

Atomic-Scale Pathway of the Pyramid-to-Dome Transition during Ge Growth on Si(001)

F. Montalenti,^{1,*} P. Raiteri,¹ D. B. Migas,¹ H. von Känel,² A. Rastelli,^{2,3} C. Manzano,³ G. Costantini,³ U. Denker,³ O. G. Schmidt,³ K. Kern,³ and Leo Miglio¹

¹*INFM and L-NESS, Dipartimento di Scienza dei Materiali della Università degli Studi di Milano-Bicocca, Via Cozzi 53, I-20125 Milano, Italy*

²*INFM and L-NESS, Dipartimento di Fisica del Politecnico di Milano, Via Anzani 52, I-22100, Como, Italy*

³*Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

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By high resolution scanning tunneling microscopy, we investigate the morphological transition from pyramid to dome islands during the growth of Ge on Si(001). We show that pyramids grow from top to bottom and that, from a critical size on, incomplete facets are formed. We demonstrate that the bunching of the steps delimiting these facets evolves into the steeper dome facets. Based on first principles and Tersoff-potential calculations, we develop a microscopic model for the onset of the morphological transition, able to reproduce closely the experimentally observed behavior.

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Three-dimensional Ge islands coherently grown on Si(001) at high temperature are well known to show a bimodal behavior, with small, shallow {105}-faceted pyramids and larger domes, exhibiting steeper facets [1,2]. In the past few years some interpretations of the bimodal behavior have been provided, mostly relying on thermodynamic arguments. Based on volumetric strain relief, surface energies, and edge contributions [3], one explanation is that pyramids and domes correspond to two minima in the energy per atom, with an activated transition from one to the other morphology [1]. The second interpretation is grounded on the chemical potential of the island, which is argued to undergo an abrupt change at a certain critical volume, corresponding to the crossover between the energy per atom for a dome and the corresponding one for a pyramid [4–6]. Therefore, no energy minima are required to explain the bimodal behavior in this picture.

When Ge is grown on Si(001) at relatively low temperature, only elongated {105}-faceted islands with narrow size distribution are observed. An interpretation of this phenomenon comes from kinetic models [7,8], where a self-limiting growth is explained in terms of kinetic slowing down occurring with increasing volume. This, in turn, should be provided by a size-dependent activation energy for adding a new monolayer to the {105} facets. In particular, Jesson *et al.* [7] suppose the additional layer to nucleate at a lower corner of the facet, where the strain is larger. Similarly, Kästner and Voigtländer [8] assume that the layer grows from bottom to top, founding their kinetic model on the stepped nature of the {105} facets. However, both the thermodynamic and kinetic models do not explain how the shape transition is microscopically accomplished. Recently, a description of how the shape transition occurs has been provided by Seifert and co-workers [9,10], suggesting a variation of the Jesson *et al.* model [7]. Here, at a critical pyramid size, new, steeper facets are supposed to nucleate close to the pyramid apex, where

the lattice parameter is more relaxed. Yet, this hypothesis was based on qualitative arguments, with no modeling.

In this Letter, we use high resolution scanning tunneling microscopy (STM), to investigate Ge islands grown on Si(001) with two different techniques. We show that the growth proceeds from top to bottom, and that the shape transition is accomplished by step bunching of incomplete {105} facets. By a suitable modeling, based on semiempirical Tersoff-potential simulations and *ab initio* results, we show that the growth modality does not need to change from small to large pyramids.

The experiments were carried out in two independent ultrahigh vacuum (UHV) setups: a magnetron sputter epitaxy (Exp_A) and a solid-source molecular beam epitaxy (Exp_B) system. In both cases substrates were first outgassed, deoxidized, and a Si buffer layer was grown to achieve a clean surface. In Exp_A , 7 ML Ge were grown on Si(001) at 550 °C at a rate of 0.3 monolayers per second (ML/s). In Exp_B 6 ML Ge were grown at 560 °C at 0.04 ML/s, followed by a 10 min growth interruption at the growth temperature. The annealing step has the effect of promoting the transition of pyramids to domes since, if the sample with 6 ML of Ge is quenched immediately after growth, only pyramids are observed [2,11]. For the STM characterization, samples were cooled to room temperature and transported to the STM chambers in UHV. The sample surface displays islands at different stages of evolution, as shown in the insets of Fig. 1 and previously reported [1,2,11]. Figure 1 shows a plot of the island aspect ratio (ratio between height and square root of the base area) versus volume together with representative STM images. Here we focus our attention on islands with shape intermediate between pyramids and domes, which will shed light on the detailed transition pathway. In Fig. 2 we present filled-state STM topographs, collected in constant current mode, of transition islands obtained in Exp_A [panels (a)–(c)] and Exp_B [(d)–(f)]. In spite of the different experimental setups and conditions,

