Real Time Observation of GeSi/Si(001) Island Shrinkage due to Surface Alloying during Si Capping

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The Si capping of Ge/Si(001) islands was observed by *in situ* time-resolved transmission electron microscopy. During the initial stages of the Si deposition, islands were observed not only to flatten but also to shrink in volume. This unexpected shrinkage is explained by taking into account the intermixing of the deposited Si with the wetting layer and a consequently induced diffusion of Ge from the islands into the wetting layer. A model of the capping process which takes into account Ge diffusion is presented which is in good agreement with the experimental data.

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During the growth of lattice mismatched semiconductors, in many systems, a strain induced transition from planar growth to three-dimensional (3D) island growth can occur (Stranski-Krastanow transition [1]). The shape of the resulting islands is usually well defined [2,3]. The Ge/Si system is especially promising for applications in microelectronic and optoelectronic devices [4] because of its compatibility with existing Si technology. In this system, small islands grow as pyramids bounded by {105}-type facets. On further growth, steeper facets are introduced and islands transform into domes [2,5,6] [Fig. 1(a)]. The size at which this transition occurs depends on the island composition [7,8]. The evolution of island shape and size during growth has been studied extensively [9]. However, less is known about the effect of depositing a Si capping layer on top of previously grown islands, a crucial step in quantum dot applications. Previous studies, based on postgrowth, *ex situ* analysis [10–12], or *in situ* low energy electron microscopy (LEEM) [13], show that the shape and size of Ge and GeSi islands change due to alloying of the deposited Si with the islands. In most studies, the data analyzed are an average over islands, so it is difficult to interpret the effect of the alloying on individual islands; LEEM [13] is an exception, showing intriguing shape changes in individual SiGe islands, but determination of 3D island volumes was not possible. Here we use *in situ* time-resolved transmission electron microscopy (TEM) to study changes in both shape and volume of individual Ge islands during capping. There are two advantages to tracking the progress of a single island in real time. First, the island can be observed under growth conditions, rather than after cooling and exposing to atmosphere as cooling may alter island sizes and shapes [3,14]. Second, measuring one island with good time resolution, rather than comparing different islands after fixed amounts of capping, enables quantitative analysis of the transformation kinetics.

Ge/Si(001) islands were examined during Si capping at temperatures between 550 °C and 600 °C. We find that, during Si deposition, the shallow (pyramid) facets grow larger at the expense of the steeper facets [cf. Fig. 1(b) for a sketch]), in agreement with previous studies [10,12,13]. The islands therefore flatten. Unexpectedly, we also observe a significant decrease in island *volume*, which is more pronounced in dislocated islands than in coherent islands. By following the development of shape and volume together, we obtain a unique insight into the dynamics of the transformation, and we develop a model that explains the transformation by considering the energetic balance between the wetting layer (WL) and the islands. This model is based on the fact that Si deposition onto WL leads to an enhanced Si content in the subsurface layers. This induces diffusion of Ge from the islands into the WL, enhancing the speed of the transformation from domes to pyramids, and, in certain growth regimes, leading to island shrinkage.

The growth experiments were carried out in a UHV TEM having gas handling facilities allowing ultrahigh vacuum chemical vapor deposition to be carried out onto a specimen while under observation. The base pressure is 2×10^{-10} Torr [15]. A slice of Si(001) wafer, chemically cleaned, was mounted in the microscope with the (001) surface viewed edge-on with the electron beam parallel to ⟨110⟩ [14]. Once in the microscope, a clean surface was prepared by flash heating the specimen (using direct current) to 1250 °C. Island growth was initiated, with the

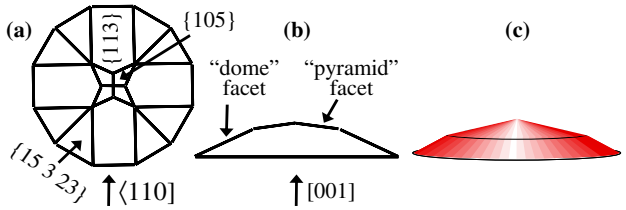

FIG. 1 (color online). (a) Schematic of the facets comprising a dome-shaped island viewed from above (i.e., along [001]). (b) Projection along ⟨110], indicating pyramid and dome facets creating apparent facet angles of 8° and 25°, respectively. (c) Approximation of a circular base used in this work.

