Lateral Motion of SiGe Islands Driven by Surface-Mediated Alloying

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SiGe islands move laterally on a Si(001) substrate during *in situ* postgrowth annealing. This surprising behavior is revealed by an analysis of the substrate surface morphology after island removal using wet chemical etching. We explain the island motion by asymmetric surface-mediated alloying. Material leaves one side of the island by surface diffusion, and mixes with additional Si from the surrounding surface as it redeposits on the other side. Thus the island moves laterally while becoming larger and more dilute.

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The self-assembly of semiconductor nanostructures by thin film deposition techniques, such as molecular beam epitaxy, has received much attention as a means of fabricating quantum dots for device applications [1–3]. The quantum dots form as surface islands via Stranski-Krastanow growth; and Ge on Si(001) has emerged as a prototypical model system for the study of this process. In this growth mode, Ge initially wets the Si surface to form a thin wetting layer which is followed by the formation of coherently strained three-dimensional (3D) islands which relieve misfit strain. Once the islands form, it is well known that they may change their size and shape during ripening [4–6]. At high growth temperatures, the islands are alloyed with Si. SiGe composition profiles inside the islands have been measured recently [7–10]. However, it is generally assumed that the composition profile has either a fourfold or cylindrical symmetry and the centers of mass of isolated islands remain fixed (see, e.g., Ref. [11]).

In this Letter, we show that semiconductor islands can and do move laterally on the substrate during postgrowth annealing. This motion is driven by an asymmetric alloying process, and leads to unexpectedly complex composition profiles in self-assembled quantum dots. We anticipate that this will be of relevance to other material systems.

The samples studied here were grown by solid-source molecular beam epitaxy (MBE). After oxide removal and Si-buffer growth, Ge was deposited at a rate of 0.04 monolayers (ML) per sec, at a substrate temperature of 740 °C. For some samples, the island layer was overgrown with 90 nm of Si and a second island layer, with identical growth parameters, deposited on top. The samples were annealed *in situ* at the growth temperature for different times, and then cooled to room temperature (RT) for the characterization. The specimens were etched with either a mixture of $HF : H_2O_2 : CH_3COOH$ [12] (BPA solution) or $NH_4OH : H_2O_2$ [13]. Both etchants selectively etch $Si_{1-x}Ge_x$ alloys over pure Si (the selectivity is 1100:1 for $Si_{0.6}Ge_{0.4}$ over pure Si in the case of BPA, while no appreciable etching of pure Si occurs for $NH_4OH : H_2O_2$), but the etching rate of BPA is orders of magnitude higher (about 110 nm/s compared to 0.007 nm/s at RT for a $Si_{0.6}Ge_{0.4}$ alloy). The samples were characterized by *ex situ* atomic force microscopy (AFM). The *same* surface areas were imaged prior to and after etching, providing unambiguous information on the island evolution and composition profiles.

Figure 1(a) displays an AFM image of SiGe islands obtained by deposition of 10 ML of Ge on Si(001) at 740 °C. The color scale allows steep and shallow facets to be distinguished according to the local surface slope with respect to the (001) plane. The islands consist of domes and ''barns'' [14], and have an average height of 41 ± 4 nm.

As reported previously, postgrowth annealing causes island coarsening and strong SiGe intermixing [5,15–18], leading to a reverse transition of domes to pyramids through intermediate shapes. This is illustrated in Fig. 1(b), which shows an AFM image of a sample obtained by deposition of 10 ML of Ge and subsequent annealing at 740 °C for 20 min. Most of the islands transform back to pyramids, labeled ''P'' in Fig. 1(b), and to transition structures [''T'' in Fig. 1(b)]. Detailed transmission-electron-microscopy characterization reveals that the islands are dislocation free. The transition structures are generally asymmetric and have one side with steep, domelike facets [the upper-left side of the transition island marked in Fig. 1(b)] while the rest of the island has mainly shallow pyramidlike {105} facets.

