Coverage-dependent self-organized ordering of Co- and Ti-silicide nanoislands along step-bunch edges of vicinal Si(111)

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We report on self-organized solid-phase epitaxially grown Ti- and Co-silicide nanoislands ordered along step-bunch edges of a vicinal Si(111) surface, as a function of the initial metal (Ti,Co) coverage. While the degree of self-ordering (in terms of step decoration) for Co-silicide islands was higher than for Ti-silicide islands, both types of island had an inverse dependence of the order parameter on coverage. In addition, the positions of the island sites were found to be correlated, and affected by the step-island and island-island interactions, leading to their alignment along the step-bunch (110) directions, even for the terrace islands. Aberration-corrected high-resolution transmission electron microscopy was used to characterize the islands’ crystal structure and growth orientation. The above findings can be understood by the use of coarse-grain modeling.

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I. INTRODUCTION

The creation of regular nanostructures such as quantum dots (QDs) and wires on semiconductor surfaces has been a focus of interest in recent years.1,2 These low-dimensional nanostructures not only are fascinating for fundamental research, due to their unique physical, electrical, and optical properties (different from those of their bulk counterparts), but are also important for technological applications, such as light-emitting diodes, solar cells, lasers, modulators, detectors, and data storage devices.1-5 One of the most attractive ways to form nanodots is to grow them epitaxially (or heteroepitaxially), where the deposit, controlled with a monolayer (ML) or even sub-ML precision, self-assembles in the form of nanosized particles and QDs, as a kinetic or thermodynamic response to the growth environment.6-16 Self-organization (SO) is a higher degree of self-assembly, generally applied to anything that drives three-dimensional (3D) islands toward greater regularity in position and/or size and shape, such as lattice mismatch between the growing layer and the substrate to achieve elastic relaxation.17 For example, elastic strain relaxation of island facet edges and island-island interactions via the strained substrate may drive SO of uniform strained islands on crystal surfaces into ordered arrays. Additional factors include the crystal symmetry of the substrate and deposited material (likely to affect the nanostructure’s shape and faceting), substrate temperature (may affect the number density of the nanostructures), deposited coverage (possibly affecting the mean nanostructure size), as well as vertical and lateral material transfer (growth rate, in-plane mobility of adatoms).17 Though mismatch strain provides a natural mechanism for the growth of dislocation-free 3D nanoislands, there may be a number of additional requirements for such islands to be used as QDs. The viability of QD-based electronics and optics does not rely solely on an individual dot size and shape, but on a collective behavior (and hence uniformity) of the dots in the array. Thus it is important to understand not only how the physical properties of these nanostructures are influenced by the growth parameters (temperature, flux, initial coverage, etc.), but also the nanostructure shape uniformity and size distribution in the array. Finally, some potential applications may require specific arrangement of the nanostructures (dots) with respect to one another.18

It has been established that in the case of thin films the interplay between surface, interface, and strain energies may drive the formation of discrete 2D or 3D compact or elongated nanoislands, and thus impede growth of flat continuous layers. On the other hand, such island growth opens new possibilities of creating novel low-dimensional devices based on quantum nanostructures. Metal silicides, e.g., Co-Si, Ti-Si, Fe-Si, Mn-Si, etc., offer a wide choice of lattice and symmetry mismatch with Si. Therefore, not only the silicide nanocrystal size can be tailored by synthesizing a phase with an appropriate mismatch, but by choosing a silicide phase with an adequately anisotropic mismatch to Si, similarly anisotropic shapes can also emerge. For example, nanowires can be grown elongated in the direction of the smallest mismatch with Si, while restricted by higher mismatch in a perpendicular direction.19 A plausible futuristic device may require patterned assembly, where nanowires interconnect ordered arrangements of nanodots, and hence it is also desirable to control the positioning of such nanostructures on the surface. One possible way to influence the location of the growing islands is to cause them to “decorate” surface irregularities and domain walls, e.g., periodic step bunches on vicinal surfaces, with the periodicity determined by the miscut angle. A regular arrangement of atomic steps on the mesoscopic scale can functionalize such surfaces as natural templates for nanodot clustering along the steps,20 thin and thick stripes,21,22 or wires (down to the size of one atom).23 The regular and well-defined steps and step bunches on vicinal surfaces provide a natural template for the nucleation of low-dimensional nanostructures.24

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particular, on vicinal Si(111), the structural characteristics and periodicity of straight and periodic steps or step bunches can be reasonably controlled by first selecting the miscut angle and then varying the magnitude and direction of the heating current during preparatory high-temperature flashes.\textsuperscript{25,26} Decoration of this kind of step bunches by CoSi\textsubscript{2},\textsuperscript{27} MnSi\textsubscript{2},\textsuperscript{28} and FeSi\textsubscript{2} (Ref. 29) nanoislands has been reported. Moreover, by carefully controlling the growth method and parameters, not only preferential occupation of the step bunches by nanoislands is possible, but even nanoisland size selection by the bunch heights.\textsuperscript{30,31} In this context, more experiments are required, particularly for SO of metal silicides, such as TiSi\textsubscript{2} and CoSi\textsubscript{2}, which are good elastic crystals and hence potential candidates for micro- and nanomachining.\textsuperscript{32} These silicides are also promising cold cathode materials for field emission, due to their high thermal and chemical stability.\textsuperscript{33} Furthermore, the low electrical resistivity and high thermal stability (CoSi\textsubscript{2} with $\rho = 16–20$ $\mu\Omega$ cm and TiSi\textsubscript{2} with $\rho = 18$ $\mu\Omega$ cm) make them potential candidates for SO nanoelectronic circuits, in addition to the well-established process compatibility with more conventional Si technology of very and ultra large-scale integrated devices, as gate, contact, and interconnect materials.\textsuperscript{34,35}