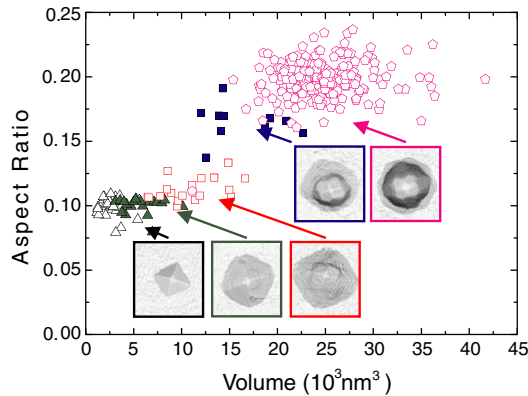


FIG. 1 (color online). Plot of the aspect ratio vs volume for Ge islands on Si(001) obtained in experiment Exp_B . Different symbols refer to islands at various stages of the pyramid-to-dome transition, as illustrated by representative STM images. Similar results are obtained for Exp_A .

similar structures are observed. The pristine pyramids are small and characterized by flat facets (see inset of Fig. 1). They grow self-similarly by the successive addition of complete layers until they reach a critical size. From this point on, atoms accumulate only at the topmost region of the islands [Figs. 2(a) and 2(d)], creating a set of steps which eventually bunch together [Figs. 2(b) and 2(e)]. As the volume increases, an extended step bunching generates steeper $\{15\ 3\ 23\}$ facets, and the transition to the dome shape is attained [Figs. 2(c) and 2(f)]. A second feature of transition islands is that they have incomplete corners, as already noticed in Ref. [2], which evolve into $\{113\}$ facets. Since the same transformations are observed upon annealing (Exp_B), or upon deposition of additional Ge (Exp_A), it is evident that the shape transition is produced mainly by the atomic flux coming from the Ge wetting layer (WL) and from the neighboring small pyramids, which are observed to disappear [2,11]. Moreover, the same results obtained by two different experimental procedures suggest that the transition islands are not the result of a frozen surface kinetics.

The flatness of the small pyramids' facets does not allow one to understand whether new layer nucleation starts at the island bottom or at the top. The absence of steps simply reveals that a very efficient step-flow mechanism takes place. At this stage, two different growth modes are still possible. Small pyramids could grow from bottom to top, as suggested in Ref. [8], until, at a critical volume, the growth modality switches to top to bottom, as shown by our experiments. The other possibility is that no change in the growth mode takes place: pyramids grow upside down regardless of their size. Simply, at some point, it starts to be convenient to develop steps in the upper region. In the following, we shall show that the latter, simpler picture better describes the island evolution.

Recently, *ab initio* calculations revealed that at the $\{105\}$ facets of the pyramids, a rebonded-step (RS) recon-

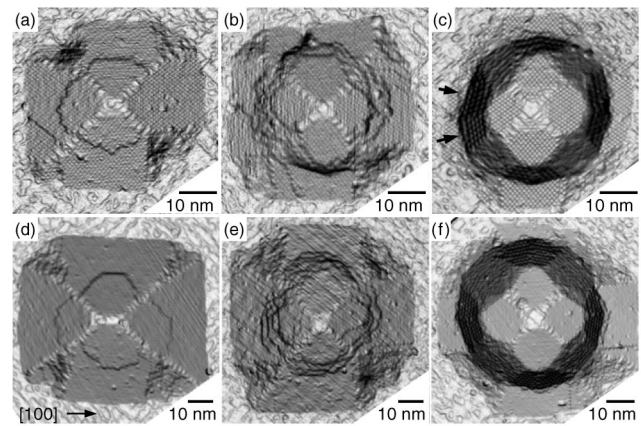


FIG. 2. STM topographs illustrating the pathway of the pyramid-to-dome evolution. Images in panels (a)–(c) correspond to Exp_A , while the three bottom panels are taken from Exp_B . The image gray scale corresponds to local surface slope with respect to the (001) plane (dark areas are steeper). Arrows in (c) point at two of the eight $\{15\ 3\ 23\}$ facets composing the dome surface.

