Self-Ordering of a Ge Island Single Layer Induced by Si Overgrowth

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We provide a direct experimental proof and the related modeling of the role played by Si overgrowth in promoting the lateral ordering of Ge islands grown by chemical vapor deposition on Si(001). The deposition of silicon induces a shape transformation, from domes to truncated pyramids with a larger base, generating an array of closely spaced interacting islands. By modeling, we show that the resulting gradient in the chemical potential across the island should be the driving force for a selective flow of both Ge and Si atoms at the surface and, in turn, to a real motion of the dots, favoring the lateral order.

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Nanometric Ge/Si(001) self-assembled islands are a prototypical example of extreme interest in the nanofabrication of ordered dot arrays, due to the relatively simple chemistry of the system and, obviously, to the wide technological importance of Si-based devices [1]. Uniformity in size and spatial ordering of self-assembled islands are critically important for practical applications. The elastic interaction between islands can improve both of them, inducing a chemical potential gradient between different islands, and, within a single island [2–4], this effect being more evident at high island density [5].

The realization of island multilayers has also been proved to enhance island size uniformity and in-plane ordering. While a mechanism based on the island-island elastic interaction through the Si spacer layers has been proposed for such a case [6,7], there is no experimental study on the effect of silicon overgrowth on island displacements and ordering for a single layer of Ge islands. This is particularly important since, in our opinion, the ordering occurring in the first layer of a multilayer structure plays a major role in promoting the vertical and lateral ordering observed in the whole structure.

In this Letter, we present an experimental procedure for obtaining Ge-island ordering on Si(001), exploiting a real lateral motion of them, by means of silicon overgrowth. The experimental results will be interpreted by a quantitative modeling based on atomistic simulations and elastic theory. The samples presented in this study were deposited by an ultrahigh vacuum chemical vapor deposition technique using high purity silane and germane. Two sample series have been realized through the deposition of variable thickness Si-cap layers on morphologically identical Ge-island layers: In series A, both the island layer (~1.5 nm Ge equivalent thickness) and the silicon cap layer were deposited at 750 °C, while in series B, the island layer (~3 nm Ge equivalent thickness) was deposited at 600 °C and the silicon capping layer at 750 °C. The sample morphology was characterized by means of a contact atomic force microscope (AFM), where finite tip-size convolution effects were taken into account in the analysis.

In Fig. 1, we first display AFM images acquired on samples belonging to series A. The as-deposited islands [Fig. 1(a)] are arranged in random positions over the Ge wetting layer. The presence of two island families, namely, small pyramids and domes [8], is evident. The average dome base width is $s = 125$ nm, and the average aspect ratio α [= (island height)/(base width)] is $\alpha = 0.18$.

The deposition of a silicon cap layer does not result in an immediate burial of the Ge islands. The supplied silicon mainly enters the Ge islands, inducing a reverse Stranski-Krastanov (SK) dynamics [9], which leads to a shape evolution from steeper domes to (partially) truncated pyramids with a larger base and to the disappearance of the small pyramids [10]. In fact, by capping with 4.5 nm Si nominal layer [Fig. 1(b)], we obtain $s = 195$ nm and

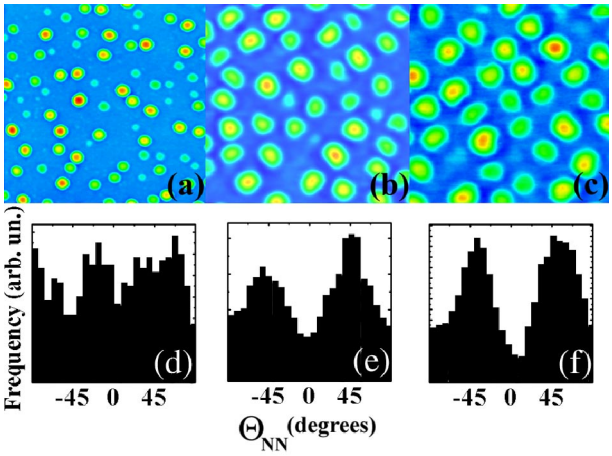

FIG. 1 (color online). $2 \times 2\ \mu m^2$ AFM images of samples belonging to experimental series A: (a) As-grown, (b) with a 4.5-nm and (c) with 6 nm-thick Si deposition. Image sides are oriented along [011] directions. In (d)–(f), we display the corresponding angular distribution of the four nearest neighbors.

