Evolution and coarsening of Si-rich SiGe islands epitaxially grown at high temperatures on Si(001)

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In this work we investigate by means of atomic force microscopy in combination with selective wet etching experiments coalescence and coarsening effects on the morphology evolution of Si-rich SiGe quantum dots and islands grown epitaxially at high temperatures on Si(001) substrates. We demonstrate that under certain growth conditions remarkably uniform island size distributions can be achieved for dome and cupola islands, while the morphological transition is dominated by coarsening and coalescence effects similar to Ostwald ripening. Under further deposition the uniformly sized cupola islands transform into larger islands with even steeper side facets (>80°). The footprints obtained from selective wet etching experiments performed on the merging islands reveal that basically all atoms of the two islands are involved in the coarsening process.

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1. Introduction

Self-assembly during epitaxial growth of semiconductor compounds with lattice-mismatch is nowadays one of the easiest ways to create homogeneous quantum dots [1]. Such quantum dots (QDs), also called nanodots or islands, attracted significant interest in the past years due to potential applications that might be based on the nanometer-sized materials [2]. Significant efforts have been made to precisely understand the mechanisms behind the growth of the QDs in order to control parameters like shape, size, chemical composition, and nucleation position. These parameters influence e.g., the optical properties but also the general addressability of the QDs [3–6]. In this work we investigate the QD/island growth in the SiGe system, which is considered as a prototype system for heteroepitaxial island growth. Induced by the lattice mismatch between Ge and Si of about 4.2%, the first layers of Ge wet the surface, forming a pseudomorphically strained film called wetting layer (WL). Under further deposition and for different growth conditions a variety of QDs form that can be identified by their surface crystal facets. Those dots are commonly named after architectonic structures: pyramids [7], domes [8], barns [9], and cupolas [10]. In general, islands with steep side facets usually form at high Ge growth temperature. The formation of such Si-rich SiGe islands grown at high growth temperatures was addressed e.g., in Refs. [10–13].

During the early formation stages of dots, supersaturation effects in the initially formed two-dimensional WL play a crucial role [6,14,15]. Exploiting these supersaturation effects allows for the formation of nanostructures with superior and novel properties. Examples include dots with a highly homogeneous size distribution [15] and perfectly ordered dots and quantum dot molecules that are grown on pit-patterned substrates and for which the inter-dot spacing can be varied almost arbitrarily [6]. Also self-elongating nanowires can be formed under annealing of supersaturated WLs at low temperatures [16].

In the ongoing morphology evolution process the different island types evolve from each other through complex shape transitions [17]. But also coalescence, Ostwald ripening and coarsening effects play a significant role in the morphological evolution process [18–32].

In this work we will show that for Si-rich SiGe islands there exist growth conditions for which the occurring islands exhibit remarkably uniform morphological shape, as well as uniform island height distributions. We demonstrate that the shape transition from one form (domes) to the other (cupolas) includes strong coalescence and coarsening effects, as traced by atomic force microscopy (AFM).

2. Sample fabrication

The samples were grown by solid source molecular beam epitaxy (MBE) on high-resistivity (>1000 Ωcm) 4 inch Si(001) wafers. After in situ oxide desorption at 950 °C for 20 min, a 45 nm-thick Si buffer layer was grown during a substrate temperatures ramp up
from 550 to 700 °C. Thereafter, 4, 6, 8, 30, 50 and 100 monolayers (ML) of Ge were deposited at a growth rate of $R_{\text{Ge}} = 0.005 \text{ nm/s}$ and a growth temperature of $T_{\text{Ge}} = 900$ °C. The samples were ex-situ characterized by a Digital Instruments Dimension 3100 AFM in tapping mode using Olympus cantilevers with sharpened Si tips with half opening angles between 10° and 15° and a nominal tip radius of 2 nm. For sufficiently large islands, therefore, facet angles as steep as 75–80° can be measured without detrimental influence of the tip geometry. The tapping mode analysis has been used since it was shown that in this mode – in combination with adequate AFM-tips – crystal facets of cupola islands can be resolved accurately [10]. The island densities were deduced from four 6 × 6 μm² sized scans for each coverage.

Additionally to the as-grown samples, we performed AFM analysis of the morphology of the same surface areas after 10 min of etching in a buffered hydrofluoric acid, hydrogen peroxide, acetic acid solution [BPA solution [29], HF:H₂O₂:CH₃COOH (1:2:3)]. From Ref. [33] it is known that this solution selectively etches Si₁ₓGeₓ alloys over pure Si. Such analysis of the island’s footprints was e.g., also performed in Refs. [29,34].