In this work, we focus on the changes in the SO of Ti- and Co-silicide nanoislands fabricated by solid phase epitaxy as a function of metal coverage on vicinal Si(111) substrates, which can be attributed to the diffusion mechanisms on Si(111), attachment-detachment kinetics, Co-Si and Ti-Si reaction, and silicide island nucleation pathways, and the mismatch of the respective silicides with Si. High-resolution transmission electron microscopy (HRTEM) was conducted on samples prepared in cross section. Special emphasis was placed on the identification of the actual crystal phase of the back reactions have also been included, i.e., dissociation

flashes at 1150–1200 °C, and the clean Si surface was slowly cooled until a well-ordered ($7 \times 7$) reconstruction appeared in diffraction and STM. Ti and Co, in the respective silicide growth experiments, were evaporated at room temperature (RT) onto vicinal Si(111) samples mounted in the VT-STM stage, and subsequently underwent a series of annealing treatments in the STM under continuous real-time imaging. The evaporation rate was calibrated by counting and measuring unreacted metal agglomerates from STM images, under incomplete surface coverage conditions, and estimating the number of atoms in the agglomerates for selected evaporation fluxes. The thickness of Ti and Co, expressed here in the equivalent ML units (corresponding to 0.96 and $1.3 \times 10^{15}$ atoms cm$^{-2}$, the areal densities of Ti and Co atoms, respectively), was controlled by tuning the time of exposure to the metal flux. We deposited low (9 ML) and high (102 ML) Ti coverages, and low (17 ML) and high (54 ML) Co coverages on vicinal Si(111) at room temperature. STM images were acquired using tunneling conditions of $0.1 < I < 0.2$ nA and $-3.0 < V < +3.0$ V in a constant-current mode and shown as current ($I$ rather than $z$) images. The LEED patterns shown here were all acquired at 80–90 eV. For statistical analyses, the images were processed using commercial (SPIP from Image Metrology) as well as home-made software specifically designed for this purpose.

HRTEM studies were performed using a monochromated and aberration-corrected FEI Titan 80–300 kV S/TEM. This field emission gun source microscope includes an image aberration corrector, providing a coincident point and information resolution of less than 0.07 nm. In addition, it is equipped with a high-resolution energy filter (Tridiem 866 ERS, Gatan), which yields an energy resolution better than 0.15 eV at an accelerating voltage of 300 kV. Cross-section sample preparation for the HRTEM investigations was optimized by comparing different preparation methods for the specific samples. A site-specific dual-beam focused ion beam system was tested as well as conventional preparation methods including the use of a tripod polishing and various mechanical (diamond) polishing procedures. Eventually the last method produced better-quality TEM specimens (thinner samples with less damage in the form of residual ion milling damage). After mechanical thinning, the samples underwent ion beam polishing using a combination of a standard precision ion beam polishing (PIPS, Gatan) as well as low-voltage ion polishing (Technoorg Linda), using milling angles of $\pm15^\circ$ and Ar ion energies of 300 eV.

III. THEORETICAL MODEL

Rather than developing an elaborate atomistic approach to study the growth kinetics of the formation of ordered silicides, we developed a coarse-grained lattice model that includes a description of the metal atoms, silicon atoms, and their association, as well as the substrate. The model is based on the division of space into cells, where each cell can contain a metal atom, a silicon atom, or a silicide species. When a metal atom and a silicon atom collide at a given site, a reaction can take place, with a rate that depends on the environment (coordination). To preserve a detailed balance, the back reactions have also been included, i.e., dissociation...
of a silicon-metal complex. The system may be described by the lattice Hamiltonian

\[ H = -\varepsilon_m \sum_{i,j} m_i m_j - \varepsilon_{ms} \sum_{i,j} m_i s_j - \varepsilon_n \sum_{i,j} n_i n_j - \varepsilon_{ns} \sum_{i,j} s_i n_j - \varepsilon_{mn} \sum_{i,j} m_i n_j - \varepsilon_{ms} \sum_{i,j} m_i s_j - \mu_j / 2 (n_i - m_i). \]

The binary variable describing the metal atom at lattice site \( j \) is denoted by \( m_j \), while that of silicon is denoted by \( s_j \), and the silicide formed when a metal atom reacts with the substrate is \( n_j \). These variables can take the value of 1 or 0 if lattice cell \( j \) is occupied or not, by a given species, respectively. In the above equation, \( \varepsilon_m, \varepsilon_{ms}, \varepsilon_n, \) and \( \varepsilon_{ns} \) are the energetic costs for creating an interface between the metal atoms, between the silicide molecules, between the metal and substrate atoms, and between the silicide and substrate, respectively. \( \mu_j \) is the chemical potential for the reaction of forming silicide in site \( j \), or the cost of forming a silicide species in vacuum.

