Step-mediated island growth: Coarsening governed by vertical lattice mismatch

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Two types of islands have formed after annealing a Co-deposited nominally flat Si(111)-(5×2)/Au surface: islands grow on terraces (terrace islands) and on steps (step islands). Upon further annealing, though of the identical kind, step islands outgrow terrace islands and eventually dominate the surface morphology, contrary to what the classical Ostwald ripening theory expects. This intriguing phenomenon of competition between two interconnecting systems is attributed to a *vertical* lattice mismatch, created by steps buried in step islands, which results in a speedy strain relaxation.

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The formation of epitaxial islands is a topic attracting great interest due in part to the potential applications as quantum dots for nanoscale devices. During growth or annealing, large islands grow at the expense of small islands to reduce the free energy associated with island edges, a common phenomenon referred in the literature as Ostwald ripening.[1] The growth kinetics of this coarsening stage has been investigated theoretically for a supersaturated solid solution[2,3] and for thin films[4] more than 40 years ago.

More recently, reports on the suppression of Ostwald ripening have begun to accumulate. Studies have shown that an island's shape can dramatically affect the growth kinetics and the late stage island size distribution.[5,6] A textbook example is the growth of Ge clusters on a Si(001) surface where huts, pyramids, and domes form at different stages in the shape evolution.[7–9] Other mechanisms have also been proposed for the suppression of Ostwald ripening in different systems. These include the creation of dislocations in strained islands,[10] the formation of stable periodic arrays of equal-sized islands,[11,12] the strain-influenced initial size uniformity,[13] a stable island size induced by edge effect,[14] a self-assembled superstructure stabilized by a short-range mechanism,[15] and the smallest hut facet being larger than the critical nucleus size.[16]

In this Brief Report we report an island coarsening mechanism governed by a surface step-mediated growth. By depositing Co onto a nominally flat Si(111)-(5×2)/Au surface, we have observed the formation of two types of islands upon annealing: the terrace islands (islands on terraces) and the step islands (islands on steps). Though we have found that both types of islands are of the identical kind, with further annealing step islands outgrow terrace islands and eventually dominate the surface morphology, in stark contrast to what can be expected from the classical Ostwald ripening theory.[17] We attribute this growth anomaly to the effect of a *vertical* lattice mismatch created by steps. This mismatch forces a step island to relieve its stress speedily, thus lowers its free energy and leads to a fast growth at early times. As time progresses, larger islands (mostly step islands) grow at the expense of smaller islands (terrace islands). Furthermore, we have also observed a size stabilization and an ordering along steps for step islands.

In the experiment, a clean Si(111)-(7×7) surface with a miscut angle of 0.3° toward the $[\bar{2}11]$ direction was first prepared according to a standard cleaning procedure.[18] Au atoms, produced by heating a Mo crucible containing Au (99.99+% pure) to 1000 °C via electron bombardment, were then deposited onto the (7×7) surface at 700 °C. After ~0.5 monolayers [MLs, 1 ML=7.83×10^{14} atoms/cm^2, the unreconstructed Si(111) surface atom density] of Au deposition, the entire surface reconstructed into a (5×2) structure.[19] Co atoms, produced by a 2-mm-diameter Co rod (99.9% pure) with electron bombardment, were then deposited onto the freshly prepared (5×2) surface at room temperature. Annealing of the Co-deposited surface between 550 and 700 °C was then performed. The evolution of the surface morphology was examined at room temperature with scanning tunneling microscopy (STM). The deposition rates for both Au and Co were at 0.01 ML/s.

After room-temperature deposition the Co atoms decorate the (5×2) surface randomly. Upon a brief annealing, distinct islands appear. At this instance there is no preference for islands to grow either on terraces or at steps. STM images displaying the morphological evolution after further annealing are shown as insets in Figs. 1(a)–1(c). In the insets, the surface steps run vertically and the step-down direction is from left to right. To emphasize the surface topography we have taken a differentiation in the $+x$ direction ($\partial/\partial x$) on the raw data to suppress the large height difference between islands and terraces.

We have developed an image analysis program capable of identifying islands and steps from raw STM data. This allows us to separate the two types of islands and carry out statistical characterization in a consistent way. Histograms of island size distributions obtained from this program are shown in Figs. 1(a)–1(c), where two distinct groups of islands representing step (filled bars) and terrace (empty bars) islands are shown. Terrace islands initially dominate the surface [see Fig. 1(a)] as step islands steadily grow and eventually become a predominant feature with a size of ~20 nm [see Fig. 1(c)]. While a net mass transfer occurs between the two types of islands, the combined island volume is conserved as indicated by the horizontal line shown in Fig. 1(d).