$\alpha = 0.052$, while for 6 nm Si capping [Fig. 1(c)], s increases up to 230 nm and α is reduced down to 0.045. A clear trend observed in Fig. 1(b), and more evidently in Fig. 1(c), is the ordering of the Ge(Si) islands in a square lattice, oriented along the elastically softer [100] or [010] directions [11–14].

We have verified that the closest 12 neighbors of the islands actually arrange in three shells, at increasing average distance, in agreement to a square lattice (not shown here). However, the best statistical analysis of the ordering is obtained by evaluating the distribution of the angles Θ_{NN} existing between the segments connecting the center of each island to those of its four nearest neighbors, with respect to the crystallographic direction [110] as a reference. The resulting histograms for the series A samples are reported in Figs. 1(d)–1(f), where the analysis has been performed over about 1000 islands per sample, i.e., over an area of approximately 100 μm^2.

While the random island arrangement in the as-deposited sample is evidenced by an homogeneous Θ_{NN} distribution [Fig. 1(d)], the Θ_{NN} distributions in Figs. 1(e) and 1(f) feature two peaks centered at about $+45°$ and $-45°$, i.e., along the [100]-[010] equivalent directions, as expected in a square lattice. Similar to the early results in Ref. [5], the island ordering is positively correlated to the surface coverage, as evidenced by the increasing peak-to-valley (P-V) ratio of the Θ_{NN} distribution shown in Fig. 2(a).

Our data clearly demonstrate that, by exposing randomly positioned ''mature'' Ge islands to a Si flux, in-plane ordering can be achieved, indicating the occurrence of real lateral displacements. Since a large island cannot move as a whole, the final displacement must be the result of a net atomic flux supplying material in the direction of motion, as nicely demonstrated by a very recent work of Denker *et al.* in the case of annealing [15]. Actually, at the deposition temperatures and on the time scale considered here, bulk diffusion is negligible. On the other hand, mechanisms involving surface diffusion are particularly effective, as confirmed by a simple Arrhenius analysis, indicating that atomic displacement as large as the island base (~ 200 nm) can potentially occur at least 10^4 times within the typical time scale of the experiment ($\sim 10^2$ s), provided the activation energy for a single atomic jump is lower than 1.04 eV. This value is nearly twice the values reported in the literature for Si/Ge atom hopping, including the diffusion across the island's facets [16]; it is also slightly larger than the value for Si_2 or Ge_2 addimer diffusion on Si(001) [17]. It is thus natural to fix our attention on the energetics of the atoms at the island facets. To this goal, we have first used classical molecular dynamics (MD) simulations based on the Tersoff potential [18].

We have considered two Ge structures on Si(001) bounded by {105} facets, located at a distance d on the [100] direction [see the inset in Fig. 2(c)]. Since we are essentially interested in lateral interactions, these pyramids were simulated by {105} ridges, having infinite extension along the [010] direction. This modeling allowed us to reduce the number of atoms involved, also relying on the self-similarity scaling, which allows us to simulate a system which is 1:10 with respect to the experiment [19]. The two ridges had a base length $s = 22$ nm and a height of 2.2 nm, lying over a 3 ML-thick Ge wetting layer and a 5.4 nm-thick Si substrate. The simulation cell was 74 nm wide along [100] (x in the following) and 5.4 nm along [010] (y), where periodic boundary conditions have been applied. The configurations considered below were optimized by a standard quenched molecular dynamics procedure, in order to obtain the mapping of the strain tensor and of the elastic energy per atom.

