Critical Role of Surface Steps in the Alloying of Ge on Si(001)

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Using low-energy electron microscopy, we show that intermixing of Ge on Si(001) during growth is enhanced on stepped surfaces and is hindered on terraces where step flow does not occur. On large terraces we have identified a dramatic and unanticipated structural rearrangement that facilitates intermixing: Pairs of steps spontaneously form and migrate over the surface, leaving alloyed regions in their wake. The driving force for step formation is the entropy gain associated with the enhanced intermixing of Ge.

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Alloy formation is a long-studied problem, and the structure and stability of many complex alloys are well understood. In contrast, less is known about the mechanisms of alloy formation, especially during growth. Here we show that step flow during growth plays a key role in the intermixing of Ge at the Si(001) surface. By the simple process of overgrowth during deposition, a larger volume of the crystal becomes alloyed with Ge, which lowers the free energy. Enhanced intermixing via step flow is frustrated on very large terraces, where step flow does not occur. On these terraces we have identified a dramatic and unanticipated structural rearrangement that facilitates intermixing: Pairs of up-down steps *spontaneously form* and migrate over the surface, leaving alloyed regions in their wake. The motion of these step pairs, or "stripes," provides a mechanism for artificial step flow, which allows enhanced intermixing. Surprisingly, we find that the modest energy gain associated with enhanced intermixing is sufficient to induce pairs of steps to nucleate and migrate over the surface.

Interest in the Ge/Si(001) system has increased significantly over the past decade, stimulated in part by the technological importance of SiGe devices [1]. However, SiGe is also attractive as a model alloy system: Si and Ge have similar properties, and the energetics of bulk SiGe alloys are fairly well understood. Above about 100 °C, Si and Ge form a random solid solution at all stoichiometries [2]. There are no ordered equilibrium alloy structures, and the driving force for alloying is essentially the increase in configurational entropy. In equilibrium, nearly all of the Ge deposited on the Si(001) surface during growth should migrate to the bulk. Complete intermixing is, however, kinetically limited in the range of typical deposition times and growth temperatures. However, several investigations have shown that, even at modest growth temperatures, submonolayer coverages of Ge will alloy into Si(001), with a significant fraction of the Ge residing in the first few surface layers [3–7].

We investigated the kinetics of alloy formation by measuring the evolution of surface morphology during growth. We deposited Ge by exposing Si(001) to digermane. In order to grow close to equilibrium, we used very low growth rates, 0.1 monolayers (ML) per minute, and relatively high growth temperatures (750 °C to 900 °C). The surface was imaged during growth using low-energy electron microscopy (LEEM) [8], and after growth using atomic force microscopy (AFM). Absolute Ge coverages were determined *ex situ* using medium-energy ion scattering, with an absolute accuracy of about 5%. The LEEM images were recorded using dark-field imaging of one of the two equivalent orientations of the 2×1 reconstruction. In this imaging mode, the contrast changes from dark to bright (or vice versa) at a ML-high surface step [8,9].

At near-equilibrium conditions, the growth of the first monolayer occurs by step flow. All deposited Ge atoms, or the Si surface atoms they displace, diffuse to surface steps where they incorporate [10]. Above a coverage of about 0.8 ML, a diffuse $2 \times N$ diffraction pattern (due to the ordering of dimer vacancy lines) is observed, which sharpens if growth is interrupted and the surface is cooled to room temperature. In the coverage range 0.8 to 1.0 ML, a dramatic change occurs on the larger terraces, as shown in the sequence of images in Fig. 1. The sequence starts after ≈ 1 ML has been deposited at 750 °C. The bright region at the center of the images is a step-free terrace that forms the bottom of a lithographically produced pit [11]. During growth, the terrace shrinks due to step flow of the bounding step. At the bottom of the center terrace a dark "stripe" appears (indicated by arrows). The stripe nucleated in the narrow channel formed at a "kissing site" where out-of-phase 2×1 domains meet [12]. A second stripe nucleates in the upper left of the terrace (outside the field of view). The change in contrast (black stripes and white terrace) suggests that the stripes are bounded by ML-high steps. That is, the stripes are either one layer lower (i.e., a ML-deep trench) or one layer higher (a ML-high hedge) than the surrounding white terrace. As we describe below, AFM images show that stripes are alternating chains of