The surface retains its (5×2) structure in regions not covered by islands.[20] The hexagonal shape of the islands emerged at early times has been preserved for both types of islands. The evolution of these two types of islands shown in Fig. 1 is typical for surfaces annealed between 550 and 700 °C. A high annealing temperature within this tempera-

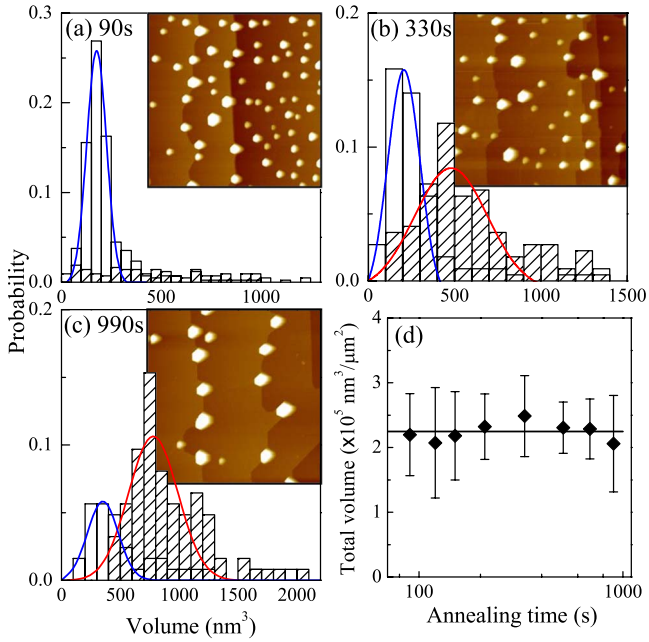

FIG. 1. (Color online) [(a)–(c)] Histogram and surface morphology of a Co-deposited Si(111)-(5×2)/Au surface. The surface was annealed at 620 °C after 0.5 ML of Co deposition. The accumulated annealing time is labeled in each panel. Gaussian curves are plotted to guide the eyes. Size of insets: 200×200 nm^2. (d) Total island volume vs annealing time. A horizontal line is plotted.

ture range speeds up the growth rate. Since there is no evidence of coalescing of islands, the island growth kinetics is governed by the formation and diffusion of mobile adatoms.

We have identified the island's chemical composition as $CoSi_2$ based on the hexagonal shape[21] and the ratio of the amount of deposited Co to the total island volume. From the occasional pining of a step by an island, such as the step island shown on the lower right center in the inset of Fig. 1(c), and the slight meandering of some steps we expect the Si atoms needed to form the $CoSi_2$ islands come mostly from steps.

To quantify the annealing process we have made log-log plots of relevant quantities as functions of annealing time for both types of islands. A linear fit to the average density of terrace islands, n_t, vs time in Fig. 2(a) (blue squares) gives $n_t(t) \propto t^{-1.09\pm0.11}$. A fit to the average volume of a terrace island, v_t, vs time in Fig. 2(b) (blue squares) has $v_t(t) \propto t^{0.62\pm0.06}$. With $m_t(t)=n_t(t)\cdot v_t(t)$, the mass density of terrace islands, we have $m_t(t) \sim t^{-0.5}$. Despite large terrace islands grow at the expense of small terrace islands, the negative exponent in t means the total mass of terrace islands actually decreases with time, or the average volume of terrace islands grows despite of a negative flux. This interesting phenomenon has never been reported since the flux is either zero (mass being conserved) or positive (atoms being added) in typical growth experiments.

The fit to the density of step islands, n_s, vs time, shown as a red line in Fig. 2(a), gives $n_s(t) \propto t^{-0.13\pm0.07}$. Since the total volume of the two systems is conserved [see Fig. 1(d)], it leads to $n_s(t)\cdot v_s(t) \sim t^{+0.5}$, where v_s is the average volume of a step island. This leads to $v_s(t) \propto t^{+0.6}$. The dashed red line

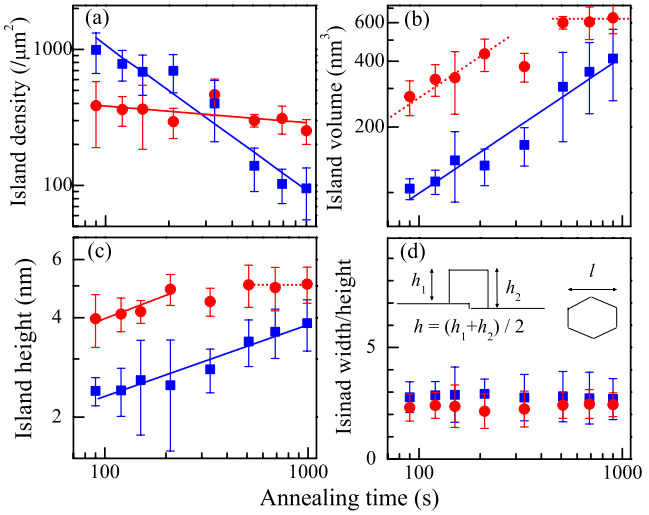

FIG. 2. (Color online) (a) Average island density, (b) island volume, and (c) height vs annealing time. Straight lines are linear fits to respective data sets. (d) Aspect ratios vs annealing time. An island's height and width are defined in the insets. Step and terrace islands are shown by red circles and blue squares, respectively. The error bar corresponds to the standard deviation of each data point.

plotted in Fig. 2(b) has a slope of 0.6 and matches well with red circles at early times. With $n_s(t)\cdot v_s(t) \sim t^{+0.5}$, i.e., a positive flux, the step islands grow.