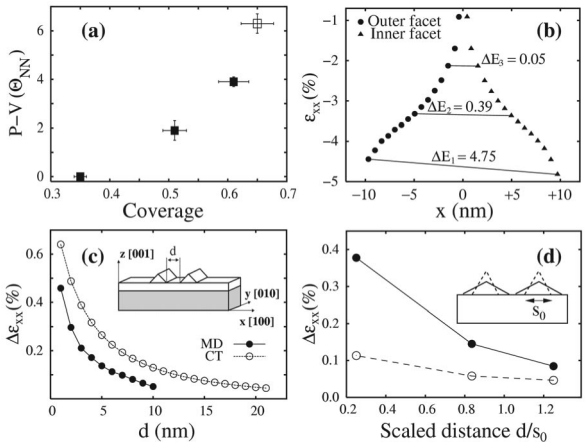

FIG. 2. (a) Correlation between the substrate coverage and the peak-to-valley intensity ratio of the Θ_{NN} angular distribution, for different samples: from left to right, Figs. 1(d)–1(f) (solid squares) and Fig. 3(d) (open square). (b) Asymmetric strain component ε_{xx} estimated by MD along the surface profile of the inner (triangles) and outer (circles) facets of one Ge ridge at a distance $d = 1$ nm from another one. The differences in the elastic energy between opposite facets, as produced by the full strain tensor, are also reported at selected island heights (ΔE_1, ΔE_2, and ΔE_3, in meV/atom). (c) Difference between the xx strain component at the opposite edges of the ridge base $\Delta\varepsilon_{xx}$ vs d: MD simulations (solid circles) and continuum approach (open circles). Inset: Geometry of the simulation cell. (d) Evolution of $\Delta\varepsilon_{xx}$ during the reverse shape transformation of the islands with capping, calculated by the continuum elastic theory. Points from right to left correspond to islands with aspect ratio 0.2, 0.1, and 0.05, respectively. Solid circles refer to pure Ge islands, open circles to progressively Si-intermixed islands (see text for details).

We analyze first the case of two pure Ge ridges at a distance $d = 1$ nm. In Fig. 2(b), we plot the ε_{xx} strain component (the largest, and by far most sensitive, component to the presence of a neighboring island) along the surface profile of the ridge. In particular, we take the average value for atoms positioned in the stripes located between 2 and 3 Å below the free surface, in order to avoid

the fluctuations produced by the surface reconstruction. Here and after we name ''inner'' the facet close to the second island and ''outer'' the opposite one. In Fig. 2(b), we quantify the total elastic energy unbalance between the two facets: Close to the bottom of the island, the atoms of the inner facet are more compressed than the ones of the outer facet, resulting in an average energy difference of 4.75 meV/atom. This effect decreases moving toward the island apex, being very small already at halfway. Similarly, the energy splitting readily disappears by moving into the bulk region of the island (not shown here) and by increasing the distance between the islands edges [see also Fig. 2(c)].

An important result of our calculation is that, due to the large compression along x of the lattice at the base of the inner facet, even the Si atoms deposited there (modeled as a cluster embedded in Ge) have an average elastic energy which is 1.71 meV/atom higher with respect to the base of the opposite facet. The same applies if a SiGe crust of four monolayers is supposed to be present at the ridge surface, slightly relaxing the energy unbalance: In this case, the difference for Si atoms at the base of opposite facets is 1.44 meV/atom on the average. Taking into account that, in the intermixed island, Si atoms occupy mainly the very bottom region [20], we can conclude that a driving force directed from the inner to the outer facet exists for them, as in the case of Ge.

Recently, Denker *et al.* [15] have experimentally demonstrated that 3-dimensional Ge islands grown on Si(001) are displaced by annealing procedure, due to a Ge flow from one side of the island to the opposite one, in order to intermix with some (accidental) accumulation of Si. In the case of two islands moving away [19], such a process requires an accumulation of Si atoms at the outer facet of the island. Our calculations also provide a quantitative explanation for the onset of such a concurring mechanism, showing that the lateral interaction produces a driving force which tends to push silicon out of the areas between two islands facing at close.

More importantly, our elastic process suggests a mechanism for stopping the island motion, when it comes close to another one. This is crucial in achieving the island ordering. In fact, as the displacing island approaches another island, a reverse flow of atoms can cause the end of the motion and drives the island arrangement in a square lattice oriented along the ''softer'' [100]-[010] directions [12,14], which are the ones allowing a shorter island distance.

Therefore, Si overgrowth promotes ordering mainly because the consequent reverse-SK shape transformation reduces the island-edge mutual distance. However, the flattening of the islands during the capping and/or the Ge-Si intermixing should lower the elastic load to the substrate and, in turn, the island interaction [12]. In order to quantify such a tradeoff, we shall leave the atomistic approach, which is computationally too expensive in addressing islands with variable shape and composition.

By using a Green function formalism for the elastic theory in the flat island approximation [21,22], we have calculated the ε_{xx} component at the surface profile of two Ge ridges at a distance d in the experimental scale. The analytic expression of ε_{xx} depends on the lattice misfit f between Si and Ge (4.2%), their Poisson ratio, the facet inclination θ, the height h, and the base length s of the two ridges. First, we have verified that this approximation holds by comparing $\Delta\varepsilon_{xx}$, the strain unbalance with distance between opposite sides of one Ge ridge at the base, against the results obtained by MD simulations. From Fig. 2(c), it is clear that the continuum-theory curves and the MD results predict the same trend of $\Delta\varepsilon_{xx}$ vs d. As we will show elsewhere, the continuum approach moderately overestimates $\Delta\varepsilon_{xx}$, partially due to neglecting the strain relaxation at the top and partially due to neglecting the anharmonicity in the Tersoff potential.