AFM scans obtained after selective wet etching for 2 min in BPA solution are shown in Figs. 1(c) and 1(d) for the same areas shown in Figs. 1(a) and 1(b). Following island removal by the etching, only plateaus remain on the exposed Si surface [19] that was formerly below the islands. These plateaus are circular for the nonannealed sample [Fig. 1(c)] and surrounded by approximately square trenches with sides parallel to the [100] and [010] directions [20]. Etching of the annealed sample [Fig. 1(d)] reveals that the Si plateaus assume a ''half-moon'' shape sur-

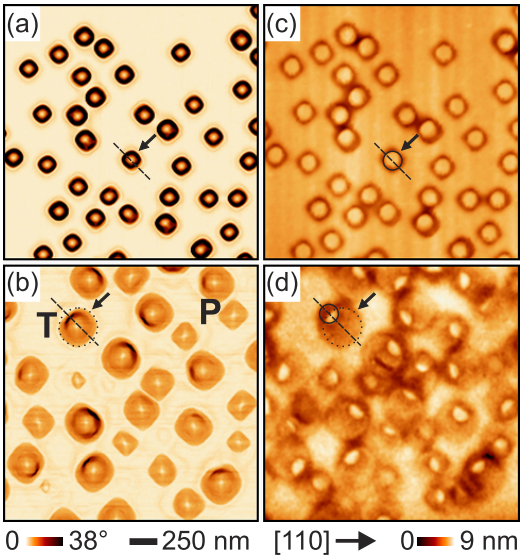

FIG. 1 (color online). AFM images of SiGe islands (a),(b) before and (c),(d) after selective etching in BPA solution. The amount of Ge deposited was 10 ML at 740 °C; color scale in left and right panels represents slope and height, respectively. In (a),(c) the sample was cooled to RT immediately after growth while in (b),(d) the sample was annealed for 20 min at 740 °C. Solid circles in (c),(d) indicate representative Si plateaus. The dashed circles in (b),(d) mark island perimeters after annealing.

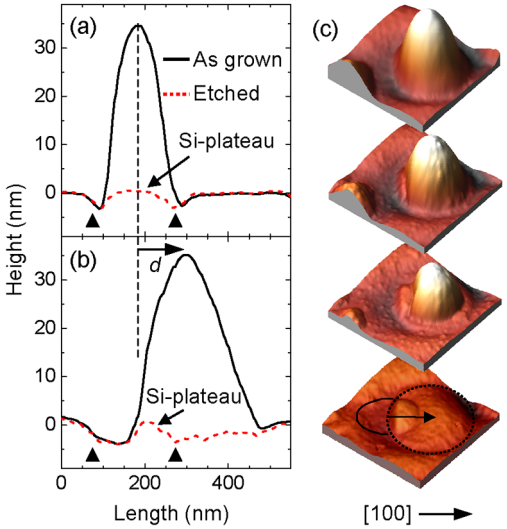

FIG. 2 (color online). AFM line scans, taken along the dashed segments shown in Fig. 1, of two representative SiGe islands (a) prior to and (b) after annealing for 20 min at 740 °C. Triangles represent the position of the trench minima around the Si plateau before annealing. (c) 440 × 440 nm^2 AFM images (3D view) of an island after sample annealing for 10 min at 740 °C (top) and subsequent etching in a $NH_4OH : H_2O_2$ solution at RT for 80, 170, and 620 min (from top to bottom). The arrows in (b) and in the bottom panel of (c) represent the displacement d undergone by the island apex during annealing.

rounded by asymmetric trenches. By comparing the half-moons with the original plateaus [see black circle in Fig. 1(c)] and measuring samples annealed for shorter periods (not shown), we find that the half-moon shaped plateaus are remnants of the original circular plateaus. While the apex of the island lies above the center of the plateau for the nonannealed sample, it is significantly displaced from the plateau center after annealing. We can thus conclude that, during annealing, islands not only intermix and change their shape, but also *move* laterally on the surface.

This is clearly illustrated in Fig. 2, where line scans of representative islands are plotted before (solid line) and after (dashed line) etching in BPA solution. The cross sections are taken along the dashed segments shown in Fig. 1. Figure 2(a) shows a typical dome-shaped island which sits on a symmetrical plateau that is uncovered after etching. Triangles below the line scan indicate the trench minima. Figure 2(b) is a transition island with domelike facets on the left side, close to a deep trench, and shallower facets on the opposite side. The etching reveals an asymmetric plateau under the steep part of the island. The area comprising the asymmetric plateau and the deep trench has exactly the same size as the plateau in Fig. 2(a), as emphasized by the triangles below the line scan. The arrow marked with d indicates the estimated distance that the island apex has moved during annealing.