Figure 2(c) shows the average island height, $h(t)$, as a function of annealing time for both types of islands. A linear fit gives $h_t(t) \propto t^{0.21\pm0.02}$ for terrace islands (blue squares), whereas $h_s(t) \propto t^{0.23\pm0.07}$ for step islands (red circles) at early times. The essentially identical exponents show that both types of islands have the same height growth rates. The aspect ratios for both types of islands are also the same and independent of the annealing time, as shown in Fig. 2(d).

The same growth rates and aspect ratios, in addition to identical chemical composition, for both types of islands lead us to conclude that we are dealing with just one kind of island. The only reason why one type of island grows at the expense of the other [see Fig. 2(a)] appears to be determined by where the islands locate. This leads us to examine what role in the island growth a step plays.

A unrelaxed step island, in addition to a lateral lattice mismatch at the island-surface interface which a unrelaxed terrace island also experiences, encounters a vertical lattice mismatch resulting from a spacing difference between a step height (0.314 nm) and the $CoSi_2$ layer-layer separation (0.309 nm) introduced by a buried step [see the left island in Fig. 3(a)]. We contemplate that a step island would have a speedy strain relaxation in comparison to a terrace island since it is strained in two directions and thus suffers a larger stress.

Figure 3(a) shows a step (left) and a terrace (right) island at the very early stage of island formation, where each island is 6 atomic layers (1.8 nm) high. Two crucial differences between the two islands stand out: (1) the step island has a hexagonal shape, the same shape for larger islands formed after further annealing; (2) the step island has a featureless top (flattop), the same structure found in larger islands,

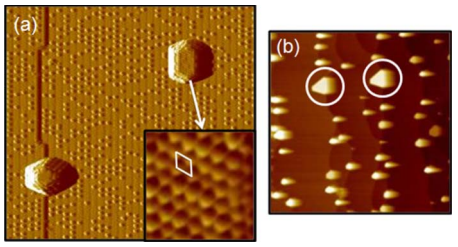

FIG. 3. (Color online) (a) Islands after the onset of formation. The round features are the "hallmark" of a (5×2) reconstruction. Image size: 56×52 nm^2. Inset: the (2×2) structure with a marked unit cell. (b) Coalescence of step islands after high-temperature annealing. Circled islands have a triangular shape. Slight fuzziness on islands' right edges was the result of a somewhat fast scan speed of the STM tip. Image size: 400×400 nm^2.

whereas the terrace island has a (2×2) structure, as shown by the inset in Fig. 3(a). Our data shows that the (2×2) structure *always* shows up on terrace islands with heights of 6 atomic layers or less. The flattop appears only on terrace islands with heights of 7 atomic layers or more. The majority of step islands, on the other hand, show the flattop even at a height of 4 layers. (We have also observed flattop step islands with a height of 2 or 3 atomic layers.) The faster transformation to reach the (near) equilibrium structure is a clear indication that the stress in step islands has been quickly relieved, a consequence directly linked to the vertical lattice mismatch.

A fast strain relaxation results in the lowering of an island's free energy, which in turn allows the step island to compete favorably against a terrace island in attracting mobile adatoms.[10] This is why, even at the early times of the coarsening process, step islands are significantly larger than terrace islands [see Fig. 2(b)].

Would step islands compete among themselves for growth? By studying the coarsening of step islands at high temperatures (>700 °C), as shown in Fig. 3(b) where most terrace islands have already dissolved, we have observed the formation of very large triangularly shaped step islands (those being circled), similar to what has been observed on a Si(111)-(7×7)/Co surface,[22] at the expense of small step islands. This "delayed" coalescence of step islands demonstrates that a step island indeed has a lower free energy per unit volume than that of a terrace island or small step islands would have dissolved long before the disappearance of large terrace islands.

We suspect that steps play little, if any, direct role in the growth of islands here. If steps were to act as one-dimensional traps which constrain trapped adatoms to move along steps, step islands would have grown at a faster rate than that of terrace islands for having a quick access to adatoms. Our results show the same growth rates for both types of islands [see Figs. 2(b) and 2(c)].