electron beam on, by reducing the sample temperature to around 600 °C and exposing it to digermane. After islands of a suitable size had formed, digermane was switched off and disilane was introduced into the chamber at a pressure of 5×10^{-7} Torr at the same temperature. This temperature was calibrated before deposition using infrared pyrometry (accuracy to within ±30 °C). As Si was deposited, changes in a single island's morphology were recorded in a dark field imaging condition. This used a 311 reflection that is sensitive to the projected thickness of the island and hence allows the island edges and substrate surface to be visualized.

In Figs. 2(a) and 2(b) we show images of a coherent island (i.e., an island without dislocations) and a dislocated island obtained during Si deposition. When viewed along the [110] direction, the steeper (dome) facet appears at an angle of 25° and the shallower (pyramid) facet at 8° [Fig. 1(b)]. The actual facet lengths are not always discernible. It is more accurate to determine the island width and height. Surfaces of the island and the substrate show up as brighter and darker lines, respectively, in the images. The island height to width ratio was determined from the images and was used to calculate the facet lengths, by assuming a dome-shaped base with pyramid facet angles set by the crystallography. Island volumes are determined assuming a circular base and the geometry implied by Fig. 2(a) [cf. Fig. 1(c)]. The exact shape assumed for the island base does not have a significant effect (<1%) on the measured island volume change.

First, we focus on the shape and size changes of the coherent island shown in Fig. 2(a). Facet lengths are plotted as a function of deposition time in Fig. 3(a), while aspect ratio and volume changes are plotted in Fig. 3(b). As

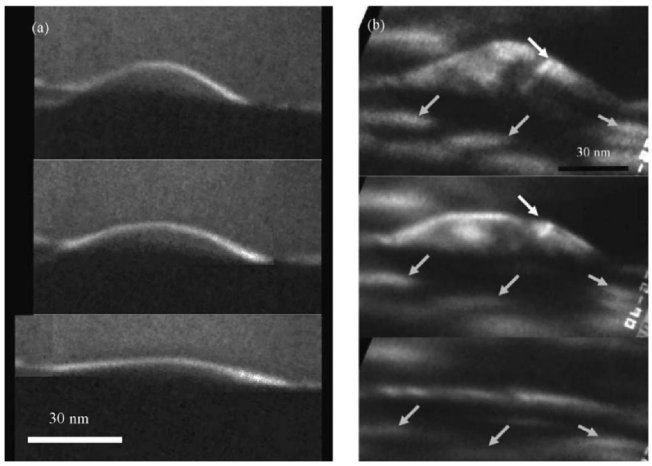

FIG. 2. (a) TEM images of a coherent SiGe island during Si deposition shown at $t = 0$, 90, and 180 s as it transforms from dome to pyramid under a disilane flux of 10^{-6} Torr. (b) Three stages of a large, dislocated dome-shaped island dissolving during Si deposition. A defect in the island is indicated by white arrows. Some small islands close by (indicated by the gray arrows) are less affected by the Si deposition.

these figures show, there is a dramatic change in the island shape during Si deposition. The length of the pyramid facet increases while the dome facet decreases until it disappears. This is consistent with previous *ex situ* observations [10,11]. The experimental data in Fig. 3(b) agrees with a starting shape of pure dome (expected aspect ratio of 0.23), and with a finishing shape of pure pyramid (expected aspect ratio of 0.07). The island volume, also shown in Fig. 3(b), stays approximately constant during the initial stages of Si deposition. After about 90 s, however, the volume starts to decrease. When the island has completely transformed into a pyramid, its volume has decreased by ~50%.