These results can be explained by lateral island motion, which occurs by material removal from the left side of the island and attachment on the right side. As a consequence of this motion, part of the initially circular Si plateau becomes uncapped and diffuses away from the compressed region at the foot of the receding left edge of the island, leaving behind a deep trench. In contrast, the remaining part of the Si plateau buried under the island is preserved, because it is never exposed to surface diffusion. (Mass transport due to bulk interdiffusion seems to be negligible under our growth and annealing conditions, as indicated by the observation of clear half-moon structures even after annealing periods as long as 10 h.) At the same time, the right island edge advances, continuously generating a new, shallower trench at its foot, which is overgrown during further island movement. The island/substrate interface [dark area inside the dashed circle in Fig. 1(d)] of the newly formed portion of the island is therefore slightly lower than the surrounding substrate.

In addition to moving laterally, the average island size increases, as seen in Fig. 3. We interpret this as due to island coarsening (the size distribution broadens with time) and, most importantly, to incorporation of Si into the islands, since the total amount of material contained in the islands is found to increase during annealing. Ultimately, the Si must come from the substrate, since that is the only source of additional material. Bulk diffusion of Si from the regions of the substrate below the islands appears to be negligible, as discussed above; and in any case it should be accompanied by migration of an equal amount of Ge into the substrate, leading to no net increase of the total volume of material in the islands. We therefore conclude

that the Si incorporated into the islands comes from the region between islands, via surface diffusion.

For annealing periods up to 10–20 min we find that the island volume increase is roughly equal to the volume of material removed from all areas below the substrate level, including the island trenches, and the depressions seen on the substrate in regions with high density of islands [20] [visible as dark areas in Fig. 1(d)]. For longer annealing times, also Si coming from regions far away from the islands is apparently contributing to the island volume increase. It is known that islands intermix during growth [10] and that SiGe intermixing occurs already during the growth of the wetting layer [21]. Moreover, when islands form, they capture material from the wetting layer [22]. We expect that this process renders the wetting layer sufficiently thin, so that Si from subsurface layers can readily reach the surface during annealing.

Si diffusion through the wetting layer provides an effectively infinite reservoir of Si at the chemical potential of bulk Si [23]. Si from this reservoir is mixed into the Ge taken from the receding side of the island, and the resulting alloy is added onto the growing side. Thus there is SiGe intermixing over a large part of the island volume, achieved *exclusively by surface diffusion*.

This alloying reduces the strain [18,24], causing the newly formed portions of the island to assume a pyramidlike shape. In Fig. 2(b), the left side of the transition island is still domelike, while the right side is pyramidlike. Etching experiments with $NH_4OH:H_2O_2$ demonstrate that the domelike side, lying above the half-moon shaped plateau, is etched faster than the remaining island part. This is demonstrated in Fig. 2(c), which shows a sequence of AFM images of an island etched for increasingly long times at RT (see figure caption for details). These results are consistent with a Ge-rich composition of the left side, which we interpret as a remainder of the original island from before annealing, and a lower Ge content of the right island side, because of the Si added to this side during the motion.

The island displacement depends on the annealing time. This is quantified by measuring the distance d between the centers of the island base before and after annealing [see bottom panel of Fig. 2(c)]. The average value of d as a function of annealing time is shown in Fig. 3. The displacement increases rapidly for short annealing times, and begins to slow down after about 20 min. Meanwhile, the average island volume increases.

In order to understand the origin of the island motion, we consider a strictly facetted pyramidal island of pure Ge. We assume that there is no composition dependence of the surface energy, and we neglect the island strain relaxation. Though highly simplified, this is sufficient to illustrate the physical origin of the lateral motion. To test for a lateral-motion instability, we assume an initial small motion, and examine whether the chemical potentials favor further motion, or tend to stop or reverse the motion.

Consider an island in which an alloy layer with Ge composition x has been formed by removing Ge from one side (or two adjacent sides) of the pyramid and adding it to the opposite side(s), along with some Si originating from the substrate via surface diffusion [Fig. 4(a)]. The difference in Ge chemical potential between the mixed side and the pure-Ge side is $\Delta\mu_{\mathrm{Ge}} = kT\ln(x) - U(1-x)^2$, where U is the strain energy per atom for pure Ge. The two terms correspond to entropy and strain energy, and both are always negative, favoring the process. (Ge motion alone contributes no change in volume or surface energy.)