The average size of step islands stabilizes at 650 ± 50 nm^3, as shown by a horizontal dashed red line at large annealing times in Fig. 2(b) [also in Fig. 2(c) for height stabilization]. To confirm this we have performed a separate experiment where 0.3 ML Co was deposited on a fresh (5×2) surface followed by a long annealing where most islands were step islands, a situation similar to what is shown in Fig. 1(c). Then additional Co atoms (0.6 ML) were deposited at room temperature. The surface morphology as a function of time was examined by further annealing at 620 °C, as shown in Figs. 4(a) and 4(b). For the first few hundred seconds of annealing the step islands formed after the first Co deposition were large compared to those formed after the second Co deposition. This allows us to separate these two groups of step islands and investigate their growth rates separately. The step island density after the first Co deposition was also obtained for double checking our counting.

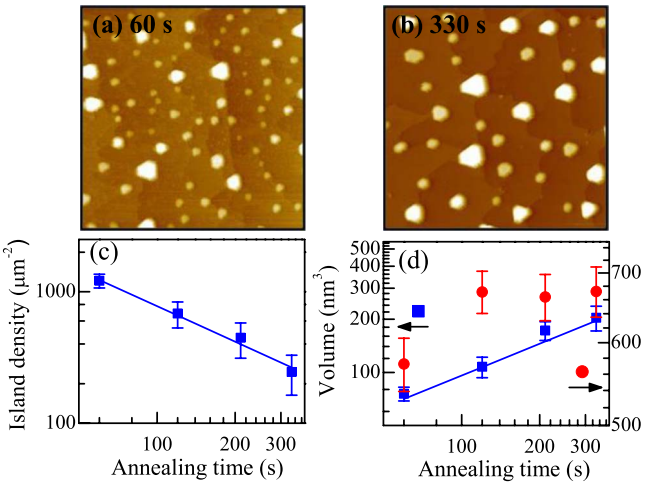

FIG. 4. (Color online) [(a) and (b)] STM images of a surface after second Co deposition. Accumulated annealing times are marked. Image size: 200×200 nm^2. (c) The average density of terrace islands vs time. (d) The average island volumes vs time for the terrace islands (blue squares) and step islands (red circles) formed after first Co deposition. The straight lines are linear fits to corresponding data points. The error bar represents the standard deviation for each data point.

Figure 4(c) is a log-log plot of the average density of terrace islands vs time after second Co deposition. A linear fit gives $n_t(t)\propto t^{-0.91\pm0.10}$. A linear fit to the average volume of terrace islands vs time shown as blue squares in Fig. 4(d) gives $v_t(t)\propto t^{0.61\pm0.07}$, agrees with the result shown in Fig. 2(b). The average size of the step islands formed after the first Co deposition is shown as red circles in Fig. 4(d). It reaches a plateau at ~680 nm^3, showing the same size-stabilizing effect as observed in the single Co deposition experiment [see Fig. 2(b)].

This size stabilization has been found in all experiments over a range of temperatures and Co coverages. It provides a self-controlled mechanism for growing islands of narrow size distribution, a topic of significant importance in nanotechnology. Since we have observed a shape transition in high-temperature annealing experiments, i.e., hexagon to triangle, we attribute the size stabilization to this shape transition.[9]

Since neither of the two types of islands is mass conserved, the classical Ostwald ripening theory is not applicable here. As a reference, for a conserved system of detachment-limited three-dimensional-islands grown on a

surface, the volume growth rate is linearly proportional to the growth time.[17] Further theoretical work is clearly needed to characterize the growth rate obtained here.

Besides the narrow size distribution, step islands also show an ordering along steps, as shown in Fig. 1(c). We have obtained the average island width and island-island separation of the step islands from a number of experiments at Co coverages ranging from 0.2 to 1 ML. The ratio of the average island width to the average island-island separation ranges from 0.2 to 0.7 in different experiments with no apparent dependence on the Co coverage. This ratio is expected to be $\sim 1/3$ for systems governed by effective long-range $1/r^2$ repulsive interactions.[23] The qualitative agreement between our results and the theoretical expectation suggests that the observed island ordering is caused by the effective $1/r^2$ repulsion, which comes from the interactions of interisland and intraisland step edges.[24]

In conclusion, the coarsening of two types of islands, the step and the terrace island, have been investigated. Despite identical structure, step islands grow at the expense of terrace islands. We attribute this unique phenomenon of competition in island growth to the presence of steps buried in step islands. The step generates a vertical lattice mismatch and induces a speedy strain relaxation which lowers a step island's free energy and further allows a faster growth at the early times of the coarsening process. This coarsening mechanism provides a self-separation of identical islands according to their locations and allows those at preferred locations to grow at the expense of the rest. Its usefulness is demonstrated by forming islands of narrow size distribution and an island ordering along steps.

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