The explicit form of the dependence of these interfacial energies on lattice sites \( i \) and \( j \) depends on the exact problem at hand, i.e., these terms can be described by short-range interactions (for example nearest-neighbor interactions) or longer-range electrostatic interactions (Coulomb, dipolar, long-rage repulsion, etc.). In this work we assume nearest neighbor interaction (limit the sum \( \{i,j\} \) to nearest neighbor) and study the formation of nanoparticles and their assembly for different classes of interactions. The chemical potential is assumed constant on the substrate and 0 elsewhere. To limit the parameter space, we focus on the range of interactions suitable for the experimental setup described above (see further discussion below).

The dynamics of the SO process has been generated using standard techniques based on a Monte Carlo scheme, similar in spirit to kinetic Monte Carlo simulation. The metal atoms perform a random walk on the substrate, biased by their interactions with each other, with the substrate, and with the silicides. Moreover, when a metal atom comes into contact with the silicon substrate it has a finite probability to react with it. In such a reaction we preserve the variable associated with the substrate (conserved order parameter, not to be confused with the step-island SO order parameter \( \eta \) described in Sec. IV A 3), while the sum of variables associated with the metal and silicide is preserved (nonconserved order parameter for each, separately). In more detail, we attempt to displace the metal atoms and silicide particles in a random direction on the lattice. Such a move is accepted with the Metropolis probability, but only if the new cell is empty. If the new position is not empty (i.e., it can be occupied by another metal, silicide, or silicon species), then we attempt to move around it. In practice, we attempt to move the metal species in the \( z \) direction (the direction perpendicular to the substrate) and then move in the \( x-y \) plane, repeating the procedure described above. In all cases, the particles cannot be suspended, and thus we allow them to relax until they meet a cell filled with any kind of species.

If, during the course of motion, a metal species comes in contact with the surface, we attempt a reaction and accept the conversion with the same Metropolis probability. In order to describe the difference in the reactivity of the silicon terraces and step-bunch stairs we add a rate parameter in such a way that the rate of chemical reaction on stairs is higher than on terraces. We use stochastic reaction probabilities, preserving a detailed balance, to model the formation and dissociation of the metal silicide.

The simulations are initiated with a random deposition of the metal atoms onto the substrate with predefined step-terrace geometric relations, which closely emulate the real substrate. These initial configurations follow as a function of a Monte Carlo sweep to track the progression of island formation and the SO process. Simulations of the lattice model include different initial metal coverages and different reaction rates corresponding to the different preselected metals. The set of parameters has been selected in such a way that the metal can react preferably with the silicon to form the corresponding metal silicide, and afterward can accumulate into 3D aggregates. It has been observed that the above conditions can be fulfilled by the following set of parameters:

- \( \varepsilon_m = 2 \), \( \varepsilon_{ms} = 2^{1/2} \), \( \mu = 3 \), \( \varepsilon_n = 5 \), \( \varepsilon_{ns} = 2^{1/2} \). With these parameters, a steplike surface with a \( 1 \times 1 \) grid cell height and width shows a very sharp concentration limit of the metal, above which the metal-silicide islands form and accumulate over the step bunches rather than at terraces, due to the lower probability of nucleation at the terraces.

IV. RESULTS AND DISCUSSION

A. STM studies

1. Ti-silicide islands

Figures [1(a)–1(d)] depict constant-current STM micrographs of as-deposited and thermally annealed Ti/Si(111) surfaces, along with the coarse-grained modeling snapshots [Figs. 1(e)–1(h)] for Ti-silicide islands (which are discussed in detail in Sec. IV C). Figures 1(a) and 1(b) capture the as-deposited and final (annealed) stages of a “low” Ti coverage (9 MLs), respectively, with the same stages simulated by our coarse-grained model for a surface coverage of 10% in Figs. 1(e) and 1(f). Similarly, Figs. 1(c) and 1(d) capture the as-deposited and final (annealed) stages of a “high” Ti coverage (102 ML), and modeled for 60% coverage in Figs. 1(g) and 1(h). A faint Si(7×7) structure can be seen in both the STM image [Fig. 1(a)] and the LEED pattern [bottom-left inset] of a low-coverage Ti/Si(111), unlike the case of a more densely covered Si(111), where the Si(7×7) structure could not be detected in the STM image and (1×1) spots were almost exclusively visible in the LEED [bottom-left inset in Fig. 1(c)]. Growth of continuous titanium-silicide layers on silicon is impeded by a large lattice mismatch, leading to the lower probability of nucleation at the terraces.
FIG. 1. (Color) STM micrographs of the as-deposited Ti on vicinal Si(111) surfaces at (a) lowest and (c) highest coverage, and heat treated at (b) 700 °C and (d) 650 °C. Corresponding 82–86 eV LEED patterns are shown in the insets. Simulated snapshots of the initial and final stages of Ti-Si chemical reaction, homogeneous over the entire surface, for (e) and (f) 10%, and (g) and (h) 60% coverage. Red, blue, and green dots correspond to the Si surface, metal particles, and silicide particles, respectively.

Flattening of the initially conical or lens-shaped islands with size during heat treatments. The initial (as-deposited) and the final (annealed) stages of the fully developed silicide islands at a higher coverage are shown in Figs. 1(c) and 1(d), with the intermediate stages of evolution presented elsewhere and for the lower-coverage surface in Figs. 1(a) and 1(b) and Fig. 2, respectively. An apparent increase in the mean island size, accompanied by decreasing island number density with temperature, is consistent with Ostwald ripening as the dominant mechanism in the late stages of growth. This mechanism is also consistent with the simulation results of our coarse-grained model shown in Figs. 2(e)–2(h). Analysis of these simulated trajectories reveals that the average island size scales with time as $t^\alpha$, as shown in Fig. 2(i), with $\frac{1}{3} < \alpha < \frac{1}{2}$.