Therefore, Ge is drawn from the bare side to add to the mixed side, if Si is supplied simultaneously. During annealing, the substrate acts as a reservoir for Si; and the difference in Si chemical potential between the substrate and the alloyed side of the island is $\Delta\mu_{\mathrm{Si}} = kT\ln(1-x) - x^2U + \Gamma V^{-1/3}$. Here V is the island volume and Γ reflects the surface energy (and also includes geometrical factors, etc.). The first two terms on the right side of the equation are always negative, so Si is always drawn from the substrate to add to the island, unless the surface energy term becomes dominant.

Note that the alloy covers the right (growing) side of the island, so on that side the pure-Ge core is not accessible by surface diffusion, and only the alloyed surface layer is relevant. But on the left (shrinking) side of the island, Si cannot be incorporated (or not to any depth beyond what is accessible by surface diffusion [23]), so the pure-Ge core remains exposed and can continue to diffuse away.

In reality, islands are not pure Ge, because some intermixing occurs during growth [8,10,25]. Nevertheless, if bulk diffusion is negligible, material can only be removed stochiometrically, so the same arguments apply (with a quantitative reduction of the energy differences). Including island relaxation and more complex shape evolution [6] would modify the effect quantitatively but not qualitatively. The important point is that this basic mechanism

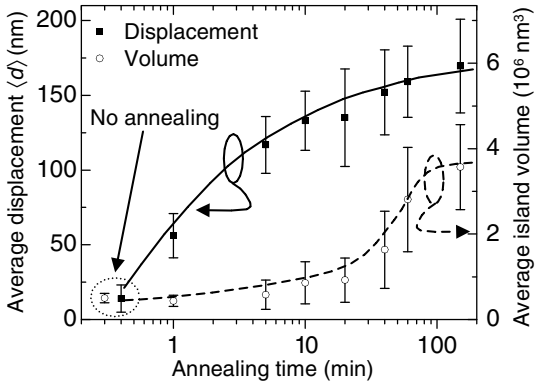

FIG. 3. Average displacement (solid squares) and volume (empty circles) of islands as a function of annealing time. Lines illustrate the main trend. (The data points corresponding to the nonannealed sample are shifted in order to be displayed in logarithmic scale.)

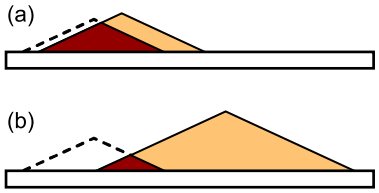

FIG. 4 (color online). Schematic model for the island movement. Dashed lines indicate the original island profile; dark and light shadings indicate Ge and SiGe alloyed areas, respectively. See text for details.

can always provide a driving force for lateral island motion, if the Si reservoir is kinetically accessible.

We have shown that, once initiated, this process of alloying via lateral motion is self-sustaining. We can also suggest a mechanism by which the motion is initiated. A detailed statistical analysis reveals a strong correlation between the *direction* of motion and the direction away from the nearest neighbor, for islands located very close to each other before annealing [26]. Thus, the elastic repulsion could drive the initial motion. However, the *magnitude* of the displacement is always comparable to the island radius and shows no obvious correlation with the proximity of other islands, consistent with our proposed mechanism.

We expect that the lateral motion can proceed until much of the original island has intermixed with Si from the substrate. However, within the approximation of fixed island shape, the chemical potential of the receding side is an average over a shrinking Ge region and an increasing alloy region (Fig. 4). This will eventually slow down the translation, as observed experimentally (Fig. 3).

Our experiments naturally raise the question whether the island motion can be suppressed. We have studied a sample consisting of a stack of two layers of islands separated by a 90 nm thick Si spacer layer [26]. We find that no appreciable displacement of the surface islands occurs after 10 min annealing. This can be explained by the surface strain modulations produced by the buried island layer which create energetically favored positions for the surface islands [27–29], suppressing lateral motion. Moreover, the annealing produces an increase of the average island volume of only 20%, while in a single layer the volume increase is about 70%, in agreement with the idea that the island motion enhances intermixing.

In conclusion, we have shown that self-assembled SiGe islands move laterally on the substrate surface during annealing by an asymmetric alloying process. This alters the compositional profile of the islands and hence their electronic properties. Our findings provide also a natural explanation for the asymmetric dome island etching, which was reported in Fig. 1 of Ref. [10]. The mechanism driving island lateral motion is not specific to Si/Ge and seems likely to occur in other material systems.

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