3. Image representations

A careful choice of the AFM image representations is necessary in order to examine and depict the morphology evolution and coarsening effects of the islands in a clear manner. In Fig. 1 the most common ways of AFM image representation are depicted. In Fig. 1(a) a 1 × 1 μm² micrograph of a large, barn-shaped island [9] that is accompanied by a transition dome [17] is shown as a three-dimensional (3D) image. Fig. 1(b–g) show two-dimensional images where the most intuitive representation type is the color coded height image (Fig. 1(b)) that it is usually not the best image representation mode. The color scale is linearly correlated to the height axis. In the adaptive height mode (Fig. 1(c)) [36] the full data height range corresponds to the full color range, but the data values are mapped to the colors in a non-linear way. The mapping function is based on inverse cumulative height distribution [36]; therefore flat areas generally get a larger slice of the color gradient which helps to see smaller height variations on the sample surface. Due to its surface sensitivity this mode is perfectly suited for picturing e.g., trenches around islands or other WL undulations. Fig. 1(d) shows AFM data of the same island in derivative mode. This mode shows high contrast of island edges and reveals sensitively changes of the slope along one direction, but it is completely insensitive to differences in the height gradient in the direction perpendicular to the calculated one.

A mixture of the two representations, height mode and derivative mode is the so-called mixed mode [36] where the respective parts can be weighted arbitrarily (Fig. 1(e)). Thus, one gains additional information by combining the two imaging techniques, albeit in a non-quantitative way since information gets lost in the mixing process.

A very informative representation mode is the so-called surface-angle image (SAI) where the local surface inclination at each AFM data point is visualized (Fig. 1(f)). The local slope is defined as the angle between the normal orientation vector [hkl] of the data point and its immediate neighbors, and the reference orientation ([001] in this case). Additionally, the color bar can be chosen in such a way, that e.g., each known SiGe island facet of the barn ({105}, {113}, {15323}, {20423}, {23420}, {111}) corresponds to one color (light blue, dark blue, green, yellow, orange and red,

Fig. 1. AFM image representation modes: The most common AFM image representations used for nanostructures, demonstrated on an example of a barn-shaped and a transition dome shaped island. (a) 3D image in lightening mode (b) standard height image (c) adaptive height image (d) derivative mode image (e) mixed image (f) surface angle image (SAI) (g) Laplacian or second derivative image. Image reproduced from Ref. [35] with the permission of the author.
respectively) as indicated on the scale bar on the right hand side. Thus, such SAI images immediately reveal the island type and the exact location of the respective facets on the islands in the AFM micrograph.

The Laplacian, second derivative representation shown in Fig. 1 (g) is most sensitive to the edges of the facets and, thus the form of the facets is depicted most clearly. Additionally, it is simple to distinguish between convex and concave shapes shown in black and white, respectively for the color scale used here.

4. Results and discussion

4.1. Morphological evolution with increasing amount of deposited Ge

In Fig. 2 3D-AFM images as well as the corresponding SAI images are plotted showing the morphological evolution of Si-rich SiGe islands with increasing Ge coverage (\(\theta_{Ge}\)). The respective coverage \(\theta_{Ge}\) was 4 ML (a), 6 ML (b), 8 ML (c), 30 ML (d), 50 ML (e) and 100 ML (f).

Before we proceed with discussion of the morphological evolution of the island with increasing amount of Ge we have to address the chemical composition of the islands grown at the high growth temperatures used in this work (900 °C). In Ref. [10] the degree of intermixing in the cupola islands was estimated from the ratio of Ge incorporated in the dots over the total island volumes measured by AFM. This yields an average Ge content of \(x = 20\%\) within the islands (not accounting for possible Ge desorption) compared to typically \(x = 40\%\) for the domes grown at 700 °C [14]. In order to determine the Ge concentration distribution in the islands discussed in this work we applied the nano-tomography method based on selective wet etching described in Ref. [37]. The NHH solution [1:1 vol. (28% NH₄OH):(31% H₂O₂)] etches selectively Si₁₋ₓGeₓ over Si for \(x\) higher than about 30% while for \(x < 30\%\) almost no etching effect is observed [38]. In our case, the NHH solution did not attack the islands even after 420 min of etching. This leads us to two conclusions. First, the average Ge content in the cupola that was estimated from the aforementioned volume considerations seems reasonable. Second, in contrast to islands grown at lower growth temperature where the island base is Ge-lean and the apex of the islands (where the elastic relaxation of the crystal lattice is largest) is Ge-rich, the intermixing has to be relatively homogenous across the cupola islands. If the apex of the island would contain Ge concentration higher than 30%, it would have been attacked by the NHH solution. Since even after 420 min of etching in NHH solution no parts of the islands were attacked, we conclude that even at the apex of the island the Ge concentration is below 30%.