struction takes place [12–14]. Such RS reconstruction dramatically reduces the density of dangling bonds and, in turn, the surface energy, virtually eliminating the stepped (001) morphology for any relevant value of the lattice parameter [15]. Therefore, it is hard to conceive a bottom-to-top growth modality based on the stepped nature of the $\{105\}$ facets [8], whatever the pyramid size. In order to further justify a top-to-bottom growth, the diffusion of single Ge atoms on the Ge(105) RS surface has been studied by *ab initio* mapping of the energy minima and of the activation energies for neighboring-minima hopping, followed by kinetic Monte Carlo simulations. An extended report about these calculations can be found in [16]. Here we just mention that diffusion turns out to be nearly isotropic, with an effective barrier ~ 0.62 eV in the base-to-top direction and ~ 0.64 eV for lateral displacements. These values suggest that at our experimental temperatures adatom diffusion is fully activated at the pyramid facets, implying that the material is not kinetically hindered from reaching the top. Moreover, any surface configuration can be explored, and a step-flow mechanism can be easily envisaged, in agreement with the STM indications. However, these *ab initio* results do not explain how we evolve from a layer-by-layer growth of small pyramids to the step bunching at the critical size. Qualitatively, we notice that material accumulation at the island upper regions appears well justified from a purely energetic point of view, because of the lattice-parameter expansion which takes place moving from pyramids base-to top [10].

In order to obtain more quantitative information, we have simulated the strain and elastic-energy distribution in realistic Ge(105) pyramids on Si(001) with a WL, by molecular dynamics with the Tersoff potential [17]. We

included the RS reconstruction and we used the same configurations and procedures described in [12]. Now, by scanning the (001) lattice parameter (a_{\parallel}) and the energy per atom ϵ_d below the {105} facets at a depth d , it is possible to estimate their average variation, as a function of the vertical height h . In Fig. 3(a), ϵ_d is plotted versus a rescaled height h/L , where L is the base side of the pyramids, 27 and 16 nm in our case. For {105} faceted pyramids the maximum value of h is $H = L/10$. For small depths, surface effects strongly shift ϵ_d to high values, while with increasing d the curves bunch to a limiting value $\epsilon_{\text{deep}}(h/L)$, which we take to be the one for $d = 6 \text{ \AA}$. Because of the increasing strain relaxation towards the top of the pyramid, ϵ_{deep} is expected to decrease and a_{\parallel} to increase with (h/L) . In fact Figs. 3(a) and 3(b) show an inverse and direct linear dependence on (h/L) , respectively. This trend is not affected by variations in size (L), nor in composition (see below).

