

etch rate diagram. It is seen that the etch rate decreases drastically for increasing Ge contents and that the solution etches selectively Si over $Si_{0.8}Ge_{0.2}$ with a selectivity of about 100:1.

The inset of Fig. 1 shows an AFM image of buried islands which were previously overgrown at 300 °C. The facet plot analysis[16] shows that traces of the {105} and {113} facets can be still distinguished, demonstrating that the shape of buried islands can be indeed revealed. (The {15 3 23} facets cannot be distinguished even when analyzing AFM images of as-grown samples due to small island size and limited resolution.) Once the buried islands are uncovered, we can analyze their composition. This is simply done by dipping the disclosed islands in a 31% H_2O_2 solution, which is known to etch selectively Ge over Si and to stop etching for SiGe alloys with Ge concentrations less than 65(±5%).[6] In other words, initially the Si capping layers are removed by etching selectively Si over Ge, and then the composition of the disclosed islands is addressed by selectively etching Ge over Si.

The morphology of the buried islands after 10 min etching in a H_2O_2 solution is shown in Figs. 2(a) and 2(b). For both overgrowth temperatures (450 and 580 °C) the etched dome islands exhibit a ringlike structure, which demonstrates that they have a Ge-rich core and a more Si-rich periphery. Similar morphologies have been recently observed after etching freestanding dome islands in the temperature range of 560–600 °C.[9]

For low temperature capping it is known that the island shape is preserved (see Fig. 1), thus it is natural that their composition profile stays unchanged. However, overgrowing SiGe islands with Si at high temperatures leads to strong morphological changes, including reduced height and increased base area.[18] Yet Fig. 2(b) shows that the Ge-rich core surrounded by the Si-rich ring survives the capping process. While we cannot rule out some bulk interdiffusion that may occur in addition to surface diffusion,[12] our results can be well accounted for by considering only surface diffusion.

We can suggest here the following scenario to account for the observed compositional profiles. There is a strong thermodynamic driving force for intermixing.[19,20] Thus, the presence of Si-rich material at the surface during capping draws Ge from the island (mainly from the exposed apex) to intermix with this added Si. The resulting more dilute alloy accumulates preferentially at the base of the island,[21] which is favorable for strain relief, but some of the Ge also spreads more widely across the surface and into the capping layer. During this mechanism the composition of the base of the as-grown island does not change, i.e., during overgrowth the Ge-rich island core is preserved [Fig. 2(c)].

In electronic applications, the "real" QD is the region of reduced band gap, defined by a high concentration of Ge versus Si (or, e.g., InAs versus GaAs). By capping at 580 °C, we obtain a smooth flat surface, yet we preserve a small core that is just as Ge rich as the original as-grown island. This is a suitable combination for device applications.

In order to investigate also the compositional profiles of buried islands grown and overgrown at higher temperatures (740 °C) we have used another etchant which etches also SiGe alloys with higher Si content, i.e., a 1:1 volume 31% H_2O_2/28% NH_4OH solution.[11] By performing successive etching experiments and imaging the same buried island after each etch step the compositional profile can be investigated in detail. Figure 3 shows the morphology and the corresponding line scans of buried islands at different stages of the etching. [Fig. 3(a) corresponds to zero etching time, i.e., it shows the morphology of the buried islands prior to Ge etching.] By comparing the etching of the buried islands with that of the as-grown islands grown under the same conditions [see Fig. 5(m) of Ref. 11] two differences can be observed. While the as-grown islands are etched almost isotropically, the buried islands are etched mainly from top to base. Their width stays initially unchanged and a small dip appears at the center of the base of the island. Both features can be explained by the fact that during Si capping the newly formed base of the buried island has a higher Si content than the top. This leads to a decreased etch rate at the periphery relatively to its top. As a consequence, the top is etched faster and this results in an etched island with a decreased height and a dip in its center [Fig. 3(d)]. Also in the case of the 740 °C sample the compositional profile of the buried island can be explained in a similar way like in Fig. 2(c) with the difference that the 740 °C as-grown island has a more homogeneous compositional profile.