From the SAI image in Fig. 2(a) it is evident that the first islands exhibit facets of dome islands (\({\{105}\}, {\{113}\}\) and \(\{15323\}\)-facets). This is in good agreement with Ref. [14]. There it was shown in a combined effort of experimental investigation of the island morphology evolution with unprecedented coverage resolution in combination with density functional theory and elastic energy calculations that subtle interplays between surface energy and volumetric energy contributions of the islands and the WL lead to an unexpected pathway in the initial formation of islands. It was found that the larger domes and not the shallower pyramids are the first energetically stable island species [14]. However, the study was performed for lower growth temperatures up to 750 °C. It is interesting that even for the high growth temperatures used in this work, where intermixing effects play a more pronounced role, this pathway still seems to hold.

By further increasing \(\theta_{Ge}\) (6 ML, Fig. 2(b)), the dome density increases to about \(1.1 \times 10^8\, \text{cm}^{-2}\) (see Fig. 2(a)) and eventually some of the domes start to merge (see black arrows in Fig. 2(b)). During this coarsening/merging process one island seems to enlarge its volume on cost of the other island. Asymmetric islands start to form that have on one side steep facets, as indicated by the yellow and red color in the SAI image.
Fig. 3. (a) Island density as a function of the Ge ML coverage. Merging, coalescence and coarsening of domes to cupolas is evidenced by a significant drop of the island density between coverage of about 6 ML and about 8 ML. (b–i) Close-up micrographs of island coarsening from domes to cupolas. AFM-SAI images were recorded on the sample where 6 ML of Ge were deposited at 900 °C. Thus, the images do not depict the time evolution of one island pair, but they are a sequence of selected island pairs on the substrate that are already in different stages of the transformation process.

Fig. 4. Tracing of the island’s footprints by selective wet etching of SiGe over Si with a BPA solution. AFM images of the as-grown islands (6 ML) in SAI mode (a) and (f), in adaptive height mode (b) and (g). AFM height images of the same islands after etching (c) and (h). The dashed grey and black lines in (b, c, g) and (h) indicate the position on which the linescans in (d, e, i) and (j) were taken. The black line represents the as-grown islands, the red line the same surface after selective etching in BPA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
of Fig. 2(b). As the deposition continues ($\theta_{Ge} = 8$ ML) again highly symmetric islands with a unimodal shape distribution are monitored by the AFM investigation. From Fig. 2(c) it can be seen that these islands exhibit the facets of cupola islands [10,39]. Those cupolas have a density of about $2.2 \times 10^3$ cm$^{-2}$, typical heights and diameters of 156 and 400 nm, respectively, and are formed with a very high uniformity and narrow size dispersion of only ±0.8%, as obtained from statistical analysis of large-scale AFM analysis. Thus, summarizing Fig. 2(a–c), we find uniformly sized domes ($\Theta_{Ge} = 4$ ML) and cupolas ($\Theta_{Ge} = 8$ ML) for a certain deposited Ge coverage. The transformation mechanism from domes to the larger and steeper cupolas will be presented in the following Section 4.2.

With further increasing deposition the islands continue to grow and, in general, become more asymmetric (Fig. 2(d–f)). Also, their maximum height increases from about 290 nm for $\Theta_{Ge} = 30$ ML to about 660 nm for $\Theta_{Ge} = 100$ ML. In this case the steepest facets found have an inclination of 80° with respect to the (001) surface, but in this case the SAI analysis is limited by the tip geometry.

4.2. Island coarsening

In Fig. 2 we have seen that for $\Theta_{Ge} = 4$ ML uniform domes are found on the surface while for a Ge coverage of 8 ML a uniform distribution of cupolas can be found. For a Ge coverage in between these two states, i.e., for $\Theta_{Ge} = 6$ ML smaller domes merge and coarsen into larger cupola islands. During this coarsening process the island density decreases from $1.1 \times 10^6$ cm$^{-2}$ to about $2.2 \times 10^5$ cm$^{-2}$, as indicated in Fig. 3(a). The densities were deduced from four $6 \times 6$ um$^2$ sized scans for each coverage. Fig. 3(b–i) aim to give some insights into the coarsening/merging process of the domes. It is very important to mention that the AFM micrographs shown in Fig. 3(b–i) are, as all other AFM images, recorded ex-situ after growth. Thus, the images do not depict the time evolution of one island pair, but they are a sequence of selected island pairs on the substrate that are in different stages of the transformation process.

In previous works it was shown that islands can move on the surface [34] in order to reduce the total energy of the system [22]. When two domes are in close vicinity, eventually their trenches start to overlap which can be seen in Fig. 3(b) where AFM images are plotted in the SAI mode. The relatively shallow trenches can be identified by the light-violet color. Already in Fig. 3(b) one of the islands is larger than the other and has, on the side facing the second island, a higher abundance of steeper facets (green color).