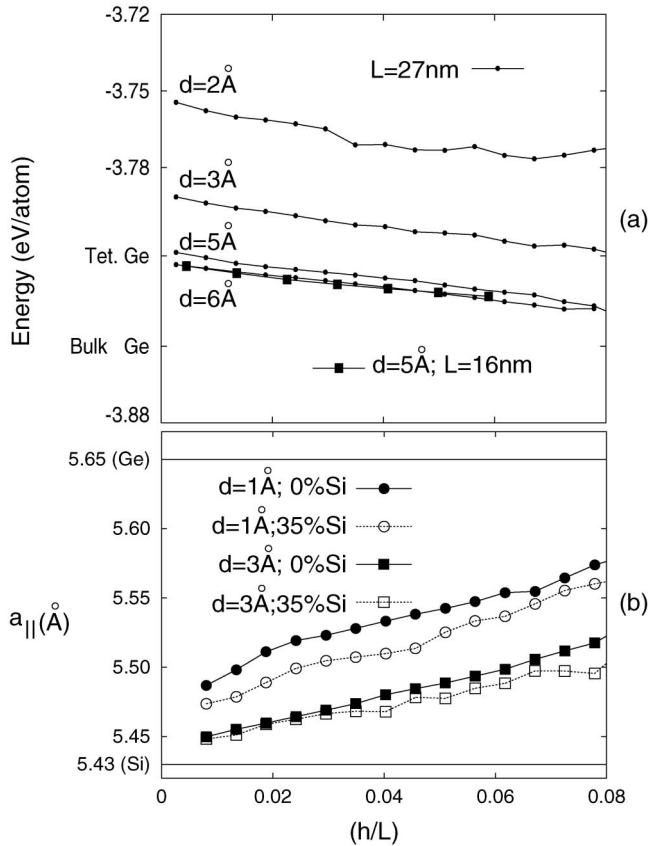


FIG. 3. (a) Energy per atom vs h/L at different depths, as computed by Tersoff-potential calculations for $L = 27 \text{ nm}$ (full curves with small, solid circles). For comparison, the energy per atom is also plotted for $d = 5 \text{ \AA}$ and $L = 16 \text{ nm}$ (full curve with large, solid squares). The energy per atom typical of bulk Ge and of Ge tetragonally strained at the Si lattice parameter are indicated. (b) In-plane average lattice parameter a_{\parallel} vs h/L for different depths, and in the presence or not of Si (35%) intermixed into the Ge pyramid.

The above results can be used to develop a model description of the experimental observations. We compare two configurations: S_0 , where a full new {105} layer has been added to a pyramid, and S_N , where the same amount of material is arranged into N partially filled layers at the top of the pyramid, bound by N steps. The latter are perfectly bunched together to form straight lines parallel to the base edge, in order to simplify the calculation. Their vertical position with respect to the island base is $H - H/\sqrt{N}$ [see Fig. 4(a)]. Let us compute the difference in the energies of these two configurations. For S_0 , the addition of one full monolayer on top of a {105} facet is morphologically and energetically equivalent to the insertion of one, parallel monolayer at the limiting depth. The increase in energy with respect to the pristine pyramid is therefore $\epsilon_{\text{deep}}(h/L)$ integrated over the whole facet area. For S_N the integration has to be limited only to the cap region and the energy for the creation of the steps has to be accounted for.

Therefore we have

$$E(S_0) = \int_0^H \gamma_{\text{deep}}(h) ds(h),$$

$$E(S_N) = N \left\{ \left[\int_{H-H/\sqrt{N}}^H \gamma_{\text{deep}}(h) ds(h) \right] + \frac{\Gamma L}{\sqrt{N}} \right\}, \quad (1)$$

where $\gamma_{\text{deep}}(h) = \epsilon_{\text{deep}}(h)\sigma_{105}$ is the energy density per unit area, with σ_{105} the {105} atomic density, that, in a first approximation, we take as constant ($\sigma_{105} = 0.025 \text{ atoms/\AA}^2$). Γ is the {105} step energy, considered as h independent for the sake of simplicity. For the surface element $ds(h)$ along the {105} facet, we used $ds(h) = 2C(H-h)dh$, with $C = 1/2 \times 10/\sin(11.31^\circ)$. In order to perform a quantitative estimate of $\Delta E = E(S_0) - E(S_N)$, we fitted $\gamma_{\text{deep}}(h) = -\gamma_{\text{deep}}^0 - A(h/L)$ on the linear trend of ϵ_{deep} reported in Fig. 3(a). The constant A turned out to be $\sim 6 \text{ meV/\AA}^2$, while γ_{deep}^0 is unimportant since it cancels out in evaluating ΔE :

$$\Delta E(L, N) = \frac{AL^2}{300 \sin 11.31^\circ} \left(1 - \frac{1}{\sqrt{N}} \right) - L\Gamma\sqrt{N}. \quad (2)$$