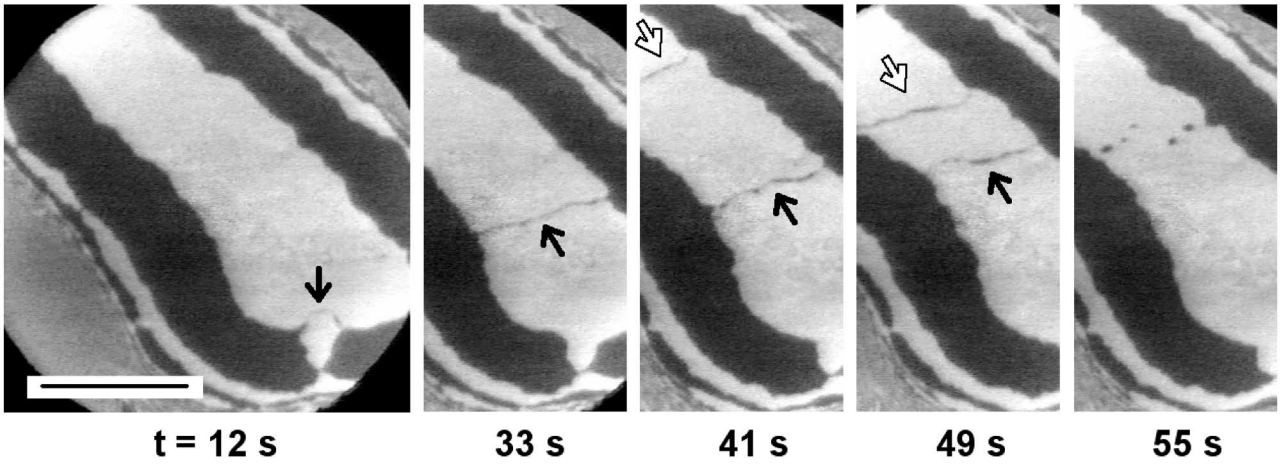

FIG. 1. Sequence of 2.3 eV dark-field LEEM images showing the nucleation and migration of two stripe features. One stripe (black arrow) emerges from the bottom of the field of view, and the other (white arrow) from the top. The stripes nucleated after one monolayer of Ge was deposited at 750 °C. When the two stripes meet, they annihilate. The images are labeled by the time after the stripes nucleate. Scale bar, 2 μm.

trenches and hedges. The stripes move rapidly across the terrace, all the while remaining connected in a continuous ribbon. The stripes do not move randomly, but in a directed fashion, never sweeping over any part of the terrace more than once. When the two stripes meet they annihilate, leaving behind small islands that coarsen away (last panel of Fig. 1).

If deposition is continued after the stripes have passed through, the surface will eventually roughen as the coverage approaches 2 ML, in agreement with the findings of Maxson *et al.* [13]. The nucleation of the stripes is not strongly influenced by the instantaneous Ge flux. If deposition is stopped when the Ge coverage is about 0.8 ML, and the surface is annealed to a slightly higher temperature, stripes will eventually nucleate (that is, stripes can nucleate even if there is no Ge flux). Not surprisingly, the speed at which the stripes advance increases with increasing temperature. Typical speeds are 80 nm/s at 750 °C, and 600 nm/s at 830 °C. As we discuss below, these speeds suggest that the driving force on the stripe is small.

The LEEM contrast suggests that the stripe structure is bounded by steps. Using *ex situ* AFM, we investigated the structure of the stripes in more detail. A LEEM image of the surface after stripe formation, and subsequent cooling to room temperature, is shown in Fig. 2(d). At room temperature, the stripes have a zigzag, or faceted, structure which consists almost entirely of low-energy *A*-type steps. An AFM image from the same region is shown in Fig. 2(e). Stripes run horizontally at the top and bottom of the image. It is clear that the stripes consist of alternating chains of ML-high islands (hedges) and ML-deep vacancy islands (trenches) [Figs. 2(e) and 2(f)]. The islands comprising the stripe are connected, and remain so even upon annealing. This connectivity is most likely caused by the fact that stripes constitute a boundary between translationally out-of-phase $2 \times N$ domains.