For larger, dislocated islands, the reduction in volume is even more significant. Some dislocated islands dissolve completely under Si deposition. They do this by introducing a flat {001}-type facet at the top, which expands during Si deposition at the expense of the dome and pyramid facets [Fig. 2(b)], again consistent with previous observations [10–13]. *Ex situ* experiments [5] have shown that a flat top facet in combination with a steep side facet becomes stable for large islands with significant Si content. A theoretical phase diagram [6] predicted this shape and showed that, in agreement with our experiments, a reduction in volume leads directly from the "steep side, planar top" facet to a planar layer without any intermediary island shapes.

We suggest, and justify below, that these changes in shape and volume observed during overgrowth are a direct consequence of the change in the stability of the islands *and the wetting layer*. In the initial stages of Si_xGe_{1-x} island formation, alloying of the deposited material (Ge) with substrate material (Si) results in a WL [i.e., the top 2–4 MLs (monolayers)] of graded composition, and the 2D to 3D transition occurs when WL reaches a "critical thickness" at a "critical composition" [16,17]. During the initial stages of Ge deposition, it is the Si from the substrate that intermixes with the WL. In a similar way it seems plausible that Si capping leads to an intermixing of the deposited Si not only with the material in the islands but also with the material in the WL.

Island shape is expected to change with composition [5] and was observed during Si capping [10–13]. But Si incorporation alone could only increase the island size, not reduce it. Island shrinkage implies that more material would leave the island than is added by Si deposition. Studies of the thermodynamics and kinetics of the intermixing of Si with a Ge_xSi_{1-x} WL [18] indicate that Si deposited on a WL with more than 3 MLs of Ge can be incorporated into only the third or possibly the fourth ML below the surface. Si incorporation into the top two MLs is thermodynamically unfavorable, while Si incorporation into lower layers is kinetically limited. Since evaporation and/or incorporation of deposited Si into bulk are expected to be negligible at our deposition conditions, there are two

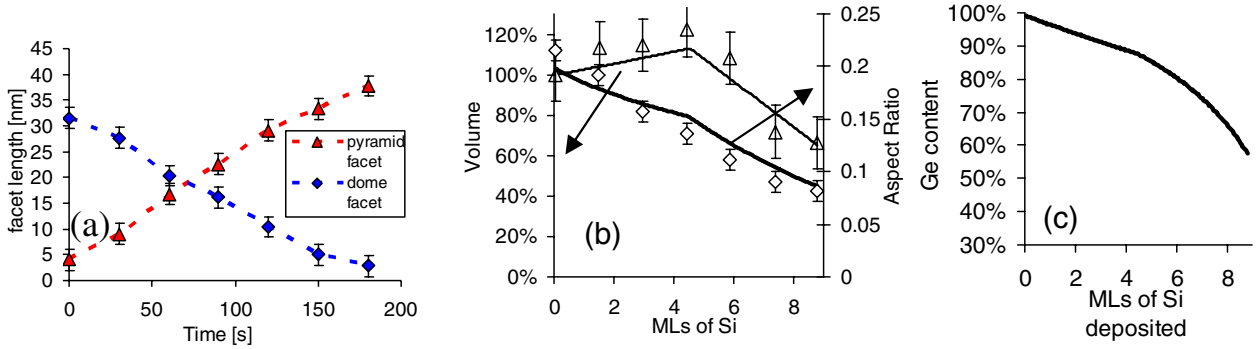

FIG. 3 (color online). (a) The pyramid and dome facet lengths for data in Fig. 2(a), assuming that the projection of the dome surface is composed of (105) and (15 3 23) facets. (b) Comparison of the aspect ratio (◇) and the volume change (△) data, measured from Fig. 2(a), with the results of the model (solid lines). (c) The decrease in the Ge content of the island predicted by the model. The change in the slope at 4 MLs corresponds to the onset of the Ge diffusion into the wetting layer (see text).

possibilities: (1) The Si starts to cap the top two Ge-rich layers. This is thermodynamically unfavorable and can therefore only be achieved by depositing the Si at low temperatures and high flux. (2) Si is incorporated into WL and changes its composition. In this case the composition of the WL may drop below the critical composition for island formation, after which the system of islands plus the WL is no longer stable and islands dissolve by diffusion of Ge from the islands into the WL. The Ge is supplied from the layers below the island surface. The surface segregation of Ge is favorable due to the atomic size difference and the comparatively lower surface energy of Ge [8]. An upper limit for the rate of island dissolution exists when the system maintains the critical composition of the WL [17]. In this case, according to Ref. [18], the top two layers would stay Ge rich while alloyed layers are added below.