Most importantly, the step bunches seem to play a leading role in the silicide formation kinetics, especially at higher temperatures, as evident from Figs. 1 and 2. The first silicide island begin to nucleate at about 550 °C, as shown in Fig. 2(a).
and these tiny nuclei are homogeneously spread all over the vicinal Si(111) surface terraces and step bunches (perhaps with an even higher probability on terraces). However, with the progress of annealing, the islands coarsen and at the same time their population migrates from terraces toward step bunches: at 600 °C the population at step bunches roughly equals that of the terraces [Fig. 2(b)], at 650 °C there is already a clear preference for the step-bunch sites [Fig. 2(c)], and at 700 °C the terraces become almost completely depleted of islands [Figs. 1(b) and 2(d)]. Naturally, the as-deposited RT state is not likely to be an equilibrium one. The as-deposited atoms are likely to “freeze” at their landing sites, because at RT they are not mobile enough to move to the energetically preferred sites at the step bunches. Annealing provides the thermal energy required to increase their mobility, leading to their migration from metastable or high-energy sites to more stable low-energy sites at the step bunches.

It should be noted that such a high degree of self-ordering by step decoration took place exclusively at a low Ti coverage (9 MLs), whereas for a higher coverage of 102 MLs only partial ordering was obtained [e.g., numerous terrace islands are visible in Fig. 1(d)]. This is consistent with our modeling results which clearly demonstrate that the concentration of the metal is crucial for SO ordering on the step bunches [Figs. 1(e)–1(h)]. At these progressive stages of evolution, both STM images [cf. Figs. 1(b), 1(d), and 2], and diffraction patterns [e.g., LEED in the inset of Figs. 1(b) and 1(d)] show the (7×7) structure, indicating that there are no free Ti atoms (from the original coverage) diffusing on the surface. In other words, the original pool of Ti atoms is exhausted, and Ti atoms for further reaction with silicon at the step bunches can only come from the silicide terrace islands, dissolving in favor of the newly formed step-bunch silicide islands. Examination of Figs. 1 and 2 leads to the conclusion that the nucleation mechanism of step-bunch titanium-silicide islands resembles that proposed for step-bunch cobalt-silicide islands,30 based on simple terrace-ledge-kink (TLK) arguments. In other words, metal atoms and small agglomerates preferentially react with silicon atoms at the step bunches, since the undercoordinated silicon atoms at the step edges are more readily available for the reaction, and the silicide islands residing at the step bunches should have a higher coordination than terrace islands. Just like Co atoms,30 the Ti atoms react with individual steps in the bunch, forming two-dimensional (2D) platelet nuclei which are free standing if the individual reacting step is at the top or middle of the bunch [Fig. 3(a)], or supported at the foot of a bunch, as depicted in Fig. 3(b). In any case, additional platelets nucleate above and below the original nucleus of a step-bunch island and stack together vertically to thicken the island [Figs. 3(c) and 3(d)]. To extend laterally, away from the parent step bunch, the growing island must consume more silicon atoms from the step bunch, causing the steps in a bunch to retreat, giving the “baylike” appearance seen in Figs. 3(c) and 3(d), and in more detail in Fig. 4. Oscillations between triangular and roughly hexagonal shapes of growing silicide islands have also been observed and explained on the basis of fast-growth crystallographic directions.38 Hence, the “best-fed” islands are those populating the step-bunch sites. In addition, they preferentially ripen at the expense of the terrace islands, by consuming them.30 Therefore, in the intermediate stages the step-bunch islands gradually become larger than the shrinking terrace islands, and ultimately they are the only ones left [Figs. 1(b) and 2(d)], spanning at least part of if not the entire step-bunch height, e.g., as in Fig. 5 (some may also cover some portion of the bunch’s top or bottom terrace as in Figs. 3 and 5).
FIG. 4. (Color online) Detailed STM micrograph of the growth process of a titanium-silicide island at a step-bunch site. (7×7) reconstruction of the Si(111) terraces is clearly visible. Note how the island consumes the parent step edges, causing them to retreat.

a. Statistical analysis

Island-island interactions. To quantitatively investigate the thermally driven interactions of the Ti-silicide nanoislands on the silicon surface, the number of first-order neighbor islands (within a 50 nm cutoff radius), hereafter known as the “count,” and the mean island-island separation distance, hereafter known as the “mean distance,” were determined at various stages of evolution (i.e., annealing temperatures). The statistical analyses were performed on a number of the highest-fidelity images. Count and mean-distance histograms, as functions of the annealing temperature, are shown in Figs. 6(a)–6(d) for a low-Ti-coverage sample, and in Figs. 6(e)–6(g) for a high-Ti-coverage sample. The central, gray histograms are the island mean-distance distributions, whereas the green histograms in the insets show the count. The variations of the mean distance and the count with temperature are summarized for a low-coverage sample in Fig. 6(h), and for a high-coverage sample in Fig. 6(i). A sharp reduction in the number of neighbors, from ∼41 at 550°C to ∼6 at 700°C for a low Ti coverage, and from ∼32 at 550°C to ∼9 at 650°C for a high Ti coverage, was accompanied by an increase in the mean distance (though much more moderate). Furthermore, simultaneously (upon heating) the islands ripened up to ∼12 nm in diameter and ∼2.5 nm in height for low Ti coverage, and up to ∼24 nm in diameter and ∼2.6 nm in height for high Ti coverage (histograms not shown). Island growth accompanied by a reduction of the nearest neighbors and larger separations is a clear fingerprint of Ostwald ripening, where larger crystals grow at the expense of smaller ones due to the Gibbs-Thomson effect.41,42