In Fig. 3(c) not only the trenches of the islands merged, but the islands are actually touching each other. From the sequence of selected island pairs (Fig. 3(c–i)) it seems that the larger island is growing on the expense of the smaller one. In Fig. 3(g) the smaller dome has already transformed back into a pyramid structure with (105)-facets that are indicated by cyan color. Eventually the larger transition cupola depletes all material from the smaller island leaving only a trench of the former island (Fig. 3(h)). Through further shape transformation the remaining island recovers a symmetric shape of a full cupola island, as indicated in Fig. 3(i) and in Fig. 2(c).

Such a strong coarsening/merging process was up to now not observed. Most likely because the shrinking process is inefficient at the lower temperatures employed in most of the reported experiments. At lower growth temperature, where the Ge concentration in the islands is high and, consequently, dislocation introduction is more likely than island capture [28,29] and merging of islands as presented here for highly diluted islands. Note also that the island density decreases by almost a factor of five when $\Theta_{Ge}$ is increased from 6 to 8 ML. This already shows that either the islands are undergoing a multiple merging process, or that small islands dissolve in a way similar to what is reported in Ref. [29].

4.3. Island footprints during coarsening and dislocation insertion

Fig. 4 depicts two AFM micrographs of merging islands ($\Theta_{Ge} = 6$ ML) in the SAI mode (Fig. 4(a) and (f)), in adaptive height mode (Fig. 4(b) and (g)) and in height mode after etching in BPA solution for 10 min. The positions of the AFM linescans presented in Fig. 4(d, e, i, j), respectively are indicated by the grey and black arrows in Fig. 4(b, g) and (c, b), respectively.

From the selective wet etching experiments in BPA (Fig. 4(c) and (h)) it is evident that there is a difference between the footprints of the domes and the ones of the merging islands. After etching of all SiGe over Si the domes exhibit a flat symmetric plateau. Similar to what was reported in Refs. [29,34] the remaining pla- teaus after etching away the former domes (Fig. 4(j)) are on average about 2 nm higher than the initial Si–Ge interface. This height difference is indicated by the dashed horizontal line in Fig. 4(j).

For the merging islands the situation is different and more complex. In contrast to the domes for the merging islands the base after etching is very inhomogeneous and in general lying below the original Si–Ge interface (Fig. 4(c) and (h) and the corresponding linescans). We will follow the behavior of the two merging islands separately, the larger “consuming island” and the smaller “providing island”. For the providing island the footprint is elevated on the side opposite to the consuming island, and is getting further below the original substrate surface in the direction towards the consuming island (see also Ref. [34]). For the consuming island there exists a flat plateau below the SiGe interface and a Si-rich bump facing the second, smaller island. Probably, this bump, which also exists in already coarsened islands (Fig. 4(d)), is a remainder of the original dome plateau [34]. This detection of the islands footprints impressively demonstrates that for both islands (also the consuming one) the coalescence/merging process not only happens via rearrangement and attachment/detachment of atoms at the island surface but that atoms of the whole island body are involved.

Fig. 5(a) shows an AFM image in SAI mode of islands after the growth of 50 ML Ge at 900 °C, and in Fig. 5(b) an AFM-height mode image of the same structures after BPA etching. It is interesting to see that the island indicated by the white arrow and the island pair indicated by the black arrow have very similar footprints after BPA etching. This indicates that the single cupola itself evolved from the coarsening process is similar to the one in the island pair marked by the black arrow.

The larger island at the bottom of the image exhibits a different footprint than the islands indicated by the arrows. The inner plateau is surrounded by more or less concentric rings. This situation
is similar to the one of dislocated islands, e.g., presented in Ref. [29].

One last point to mention is the depression that can be found in the inner plateau of the three larger islands at the lower part of Fig. 5(b). This depression has on average an opening diameter of about 100 nm and a depth of 17 nm and might be correlated to the formation of dislocations in the islands. One more indication for dislocation formation in cupola islands can be found in Fig. 2(f) where dark arrows indicate a depression in the island’s facet which might arise from the threading end of a dislocation line that ends at this facet. A more detailed analysis of the formation of dislocation in such islands, which was performed e.g., in Ref. [40], exceeds the scope of this work.

5. Conclusion

In this work we investigate by analyses based on atomic force microscopy in combination with selective wet etching experiments coalescence and coarsening effects on the morphology evolution of Si-rich SiGe quantum dots and islands grown epitaxially on Si(001) substrates. We demonstrate that under certain growth conditions remarkably uniform island size distributions can be achieved for dome and cupola islands, while the morphological transition is dominated by strong coarsening effects similar to Ostwald ripening. We expect that our work provides a better understanding of the fundamental mechanisms governing the evolution of self-assembled islands in different strained material systems.

Acknowledgements

The Laplacian AFM transformation depicted in Fig. 1 was generated by the XIm program kindly provided by A. Rastelli [37]. The work was supported by the Austrian Science Fund FWF (Contract No. SFB02502). Additionally, Moritz Brehm acknowledges financial support from the Austrian Science Fund (FWF): J3328-N19.

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