Clearly, there is a driving force that causes the stripe to advance. However, the stripes themselves are not energetically favorable. They nucleate, move in a directed fashion over the surface, and annihilate at the opposite side of the terrace. Low-energy electron diffraction measurements imply that the structure of the near-surface region is not significantly changed by the passage of the stripe. If the temperature is rapidly lowered after a stripe nucleates, the stripe will stop moving. Using a selected-area aperture, we recorded electron diffraction patterns from ≈ 2 μm regions of the surface both behind and in

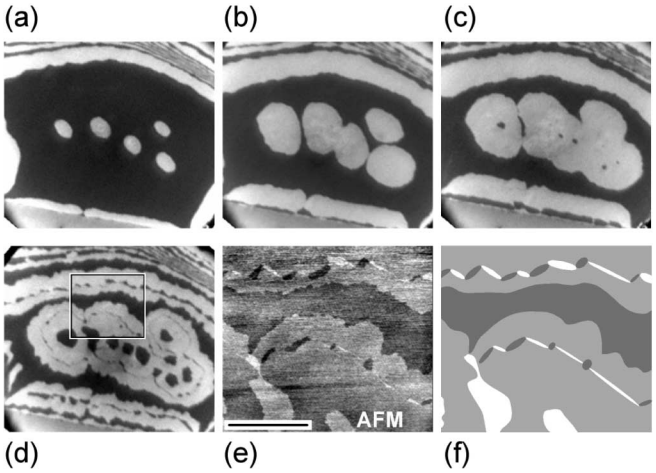

FIG. 2. (a)–(d) LEEM images of 1 ML/min Ge growth on Si(001). (a) First-layer islands (white) nucleate and (b) coalesce into a "mesa." (c) Second-layer islands (black) nucleate on the mesa layer. (d) Stripes form at the center of the mesa and rapidly move out to the edge. (e) AFM image showing the detailed structure of the stripe. The image corresponds to the boxed area in (d). The stripes are an alternating chain of vacancy islands and adatom islands. Scale bar, 1 μm. (f) Schematic of the stripe structure shown in (e). ML-high islands are white, ML-deep pits are dark grey.

front of a frozen-in stripe. Both areas exhibit sharp $2 \times N$ diffraction patterns, where N is the same for both regions (typically $N = 10$ to 12 depending on the Ge coverage [3]), with no discernible difference in the intensity-versus-voltage profiles.

We now show that the passage of the stripe enhances the migration of Ge to deeper layers of the substrate. To do this, we prealloyed selected regions of large terraces. We find that stripes will not pass through the alloyed areas, implying that the driving force on the stripe is directly related to alloy formation. Etching Si(001) with oxygen at elevated temperature leads to the formation of ML-deep etch pits [14]. During Ge growth, the bottoms of these pits are directly exposed to Ge, which becomes incorporated in the surface layer, and to a lesser degree in the near-surface region [3–7]. Step flow at the pit boundary effectively moves the alloy one layer deeper into the crystal via overgrowth, with no kinetic barrier. That is, the alloyed volume of the crystal is increased (by one layer) in regions of the surface where step flow has occurred. The amount of alloyed Ge will depend on the instantaneous Ge coverage. At the start of Ge growth, step flow can bury only small amounts of Ge because the total Ge coverage is initially small. At later stages of growth, when the concentration of Ge in the surface layer is large, overgrowth by step flow can lead to more incorporation. The process is shown schematically in Fig. 3(a). When the pits fill in, there will be a gradient in the distribution of incorporated Ge [Fig. 3(b)] and the largest subsurface concentrations will occur at the center of the pits (i.e., at the later stages of growth). For islands, the situation is reversed [Fig. 3(b)]. At the start of growth, step flow of the island perimeter will bury small amounts of Ge. At the later stages of growth, when the islands are large, more Ge is buried because the total Ge coverage is large.