Step-island interactions. Figure 7 depicts distributions of the fraction of the total area covered by the terrace islands (left) and step-bunch islands (right), respectively, as a function of temperature for both low [Figs. 7(a)–7(d)] and high [Fig. 7(e)] Ti coverage. Gradual depletion of the terrace islands in favor of the step-bunch islands with temperature is evident, supporting the earlier conclusion made on the basis of qualitative observation of Figs. 1 and 2. Such a SO may be referred to as “step decoration,” where the annealing temperature plays an important role as a primary activation for the adatoms to reach the step-bunch edges with a higher probability than to form islands on terraces, as depicted in Figs. 1(a) and 1(b) for 9 MLs of Ti. Clearly, if the coverage is too high, as in Fig. 1(c), the mean free path is shorter than the terrace width, and terrace islands cannot be avoided even at high temperatures, as in Fig. 1(d), for 102 MLs of Ti.

The azimuthal distributions of the silicide islands are shown in Figs. 8(b)–8(f), with the mean island-island separation (along the parent step edge) distributions in the insets. As step bunches are the major sinks for the islands, the size of such a capture zone can be estimated by finding the proximity of the islands to the step bunches on both the up and down terraces [Fig. 8(a)]. Obviously, such an analysis cannot apply to well-ordered cases, e.g., Fig. 1(b), since it requires a statistically valid sampling of terrace islands, such
as in the case of a high Ti coverage [cf. Fig. 1(d)] to have a meaningful measure of their proximity to step bunches. Only terrace islands are included (step islands are excluded for the sake of clarity), with the positive (negative) side representing the up (down) terrace of the bunch. It is evident from Fig. 8(a) that the capture (denuded) zone is wider on the up terrace (∼15 nm) than on the down terrace (∼10 nm). In other words, there is a high probability for islands within 15 nm of the step bunch at the up-terrace side to end up at the step bunch itself. In contrast to that, islands at the down terrace of the step bunch can get closer to the bunch by ∼5 nm without being drawn onto it. This asymmetry by itself does not directly shed light on the physical origins of step attachment-detachment kinetics. It could be argued, for example, that this may indicate the absence of an Ehrlich-Schwoebel (ES) barrier which prevents adatoms at the up terrace from descending down the step edge, or even a negative ES barrier. However many islands, such as the ones depicted in Fig. 5, partially cover step bunches, and the up terrace of those bunches may be pinned to that up terrace by an ES-type barrier.

Azimuthal distribution histograms were generated from the statistical data which included all the islands in each image, with step intervals (∆θ) of 10° and angles calculated from vectors connecting the selected neighboring islands along each azimuth. A progressive alignment of the islands, towards the step angle (∼45°), with increased annealing temperature clearly emerges for the low-Ti-coverage sample [Figs. 8(b)–8(e)], shifting from relatively misaligned 50°–60° at low temperatures [Figs. 2(a) and 8(a)] to the 45°–55° sector at 700 °C [Figs. 1(b), 2(d), and 8(d)]. However, this was not the case for the high-Ti-coverage sample, shown in Fig. 1(d), where the islands never seemed to reach the same degree of alignment [Fig. 8(f)], regardless of the annealing temperature. Finally, the interisland separation distributions along the step edge, shown in the insets of Fig. 8, are broad, and do not seem to improve with temperature (except slightly for the high-coverage sample [inset in Fig. 8(f)]).

2. Co-silicide islands

Constant-current STM micrographs of a low-coverage Co/Si(111) sample (17 MLs) before and after the anneal are shown in Figs. 9(a) and 9(b), respectively, whereas the high-coverage Co/Si(111) sample (54 MLs) before and after the anneal is shown in Figs. 9(c) and 9(d), respectively. The panels showing the modeling results in Figs. 9(e)–9(h) are discussed below, in Sec. IV C. Similarly to the case of low- and high-coverage Ti/Si(111), with discrete and compact 3D titanium-silicide islands formed upon annealing, the compact 3D cobalt-silicide islands on a low-coverage Co/Si(111) surface underwent an identical shape transition of progressive apex truncation with the thermally growing island size [Fig. 9(b)]. However, unlike the case of Ti/Si(111), irregular 2D islands, forming a quasicontinuous cobalt-silicide layer, were observed at high coverage [Fig. 9(d)]. Therefore the (7×7) structure, characteristic of Si(111), that vanished from STM [Fig. 9(c)] and LEED [inset in Fig. 9(c)] when the Si(111) surface was “buried” underneath 54 MLs of Co, was not regained in either STM or LEED [Fig. 9(d)].
It can be speculated that the high density of Co adatoms in this case significantly shortens their mean free path, preventing them from reaching the step-bunch edges prior to colliding with their neighbors and nucleating terrace islands, and also favors coalescence between impinging neighbor islands over Ostwald ripening. The reason this does not happen in the high-coverage titanium silicide could be a result of its high lattice mismatch with silicon, which creates a barrier for adatom attachment to the forming silicide islands and self-limits their growth.\textsuperscript{38} Comparison of the final stages yields apparently much better SO, in terms of step decoration, of the low-coverage compact cobalt-silicide islands [Fig. 9(b)] than for the analogous low-coverage titanium-silicide islands [Fig. 1(b)] [let alone high Ti-coverage, as in Fig. 1(d)]. This is, again, captured by the coarse-grained simulations, which show nearly all cobalt-silicide aggregates at the step bunches [Fig. 9(f)]. Moreover, uniformity of the titanium-silicide step-bunch island sizes and intersilicide separations [cf. Fig. 1(b)] cannot compete with an apparently much higher uniformity of cobalt-silicide islands [cf. Fig. 9(b)] (determined by the height of their parent step bunch)\textsuperscript{30}). Evolution of the Co/Si(111) surfaces in the intermediate annealing stages, recorded by real-time STM observations, was reported in detail elsewhere.\textsuperscript{30,31,45} Below, a detailed statistical analysis of cobalt-silicide islands SO is presented and discussed.