If we assume that possibility (2) is the case during our experiments, we can develop a simple, semiquantitative model that explains the experimentally observed shape and size evolution during capping. Assuming the maximum rate of Ge diffusion from the islands into WL, the amount of Ge, $\Delta N_{\mathrm{Ge}}^{\mathrm{wet}}$, diffusing in one time step, is $\Delta N_{\mathrm{Ge}}^{\mathrm{wet}} = \frac{c_{\mathrm{critical}}^{\mathrm{wet}}}{1-c_{\mathrm{critical}}^{\mathrm{wet}}} \Delta N_{\mathrm{Si}}^{\mathrm{wet}}$ [19], where $\Delta N_{\mathrm{Si}}^{\mathrm{wet}}$ is the number of Si atoms deposited onto the WL during this time step and $c_{\mathrm{critical}}^{\mathrm{wet}}$ is the critical WL composition. $\Delta N_{\mathrm{Si}}^{\mathrm{wet}}$ depends on the available WL surface per island (i.e., the surface coverage) and on the Si deposition rate ($\Delta N_{\mathrm{Si}}^{\mathrm{wet}} = k \frac{1-\mathrm{coverage}}{\mathrm{coverage}} r^2 \pi$, where k is a constant determined by the deposition rate and r the island radius). Similarly, the number of Si atoms deposited on the surface of the island, $\Delta N_{\mathrm{Si}}^{\mathrm{island}}$, is a function of the surface area of the island and the deposition rate. Finally, since no Ge is being deposited, $\Delta N_{\mathrm{Ge}}^{\mathrm{island}} = -\Delta N_{\mathrm{Ge}}^{\mathrm{wet}}$. The size change $\Delta N^{\mathrm{island}}$ of the island is then $\Delta N^{\mathrm{island}} = \Delta N_{\mathrm{Si}}^{\mathrm{island}} - \Delta N_{\mathrm{Ge}}^{\mathrm{wet}} = \Delta N_{\mathrm{Si}}^{\mathrm{island}} - \frac{c_{\mathrm{critical}}^{\mathrm{wet}}}{1-c_{\mathrm{critical}}^{\mathrm{wet}}} \Delta N_{\mathrm{Si}}^{\mathrm{wet}}$, and the composition $c(t + \Delta t)$ of the island after a time step Δt is $c(t + \Delta t) = \frac{c(t) N^{\mathrm{island}} - \Delta N_{\mathrm{Ge}}^{\mathrm{wet}}}{N^{\mathrm{island}} + \Delta N^{\mathrm{island}}}$.

These expressions were used to determine the change in island volume, composition, and hence aspect ratio [20] as a function of deposited Si with the parameters in the model resembling as closely as possible the experimental parameters. We assume a constant Si deposition rate, that the island is composed of 100% Ge prior to Si deposition with a volume of 10^6 atoms, and that the critical composition (in line with predictions in [17]) is 23% Ge. Surface coverage, which is not known in our experiments, is used as a fitting parameter and set at 5%. The facet lengths are optimized after each deposition step for the new island composition and volume by minimizing the total energy of the island using a similar process and the same values for the surface and strain energy as in Ref. [8].

Comparison of the experimental data to values predicted by this model is shown in Fig. 3(b). This comparison suggests that the onset of Ge diffusion in the experiment commences at about 90 s. This may be because the composition of the WL actually exceeds the critical composition at the start of the Si deposition. As a consequence, the slope of the theoretical curve in Fig. 3(c) changes at about 4.5 MLs when the Ge diffusion starts. While the onset is abrupt in the model, it is expected to be more gradual in the experiment due to kinetic effects. This gradual onset and the experimental measurement errors may explain why it is not directly visible in the data.