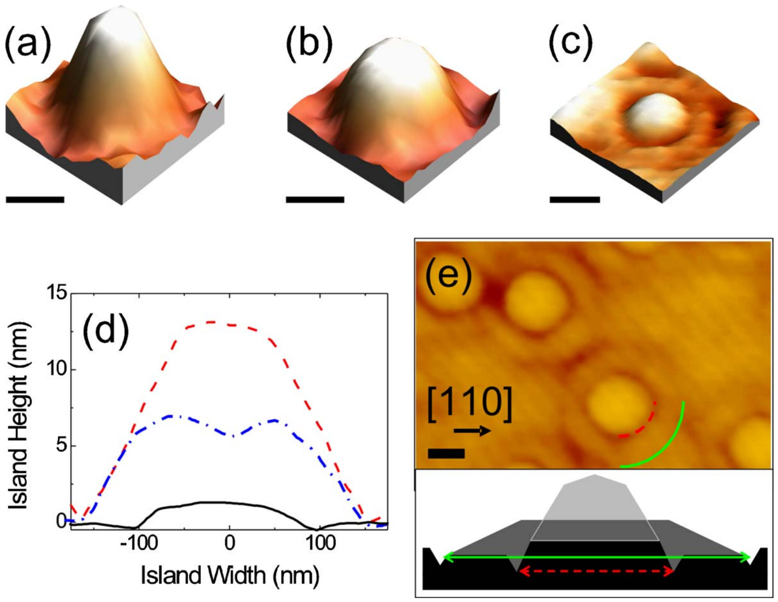

FIG. 3. (Color online) [(a)–(c)] AFM images of buried islands after different etching times. (a) corresponds to zero Ge etching time. (d) shows the corresponding line scans, which demonstrate that the buried islands have a more Si-rich periphery. (e) AFM image of the surface after the buried islands have been completely etched away. The (red) dashed arc displays the trench of the as-grown (light gray) island which is carved into the Si (black) substrate while the (green) solid arc corresponds to the perimeter of the buried island (darker gray). The arrows in the inset elucidate the origin of the arcs seen in the AFM picture. Scale bars correspond to 100 nm.

Figures 3(c) and 3(e) show the surface of the sample grown and overgrown at 740 °C after the buried islands have been completely removed. A double ring structure can be identified. The first ring (indicated by the dashed red arc) corresponds to the trench of the initial freestanding island while the second (solid green arc) to the perimeter of the buried island. The outer ring is probably a second trench created around the island during the initial stages of capping. However, we cannot fully rule out strain enhanced etching rate for the KOH solution. It is seen that the two rings are rather concentric. This suggests that no lateral motion has taken place during Si capping of the MBE grown samples. This is in contrast to the striking lateral motion observed during extended annealing of uncapped islands.[10] Interestingly, our result is different than that of Capellini *et al.*[15] in which SiGe/Si(001) islands grown by chemical vapor deposition were studied.

For a very slow capping process (which is equivalent with annealing on a short time scale) one would expect that the islands should move laterally on the surface as is observed for postgrowth annealing experiments of freestanding islands.[10] The absence of a motion in our capping experiment is most probably due to the fact that the kinetics for the lateral motion are too slow. If one embeds the islands too fast, as it seems to be our case, Si covers all facets and prevents bare Ge from being exposed and intermix. In order to study whether a decreased Si overgrowth rate would allow islands to move, one more sample was grown in which the overgrowth rate was reduced from 0.7 to 0.2 ML/s. Nevertheless, no signs of island motion can be traced, i.e., even this reduced overgrowth rate is too fast to allow a lateral island motion.

In conclusion, we have investigated the 3D compositional profiles of buried SiGe islands. We find that even for samples overgrown at 580 °C where strong morphological changes take place, the islands do not become diluted throughout, they still exhibit a Ge-rich core. For samples grown at higher temperatures, our experiments show that the newly formed base has a higher Si content than the top of the buried island. By analyzing the structure around this high temperature buried islands we find that no lateral motion takes place during embedding in the Si matrix.

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