### a. Statistical analysis

**Island-island interactions (low Co coverage).** Temperature-dependent mean distance and count histograms, for the low Co coverage, can be seen in Figs. 10(a)–10(d) and their insets. Gray histograms express the mean-distance distributions of islands for every temperature, and the green ones in the insets.
FIG. 10. (Color online) (a)–(d) Gray: Distribution histograms of the mean separation distance between cobalt-silicide islands on a Si(111) surface with low initial coverage of Co. Insets in green: histograms of nearest-neighbor islands. (e) Summary of the mean-distance and neighbor-count data points plotted as a function of temperature. Variations of these two parameters with temperature were even more profound than in case of Ti/Si(111); the number of nearest-neighbor islands (green insets) decreased from ~60 at 350 °C to ~2 at 500 °C, and the mean island-island separations increased from ~31 nm at 350 °C to ~38 at 500 °C, as summarized in Fig. 10(e). This was also accompanied by corresponding growth of the islands themselves up to ~18 nm in diameter and ~4.5 nm in height (histograms not shown). Again, these findings indicate Ostwald ripening as the main island coarsening mechanism. Not only island-island interactions are strongly affected by heating, but step-island interactions as well, as presented below.

Step-island interactions (low Co coverage). Just as in the case of titanium-silicide islands, interactions of cobalt-silicide islands with the Si(111) step bunches were explored in three principal directions: preferential occupation of step bunches relative to terraces; alignment of the islands with the direction of the step edges; and establishment of island periodicity along the parent step bunch. With respect to the first criterion (step decoration), Fig. 11 shows the fraction of area covered by step bunches (left-hand side) simultaneously with the fraction covered by the step-bunch islands (right-hand side) as a function of temperature. This figure clearly demonstrates gradual “pumping” of the terrace islands [still a majority at 350 °C; see Fig. 11(a)] toward step bunches with increasing temperature, until ultimately at 500 °C a vast majority of the islands populate the step bunches [Fig. 11(d)]. This population inversion is clearly evident from the STM image in Fig. 9(b), with the islands located exclusively at the step bunches, and the terraces turned into denuded zones.

FIG. 11. (Color online) (a)–(d) Distribution of the fraction of total area covered by the terrace islands (left-hand side) and step-bunch islands (right-hand side) as a function of annealing temperature, for the low Co coverage on vicinal Si(111) surfaces.

Figure 12 demonstrates the effect of interaction with the step bunches on the entire population of islands. Already at 350 °C the majority “senses” the step bunches in a −35° to −45° angular sector and aligns accordingly, with a broad distribution of angles [Fig. 12(a)]. However, by 500 °C the distribution is very sharp, indicating that all the islands are aligned exactly with the steps [Fig. 12(d)].
measurements show that $\eta$ for titanium-silicide islands on a high-Ti-coverage Si(111) surface and improves up to $\eta \sim 0.73$ for lower Ti coverage (after a 700 °C anneal). However, the highest value of the order parameter was obtained for cobalt-silicide islands at a low Co coverage, $\eta > 0.90$ (after a 500 °C anneal). Naturally, highly covered Co/Si(111) was irrelevant. The variation of the order parameters of titanium- and cobalt-silicide islands with temperature is plotted in Fig. 13 for the two best-ordered cases, namely, low Co coverage (on the left) and low Ti coverage (on the right). The data points plotted against reciprocal absolute temperature could not be fitted with an Arrhenius-type function. Therefore they are plotted as a function of temperature in degrees Celsius and fitted with a logarithmic growth function, $\eta = \eta_0 \ln(T - T_0)$, merely to guide the eye. The best fits were obtained with the $\eta_0$ coefficient = 0.13 and $T_0 = 544$ °C for titanium-silicide islands, and $\eta_0 = 0.18$ and $T_0 = 345$ °C for the cobalt-silicide islands. Perhaps the physical meaning of $T_0$ may be understood as the onset of ordering, as roughly at these respective temperatures the first titanium- and cobalt-silicide islands were nucleated, i.e., essentially the SO begins with the formation of the first islands.