The fact that, for a realistic set of parameters, changes in both volume and aspect ratio [Fig. 3(b)] are predicted well by the model suggests that island shrinking is indeed induced by Ge diffusion from the island to the WL. This is consistent with *ex situ* investigations [10] which show that island shrinkage is kinetically limited only at Si deposition below 450 °C. In our experiments, island composition could not be measured directly during the transformation. However, large compositional changes have recently been measured during Si capping [13] and are in good agreement with our model predictions [Fig. 3(c)]. It is also important to realize that all the processes involved in the model are surface processes and do not require bulk

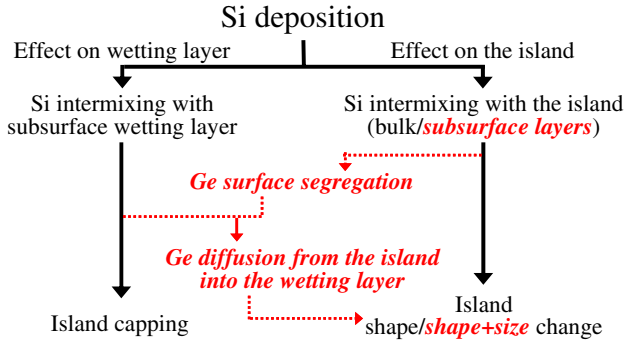

FIG. 4 (color online). Schematic of the changes in the wetting layer and the island during the capping process with the modifications proposed in this Letter are shown in italics/dashed lines.

diffusion, which has been shown to be too slow at the temperature considered here to have a significant effect [21]. The results of the modeling in Figs. 3(b) and 3(c) are not fully quantitative for two reasons: (i) the surface coverage was estimated, and (ii) there are uncertainties in the values for the surface energies because the exact reconstructions are unknown for some of the facets involved. Nevertheless, the good agreement between experiment and theory gives confidence in the model.

We finally consider the morphological evolution of dislocated islands which exhibit even more dramatic decrease than coherent islands and may even disappear completely. In the case of coherent islands, a misfit strain arises due to the difference in Ge content between the deposited material and the substrate. Introduction of dislocations partially relieves the strain. Since the critical thickness and composition at which the 2D to 3D transition occurs of course depend sensitively on the strain, WL composition $c^{\text{wet}}_{\text{critical}}$ surrounding dislocated islands is likely to be different from that of coherent islands. This affects the island dissolution rate and, depending on the composition, could result in complete disappearance of the island. Surface adatom mobilities are also influenced by strain and could contribute to the observed behavior.

In summary, during overgrowth of coherent dome islands, we find a shrinkage in island volume that occurs simultaneously with the dome to pyramid transition. We can account for this change using a model that combines features that are known to occur during capping (intermixing in the island adn contributing to the shape transformation) with processes taking place in the wetting layer. A schematic of this model is shown in Fig. 4. Both the complete reversal of island growth (i.e., dissolution) in the case of dislocated islands and the partial reversal (dome to pyramid transformation) for coherent islands can be understood by taking into account the balance between the wetting layer and the islands and the interplay of kinetics and thermodynamics during capping. These results provide insights into atomic processes that control quantum dot size and consequently electronic and optical properties. Furthermore, the preferential dissolution of dislocated islands may be important in fabricating defect free devices.

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[19] If for every deposited Si atom at a critical composition c more than $c/(1-c)$ Ge atoms were to diffuse from the islands, the critical composition would be exceeded and the system island + WL would be stable.
[20] The island was assumed to be composed of two parts, the bottom of the island with a facet angle of 25° and the top with a facet angle of 8°. For a given c and V, the optimum facet length was determined from the values for the strain and surface energies for pyramid and dome-shaped island from previous atomistic modeling [8]. The aspect ratio was determined by varying the ratio (pyramid facet length)/(dome facet length) until the total energy of the island is equal to the energy of a pyramid shaped island with equal volume and composition.
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