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One-dimensional Ge nanostructures on Si(001) and Si(1 1 10): Dominant role of surface energy

Structures unidimensionnelles de Ge sur Si(001) et Si(1 1 10) : rôle dominant de l'énergie de surface

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ABSTRACT

Ge/Si(001) is a prototypical system for investigating three-dimensional island self-assembly owed to the Stranski–Krastanow growth mode. More than twenty years of research have produced an impressive amount of results, together with various theoretical interpretations. It is commonly believed that lattice-mismatch strain relief is the major driving force leading to the formation of these islands. However, a set of recent results on Si(001) and vicinals point out that, under suitable conditions, this is not the case. Indeed, we here review experimental and theoretical results dealing with nanostructures mainly determined by surface-energy minimization. Results are intriguing, as they reveal the existence of magic sizes, show the presence of very peculiar morphologies, such as micron-long wires, and distinguish among attempts to facet the wetting-layer and true SK islands.

RÉSUMÉ

Le système Ge/Si(001) constitue un prototype pour l'étude de l'auto-assemblage des îlots tridimensionnels dans le cadre de la croissance Stranski–Krastanov. Plus de vingt ans de recherches on produit une quantité impressionnante de résultats, ainsi que des interprétations théoriques variées. Il est communément admis que la relaxation de la contrainte due au désaccord de maille est la force motrice dominante qui mène à la formation de ces îlots. Cependant, de nouveaux résultats sur Si(001) et sur des surfaces vicinales indiquent que, dans des conditions adaptées, ce n'est pas le cas. En effet, nous rapportons ici des résultats expérimentaux et théoriques décrivant des nanostructures qui sont essentiellement déterminées par la minimisation de l'énergie de surface. Ces résultats intriguent, car ils révèlent la présence de tailles magiques, et montrent la présence de morphologies très particulières, comme des fils de longueur micronique. De plus, elles mettent en évidence les différence entre les tentatives de facettage de la couche de mouillage et la formation de véritables îlots Stranski–Krastanov.

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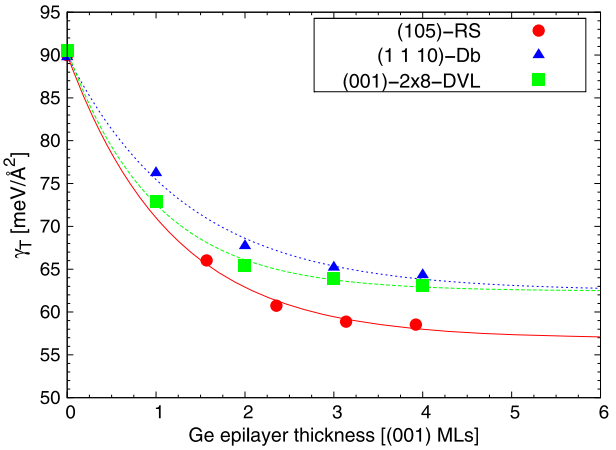

Fig. 1. From Ref. [27]. Trend of the surface energy density γ as a function of epilayer Ge thickness N for three different orientations. Color figure available on the web.

1. Introduction

More than twenty years have passed since the first seminal reports on three-dimensional (3D) Ge islands on Si(001) were published [1,2]. Massive research followed, as Ge/Si was soon recognized as a prototypical, simple-enough system following the Stranski–Krastanow (SK) growth mode. As such, its profound understanding could lead to the development of predictive models for other, technologically more appealing but more complex, heteroepitaxial lattice-mismatched systems such as III–V compounds (see, e.g., [3–7]). Reviews on Ge/Si (and, Ge_xSi_{1-x} alloys on Si(001), showing a similar behavior for high enough Ge concentration x) SK growth can be found in Refs. [8–13]. We now know that typical 3D islands tend to change morphology during growth, evolving from low height-to-base aspect ratios R to large R values as their volume increases (see also [14] and references therein). A multitude of islands shapes were indeed observed, starting from small mounds [15,16], leading to {105}-faceted pyramids ($R \sim 0.1$) and huts [1,17], to larger-volume (V) multifaceted domes ($R \sim 0.2$) [18,19], barns [15] ($R \sim 0.3$) and cupola islands ($R \sim 0.4$) [20] with increasing V. What typically defines an island of each family is the set of different exposed facets.

Some general features of Ge/Si SK growth are now well understood. As the first layer of Ge is deposited, a strong driving force determines perfect wetting, to saturate highly-energetic Si dangling bonds with the weaker Ge ones. As a result, the film surface energy γ_{WL} drops. If a second Ge layer is now added, the interface-effect due to the presence of the Si substrate below is still strong (owed both to electronic [21] and elastic [22] effects), so that the surface energy γ keeps on dropping. If N is the number of deposited layer, this effect in semiconductors is well described by an exponential decrease of the surface energy with N [23], convergence to the $N \to \infty$ limit being controlled by a system-specific *wetting factor*. To add on complexity, the WL typically changes its reconstruction with increasing N [21,24–26], without however affecting the general $\gamma_{WL}(N)$ behavior described above. Examples of the $\gamma_{WL}(N)$ dependence as obtained by ab initio calculations are given in Fig. 1 for the orientations of direct relevance for the problem discussed in Sections 4 and 5. It is clear that the driving force for wetting decreases with N, so that departure from a simple 2D WL configuration is increasingly facilitated with WL thickness, provided there is a driving force for doing so. Obviously, this additional driving force is provided by strain relaxation. A planar WL configuration determines biaxially compressed Ge (Ge lattice parameter being ∼4% larger than the Si one), only partially reacting through a tetragonal relaxation of the elastic energy. Formation of 3D structures introduces further degrees of freedom allowing for R-dependent lowering of the volumetric elastic energy density ρ_{is}, higher R values leading to lower ρ_{is} [12]. On the other hand, islands with high R values also determine an increased additional-surface exposure [12,14], scaling as $V^{2/3}$, so that the following simple interpretative scheme emerges. Provided that the WL is thick enough (above some ∼3 ML, but see discussion in [28]), 3D islands are formed. At small V, only low-R islands can be observed as evolution towards optimal (high-R) strain relaxation is hindered by surface-energy costs. As the volume increases, however, volumetric strain relaxation dominates and high-R structures are eventually formed. Although this simple description seems to yield a qualitative explanation of the experimental findings, a substantial upgrade of the theory is needed in order to account for a semi-quantitative description of the Ge/Si(001) behavior. A general discussion is presented in the next section, considering various additional effects which can significantly alter the simplified description presented in this Introduction. Then, in the remaining sections of the manuscript, we shall review recent theoretical and experimental results demonstrating that the very concept of islands being created as a result of strain relaxation frustrated by a flattening surface-energy driving force does not apply under peculiar conditions. This leads to a new class of Ge/Si nanostructures of major scientific interest, whose potential for applications has not been yet explored.