3. Order parameter

Just like the other three SO parameters discussed above (alignment of the islands with the direction of the step edges, island periodicity along the parent step bunch, and size uniformity of the step-bunch islands), the fourth parameter, namely, the relative degree of step-bunch population by the islands, can be quantified by defining an order parameter ($\eta$), where $\eta = \text{number of step-bunch islands}/\text{number of step-bunch islands} + \text{number of terrace islands}$). Thus, in the extreme limit of only populated terraces $\eta = 0$, and in the ideal extreme limit with only populated step bunches, $\eta = 1$. Our measurements show that $\eta \sim 0.32$ (after a 650 °C anneal) for titanium-silicide islands on a high-Ti-coverage Si(111) surface and improves up to $\eta \sim 0.73$ for lower Ti coverage (after a 700 °C anneal). However, the highest value of the order parameter was obtained for cobalt-silicide islands at a low Co coverage, $\eta > 0.90$ (after a 500 °C anneal). Naturally, highly covered Co/Si(111) was irrelevant. The variation of the order parameters of titanium- and cobalt-silicide islands with temperature is plotted in Fig. 13 for the two best-ordered cases, namely, low Co coverage (on the left) and low Ti coverage (on the right). The data points plotted against reciprocal absolute temperature could not be fitted with an Arrhenius-type function. Therefore they are plotted as a function of temperature in degrees Celsius and fitted with a logarithmic growth function, $\eta = \eta_0 \ln(T - T_0)$, merely to guide the eye. The best fits were obtained with the $\eta_0$ coefficient = 0.13 and $T_0 = 544$ °C for titanium-silicide islands, and $\eta_0 = 0.18$ and $T_0 = 345$ °C for the cobalt-silicide islands. Perhaps the physical meaning of $T_0$ may be understood as the onset of ordering, as roughly at these respective temperatures the first titanium- and cobalt-silicide islands were nucleated, i.e., essentially the SO begins with the formation of the first islands.

B. Cross-section HRTEM

The crystal phase and structure of the Co-silicide islands could easily be identified by STM and determined as a bulklike CoSi$_2$ fluorite-type structure. However, the structure of the Ti-silicide islands could not be easily and unambiguously determined by STM, and hence HRTEM was employed. Figure 14 presents a cross-section HRTEM micrograph of one of the Ti-silicide islands located directly at a step, with the incident beam direction parallel to Si {110}. Ti silicides can crystallize in several phases as a function of Ti and Si composition, thickness, and heat treatment. From fast Fourier transform analysis of the island (shown in the inset on the right of Fig. 14) and accompanying electron diffraction simulations, it was determined that the island consists of the complex hexagonal Ti$_5$Si$_3$ phase (space group $P6_3/mcm$, no. 193) with its {1012} planes parallel to the Si {111} planes. It should be noted that diffraction from Ti$_5$Si$_3$ along a [241] zone axis can be easily mistaken for a C49 TiSi$_2$ [514] zone axis, which may explain the multitude of reports on TiSi$_2$ islands and the few on Ti$_5$Si$_3$. Detailed multislice image simulations of the atomic column contrast were required to match the intensity maxima observed in the HRTEM micrographs and to confirm the Ti-silicide phase and corresponding zone axis. Numerous islands located at the steps were imaged and analyzed in the same way, and a second example is shown in Fig. 15. It was found that all of the islands which could be resolved and analyzed exhibited the hexagonal structure of Ti$_5$Si$_3$ with the preferred orientation described above. Additionally, special emphasis was put on the identification of the substrate-island interface itself. The formation of amorphous or crystalline interfacial layers, which may evolve to overcome the lattice mismatch in the growth direction, would be expected to affect the electronic properties of the islands. Considering the complicated substrate morphology at the steps, which can consist of a series of monatomic layer steps, the image contrast has to be analyzed carefully to avoid misinterpretation regarding the structure. It is thus necessary to find areas on the sample that have a negligible gradient in thickness (parallel
to the electron beam) and achieve imaging conditions where both the island and substrate are in focus at the same time.

An example of a rather blurred contrast at the substrate-island interface is shown in Fig. 15(a), where the exact interface position can be determined only roughly with an accuracy of approximately 1–2 MLs (although a heteroepitaxial relationship is apparent), unlike the micrograph shown in Fig. 15(b), where the substrate-island interface is precisely resolved. The monatomic steps of the substrate can easily be determined from the contrast, and the morphology of the island in projection can be determined. Consequently, no interlayer between the Si(111) substrate and the island was detected. These results demonstrate that at least some of the islands grow coherently and heteroepitaxially with the substrate.

C. Coarse-grained modeling

To gain a deeper understanding of the growth kinetics and the formation of the ordered nanoparticle structures, we employed the coarse-grained model described in Sec. III. Two generic cases that differ with respect to the reaction rate on the step bunches were examined. In the first symmetric case, the rate of reaction was uniform on the entire surface (no difference in reactivity between steps and terrace). Simulated trajectories for this regime are shown in Figs. 1(e)–1(h). These results seem to be consistent with the experimental observations for the corresponding Ti coverage on Si [Figs. 1(a)–1(d)]. The coverage of the metal plays a crucial role in SO on the step bunches even when the reactivity on the step bunches and on terraces is the same. For the lower metal coverage, ordering on the step bunches is almost perfect, whereas for higher coverage on vicinal Si. Typical simulated snapshots are shown in Fig. 1(f). When the Co coverage is increased to 100%, the terrace agglomerates dissolve (as a part of an ongoing ripening process) by detachment of monomer units, which then diffuse toward the larger agglomerates at the step bunches, which consequently coarsen at the expense of the terrace agglomerates. For the longest simulation time (analogous to the highest temperature) this depletion is nearly complete [Figs. 2(f)–2(h) and 2(b)–2(d)].