We tested this hypothesis by observing Ge growth both on large terraces with etch pits (Fig. 4), as well as terraces where islands nucleate (Fig. 2). We consider the case of the pits first. During Ge growth, the pit, imaged white, slowly fills in due to step flow. At some point during Ge deposition, the pit completely disappears [Fig. 4(b)]. Note that, once the pit fills in, no steps remain on the large terrace, and there are no structural inhomogeneities other than the fact that step flow has occurred over the region where the pit was located. As the Ge deposition proceeds, and the coverage approaches 1 ML, a stripe nucleates [Fig. 4(c)]. The stripe moves rapidly over the surface, but avoids passing through areas of the surface where the large pit was located. In fact, the stripe will not pass through the center of the largest prealloyed regions, where the alloyed Ge concentration is largest [Fig. 3(b)], but will flow around them, forming a closed loop [Figs. 4(e) and 4(f)] [15]. The stripes clearly avoid areas of the surface where significant amounts of Ge have already been incorporated in subsurface layers. When the stripe enters a region with an enhanced subsurface Ge concentration, the driving force causing the stripe to advance disappears.

Stripe formation on islands is shown in Fig. 2. In this experiment, the flux of Ge was large enough to cause island nucleation during growth. An image of a large terrace with five islands is shown in Fig. 2(a). As growth proceeds, the islands coalesce into a connected "mesa" [Fig. 2(b)]. Eventually, a second layer of islands nucleates on the mesa [Fig. 2(c)]. At this point, the total Ge coverage is close to 1 ML and stripes appear [Fig. 2(d)]. The stripes move very rapidly outward from the center of the white mesa, but stop abruptly before reaching the perimeter, where the subsurface Ge concentration is largest [Fig. 3(b)]. This behavior results in the curious topology shown in Fig. 2(d): There is a continuous stripe that traces the perimeter of the mesa a distance 100 to 300 nm in from the edge. Both this structure and the one shown in Fig. 4(f) for the pit are consistent with the conclusion that

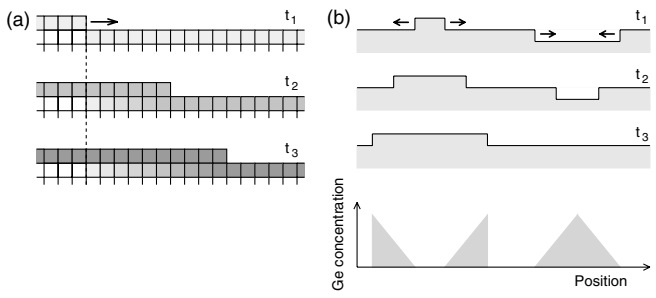

FIG. 3. (a) Side view of a surface step growing via step flow at times $t_3 > t_2 > t_1$. The grey scale schematically indicates the Ge concentration "buried" by the advancing step. (b) Side view of a terrace with a pit and an island. The graph shows the distribution of subsurface Ge after the pit has filled in and the island has grown.

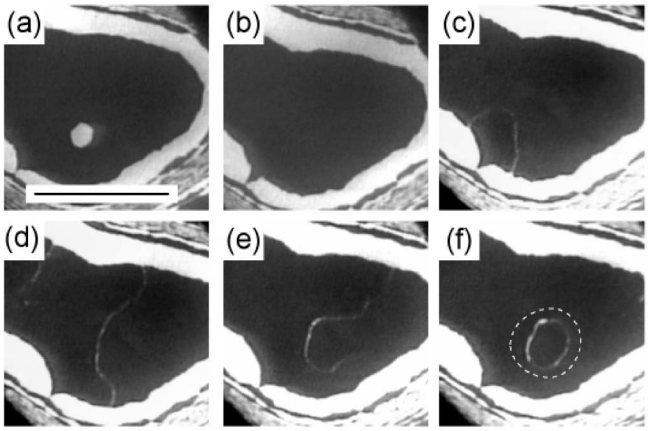

FIG. 4. LEEM images of Ge growth on a terrace with a ML-deep pit (800 °C). The ML-deep pit fills in during Ge deposition via step flow. The stripe does not pass through the area where the pit was located. Instead, the stripe forms a ring, surrounding the area were the concentration of subsurface Ge is largest. The dotted line in (f) indicates the size of the pit at the start of Ge growth. Scale bar, 3 μm.

stripes avoid areas of the surface where step flow has already led to significant and deeper subsurface Ge incorporation.