The first term in Eq. (2) tends to make the stepped state lower in energy; the second one acts in the opposite way. Since the step contribution is linear in L , while the surface-covering contribution scales as L^2 , small pyramids will remain flat, while larger pyramids will develop step bunching [see Fig. 4(b)]. The size at which the transition from S_0 to S_N takes place will depend on Γ , the only free parameter of the model. In order to predict that stepped pyramids become lower in energy for values of L comparable to the experimental ones reported in Fig. 1, we need to set $\Gamma = 12 \text{ meV/\AA}$. While no information is available on Γ for the {105} steps, this value appears reasonable, on the grounds of experiments on Ge(001) steps [18,19]. By increasing L above $\sim 50 \text{ nm}$, the model also predicts that the convenient number of

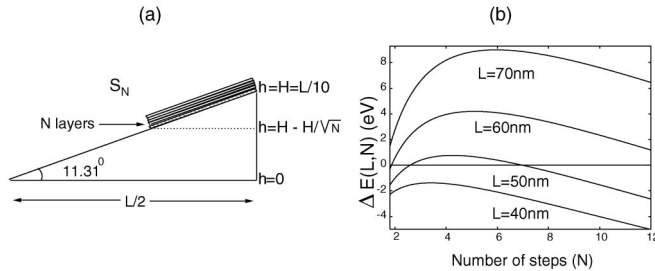


FIG. 4. (a) Geometry of the configuration S_N , characterized by N steps bunched together. (b) Energy difference between the flat-facet state (S_0) and the stepped state (S_N) plotted as a function of the pyramid base L and of the number of steps N for $\Gamma = 12 \text{ meV/\AA}$.

bunched steps [i.e., the N value which maximizes $\Delta E(L, N)$ for a given L] increases with L ; see Fig. 4(b). This is in agreement with the experimental results of Fig. 1. We incidentally note that standard aspect ratio vs volume analysis cannot reveal the critical size at which the transformation sets in, and accurate STM images are needed.

Our model, formally equivalent to the one proposed by Jesson *et al.* in a different context [7], is very simple and contains several approximations. The major one, that we have not yet discussed, is the negligence of the role played by some Si intermixing, which is always present [20–22]. As shown in Fig. 3(b), the lower portion of the pyramid is more likely to accommodate Si atoms, due to the smaller values of a_{\parallel} , as experimentally reported in Refs. [20,22]. This is also confirmed by our Monte Carlo simulations of 35% Si intermixing at $T = 900 \text{ K}$ [23], and by the careful analysis reported in Ref. [21]. Being mostly concentrated in a part where the lattice parameter is already close to the proper one, the Si atoms occupying the island base do not cause any relevant change in the a_{\parallel} vs (h/L) trend, as demonstrated in Fig. 3(b). Taking also into account that, due to the lower surface tension, a floating Ge layer is always expected to cover the pyramid facet (as confirmed in Ref. [21]), we conclude that surface kinetics should not be dramatically dependent on intermixing, at least for the initial stage of the transformation, described by our model and leading to the step-bunching process. As mentioned above, the complete evolution to domes is also produced by a “rounding” of the pyramid corners (see Fig. 2). This effect may be correlated with the presence of Si-rich regions at the pyramid corners [20], rendering the attachment of Ge adatoms unfavorable. Additional theoretical effort, however, is still needed in order to clarify this issue.

We notice that, based on the STM observations, the model assumes atomic diffusion across the $\{105\}$ steps of the transition islands to be possible, even if the barrier for the corresponding process is unknown. Lowering the temperature, the process could be hindered, qualitatively changing the island evolution. Despite its simplicity, the

model captures the essential features of the Ge island evolution, showing that no changes in the pyramid top-to-bottom growth modality is needed in order to account for the observed onset of the step bunching, which ultimately produces the transition to the dome shape.

One final comment has to be stated about our analysis: the model considers the energetics of different configurations for an additional Ge monolayer reaching the $\{105\}$ facet, and not the global thermodynamics of the system. It cannot be excluded that by rearranging the atoms composing a pyramid with extended step bunching into a (small) dome geometry, with larger (still unknown) surface energies, but lower volume contribution (see, e.g., Fig. 3 of Ref. [4]), one obtains a lower-energy structure. However, the sequence flat pyramids—stepped pyramids—domes appears strongly favored from a kinetic point of view, since it allows the shape transformation to occur by surface diffusion only, without needing any bulk reshuffling of the atoms.

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*Email address: francesco.montalenti@unimib.it

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