We find that such island coarsening is consistent with Ostwald ripening. This also seems to be the leading coarsening mechanism observed in the experiments. Figure 2(i) depicts the average number of particles in an island (average cluster size) as a function of time on a log-log scale. The long-time behavior can be fitted to a scaling law of $R \propto t^\alpha$, with $\alpha \approx 0.4$. In the limit that ripening is governed by attachment-detachment of monomers we expect $\alpha = 1/2$, in contrast to the diffusion-limiting case where the scaling law is $\alpha = 1/3$. Therefore, we find that growth of the islands is likely to be governed by both attachment-detachment of metal-silicide units from the agglomerates and their rate of diffusion.

In the second, asymmetric, case, the reaction rate at the step bunches was chosen to be twice as fast as that on terraces. This condition seemed to reproduce the results of Co coverage on vicinal Si. Typical simulated snapshots are shown in Figs. 9(e)–9(h) alongside the corresponding experimental results for Co on vicinal Si [Figs. 9(a)–9(d)]. Indeed, the SO on the step bunches in the simulations is close to perfect [Fig. 9(f)], even better than that of the simulated Ti-covered surface [Fig. 1(f)]. When the Co coverage is increased to 100%, the metal-silicide particles start to form quasi-two-dimensional islands covering both the bunches and the terraces, consistent with the experiments for high Co coverage [Fig. 9(d)].

The difference between Co and Ti seems to be correlated with the relative reactivity of the step bunches versus terraces, which in the present study is set by the rate of reaction. At low coverage this is not significant, since the energetics favors nucleation and growth of islands at the step bunches anyway, and the metal atoms in both symmetric and asymmetric cases can diffuse there. Thus, in both cases, the nucleation of islands is faster, and larger islands form at the step bunches. In the course of Ostwald ripening, islands that nucleate and grow on terraces eventually decompose in favor of step-bunch islands.

Structures of this type are shown in Figs. 1(b) and 1(f), Fig. 2, and the formation of the ordered nanoparticle structures, we explore this regime are shown in Figs. 1(e)–1(h). These results seem to be consistent with the experimental observations discussed above and provide a possible explanation for
The long-time behavior could be fitted to a scaling law: \( R \propto t^\alpha \), with \( \alpha \approx 0.3 \) for high Ti coverage and \( \alpha \approx 0.7 \) for Co. Ordering of cobalt-silicide islands was also superior according to three additional figures (Fig. 16(c)–16(h)). Therefore, our simulations support the proposed “bottom-up” growth mechanism. This mechanism seems to apply to both symmetric and asymmetric cases of reaction rates. The variations in the average cluster size as a function of time once again demonstrate Ostwald ripening with a power law \( \alpha \approx 1/2 \) [Fig. 16(h)], indicating that under the current set of parameters, the process is governed by attachment-detachment of monomers.

**V. SUMMARY AND CONCLUSIONS**

Low and high coverages of Ti and Co were deposited at room temperature onto atomically clean vicinal Si(111) substrates. Except for the case of high Co coverage, thermally activated formation of the respective metal-silicide phase was in the form of Vollmer-Weber compact and discrete 3D nanoislands. Further annealing treatments caused partial spatial ordering of the silicide islands, expressed via their preferential occupation of the vicinal Si(111) step-bunch sites at the expense of the terraces, which became gradually devoid of islands. Within the scope of the experiments, the most important factor affecting the self-ordering process appears to be the initial metal coverage. With a metal coverage of many tens of equivalent MLs, self-ordering is either impossible (as in the high-Co-coverage case) or rather limited (order parameter \( \eta \sim 0.3 \) for high Ti coverage). A trivial interpretation of this phenomenon, within the framework of the so-called terrace-ledge-kink model, is simply that the longer mean free path of sparse adatoms is more likely to assure their “safe” arrival at the preferred (in terms of coordination) sites at the step-bunch edges, rather than impinging on their neighbors on terraces and nucleating islands. A much higher degree of step decoration (\( \eta \sim 0.7 \)) was achieved with a few equivalent MLs of Ti, and even better (\( \eta \sim 0.9 \)) for Co. Ordering of cobalt-silicide islands was also superior according to three additional figures of merit, namely, the degree of alignment with the step-bunch orientation, uniformity of the step-bunch island sizes, and uniformity of the mean island-island separations along the parent bunch (periodicity). Cross-sectional HRTEM studies...
indicate that most of the Ti-silicide islands crystallize in the hexagonal Ti$_2$Si$_3$ structure, rather than in the more frequently reported C49 and C54 Ti$_2$Si$_3$ structures. The experimental results are corroborated with the findings of coarse-grain modeling showing almost complete ordering of metal silicides over the step bunches for lower initial metal coverage (in contrast with higher coverage, where no significant ordering was observed to take place). It seems that while the initial metal coverage is the most important first-order factor, intrinsic physicochemical differences between various metal atoms, e.g., Co and Ti (and between their respective and silicides), such as diffusivity, attachment-detachment kinetics, lattice mismatch between a silicide and the silicon substrate, etc., play a role as well. In addition, one of the possible directions for future investigation is to have several different coverages for a role as well. In addition, one of the possible directions for

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46. Joint Committee for Powder Diffraction Standards (JCPDS) files 
No. 10-0225, No. 35-0785, No. 27-0907, and No. 23-1079 
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