The fact that stripes avoid areas where step flow has occurred indicates that the driving force on the stripe is related to alloying. We now show that the stripe speed is consistent with a picture in which the driving force for stripe motion is the increase in alloyed volume that occurs during step flow in the vacancy island sections of the stripes. On the time scale of the experiment, some number of layers near the surface will become alloyed. For simplicity, assume that the first L subsurface layers are in complete equilibrium with the deposited Ge, but that migration of Ge to layer $L + 1$ does not occur [16]. The value of L is determined by the time scale of the experiment (i.e., Ge flux) and the kinetics of subsurface migration of Ge. Step flow effectively increases L by 1, by adding an additional alloyed layer to an already-equilibrated L-layer alloy. Increasing the volume over which the alloy is equilibrated increases the configuration entropy, lowering the free energy. Using first-principles values for the binding energies of Ge in various subsurface sites [7], the free energy gain associated with step flow can be estimated. For example, for a Ge coverage of 1 ML at 830 °C, the free energy gain associated with allowing five layers to equilibrate rather than four (i.e., $L = 4$) is about 10 meV/surface atom [17]. This value is the difference in surface energy between regions in front of and trailing a flowing step. In terms of this model, the motion of the stripe enhances alloy formation by "artificial" step flow over the vacancy island parts of the stripe. The leading edge of the stripe exposes the second layer, allowing some Ge to migrate to layer $L + 1$. The trailing step of the stripe reburies the second layer. We now show that the speed of the stripe is consistent with energy gain associated with step-flow overgrowth. The speed of the stripe, v, is proportional to the free energy difference between the leading and trailing terrace, $\Delta\gamma$: $v = (\Gamma/k_B T)\Delta\gamma$, where T is temperature, k_B is Boltzmann's constant, and Γ is the stripe mobility. A similar expression was used by Schmid *et al.* to analyze island motion during alloying [18]. If the stripe mobility is equal to that of a step on Si(001), approximately 5000 nm^3/s [19], then the stripe speed of 600 nm/s at 830 °C corresponds to $\Delta\gamma = 2$ meV/surface atom. Thus, the speed of the stripe is consistent with an entropic driving force for alloy formation. Of course, chemical and elastic effects might also influence near-surface intermixing, although they do not seem to play a central role in the stability of bulk SiGe alloys [2].

We have shown that step flow during growth influences interfacial mixing in a way not previously identified. If alloy formation by step flow is frustrated by the local absence of steps, the surface will spontaneously generate excess step pairs ("stripes") to facilitate intermixing. As the stripes move over the surface, subsurface layers are transiently exposed, allowing Ge to migrate deeper into the bulk. The stripes never retrace their path, while avoiding areas of the surface where enhanced alloying has already taken place. For Ge/Si(001) the driving force for alloy formation is not particularly strong (entropic). For highly exothermic alloys systems, spontaneous step formation and migration may play an even more important role in alloy formation.

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[15] The loops will shrink very slowly, in a manner consistent with island coarsening. That is, they shrink to reduce the overall step length at the surface.
[16] This simple approximation, suggested to us by Tersoff, is motivated by first-principles calculations [7] that show that the barrier for Ge migration increases with depth.
[17] As in [7], we assume the Ge atoms are noninteracting. The free energy gain is not strongly dependent on the choice of L: for $L = 2$, $\Delta\gamma = 15$ meV/atom, whereas for $L = 5$, $\Delta\gamma = 7$ meV/atom.
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