Subsequently, we have considered islands of the typical experimental size and geometry prior to Si capping (dome islands, with a base length $s_0 = 120$ nm and height $h_0 = 24$ nm), and we have calculated the changes in $\Delta\varepsilon_{xx}$ accompanying the shape transformation in three steps, from domes, to pyramids, to truncated pyramids. In particular, we have fixed the island centers at a distance of 2.25 s_0 and decreased the island aspect ratio from 0.2, to 0.1, to 0.05 [see the inset in Fig. 2(d)] while keeping constant the island volume, as indicated by the experimental observations [10].

As shown in Fig. 2(d) by the solid lines connecting the three steps, we found that, despite the decrease in the island aspect ratio, the reduction in the scaled distance between the island edges leads to a sizable raise in the strain difference between the inner and outer facets. A further process, however, must be taken into account. During the inverse shape transformation, the average Ge concentration c_{Ge} within the islands progressively decreases, from $c_{\mathrm{Ge}} = 0.55$ in domes, to $c_{\mathrm{Ge}} = 0.40$ in pyramids, and finally to $c_{\mathrm{Ge}} = 0.3$ in the truncated pyramids (immediately before the burial of the islands), as shown by x-ray absorption spectroscopy measurements on similar samples [10]. In our calculations, the change in Ge content was taken into account by taking an effective misfit $f(c_{\mathrm{Ge}})$ linearly proportional to c_{Ge}. As shown by the dashed line in Fig. 2(d), despite the reduced Ge content lowering the elastic load with the reversed shape transformation, the qualitative behavior of the strain difference remains the same of the solid line.

If our interpretation of the ordering process is correct, an increased ordering can be experimentally obtained by enhancing the elastic repulsion through a higher average Ge content and a higher island density. The experimental series B has been conceived to verify these expectations: The larger amount of deposited Ge and the lower Ge-island growth temperature entailed an higher density of Ge-rich domes [23], resulting in closer and less intermixed islands upon Si capping.

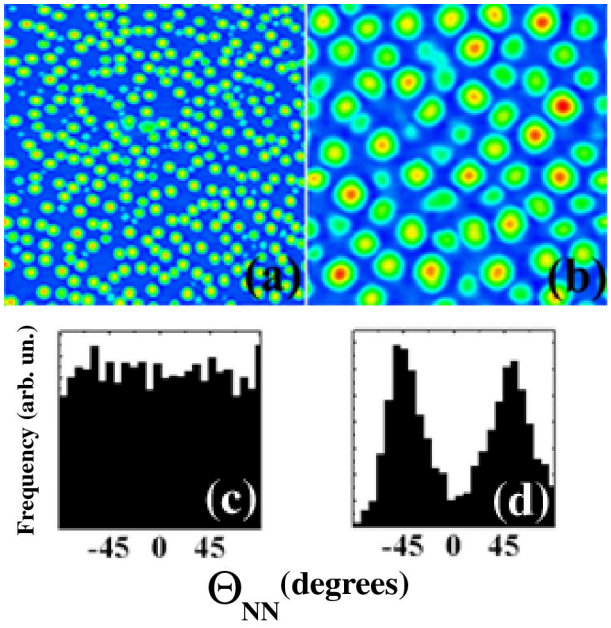

FIG. 3 (color online). $2 \times 2\ \mu m^2$ AFM images of samples belonging to experimental series B: (a) As-grown sample at 600 °C. (b) The same after 6 nm Si capping at 750 °C. In (c) and (d) are the corresponding angular distributions at first neighbors, as in Fig. 1.

In Fig. 3, we report the AFM images of two samples of series B: (a) an as-grown island layer and (b) a 6-nm Si capping of the island layer. It is clear that in the latter case the ordering is more pronounced with respect to the one observed in series A, at the same silicon deposition [Fig. 1(c)]. In fact, the *P-V* ratio of the Θ_{NN} distribution has increased from 3.9 to 6.3, actually corresponding to a larger surface coverage [open square in Fig. 2(a)].

In conclusion, we have shown that the ordering process of Ge(Si) islands is confirmed to be proportional to the actual coverage of the substrate, even in the case where the decreasing island distance is obtained by Si intermixing, via overgrowth. In addition to that, we explained this process to be generated by an actual displacement of mature islands, completing and relating to the ordering very recent complementary experiments by molecular beam epitaxy [15,20]. Finally, we have quantitatively supported our interpretation of the island displacement as originated by the elastic interactions, showing that a chemical potential gradient is present across neighboring islands, for both Ge and Si atoms.

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