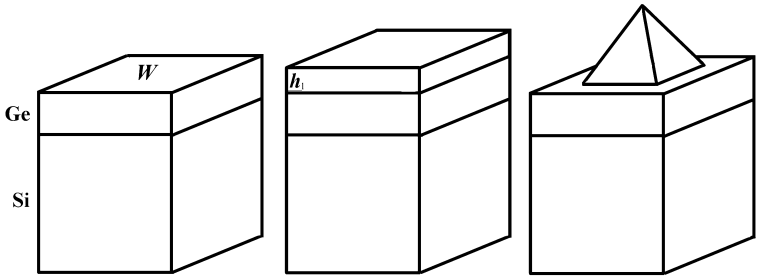

Fig. 2. Starting from a WL made of N Ge layers (left), we evaluate the energy difference ΔE between a configuration where an additional volume V of material creates a partially covered $N+1$ flat layer (central), producing local thickening h_1, and the alternative configuration where an island of volume V is formed over the N-layer thick WL (right). Only the portion of area $W = V/h_1$ of the full WL is shown.

2. Complex phenomena

The tendency towards increasing aspect ratios with V does not persist at any volume, as large enough islands eventually find it more convenient to follow a different relaxation channel. Above some critical volume V_d, indeed, misfit dislocations are introduced, fully altering the growth modality. Typically, a plateau in the $R = R(V)$ curves is seen experimentally as plasticity sets in [29–32]. While plasticity in 3D islands is an extremely interesting subject, surely demanding for further research, here we shall restrict our analysis to coherent islands, for which another key process was not described in the Introduction. Ge and Si have a negligible enthalpy of mixing. As the tetragonal energy density of Ge biaxially strained at the Si lattice parameter is $\rho_{WL} \sim 40$ meV/atom (or, $\sim$1.4 eV/nm^3 if expressed as volumetric density) [12], at typical growth temperature ($T \gtrsim 400\,^\circ$C [12]) one expects Si/Ge mixing entropy ($\propto kT$, k representing the Boltzmann constant) to be highly competitive with strain relaxation [33–36]. Actually, full free-energy minimization of a system composed of a few ML Ge on a virtually infinite Si substrate would lead to complete Ge dilution into Si. The reason why this does not occur, allowing us to observe the fascinating SK process, is determined by kinetics. Bulk diffusion, indeed, is typically frozen [37] (or, at least extremely slow below $T = 750\,^\circ$C [38]), so that mixing needs to occur by surface diffusion only (i.e. by surface atomic exchanges [37,39,40]). And this is hindered by the tendency towards exposing Ge atoms only for minimizing surface energy. As a net result, 3D islands form, but they do contain silicon mixed with Ge [41,42]. As expected from both kinetic (exchange processes being faster) and thermodynamic (stronger entropy of mixing) arguments, the Ge content x in the islands is a decreasing function of temperature. For instance, in the Molecular Beam Experiments described in Ref. [14], already at a growth temperature $T = 620\,^\circ$C islands are half filled with Si, becoming Si-rich at $T = 700\,^\circ$C ($x = 0.36$). For a fixed x, comparing the stability of differently shaped islands is not particularly demanding, as, in essence (and using some simplifying assumptions on surface energies [43]), one simply needs to rescale the effective lattice/island misfit. This results in a rescaling of the typical critical volume V_c for island formation scaling as $V_c \propto x^{-6}$, as confirmed experimentally [12,14,44]. If x changes during the evolution, but the corresponding values of x are known, then the search for optimal shapes can still be carried out with relative ease [43]. But if one wants to develop a model actually predicting how x changes during growth under the combined effect of deposition, intermixing and strain release, then the task becomes quite formidable. A set of increasingly refined continuum models able to tackle such complexity have been introduced by Tersoff [45–48] and various coworkers. While so far implemented only in $1+1$ dimensions, such models were shown to capture, at least qualitatively, the typical experimental behavior. Impressive 3D continuous models of heteroepitaxy have also been presented, but their treatment of intermixing is missing or incomplete (see, e.g., [49–52]).

It must be noticed that typical x values here above reported for a given growth temperature referred to experiments where Ge was deposited by Molecular Beam Epitaxy (MBE). Recent results [53] obtained by using a faster (0.1 nm/s, some 100–1000 faster than typical MBE ones) deposition technique, allowed for kinetic suppression of intermixing, so that islands with unprecedented x were obtained.

3. Modeling the stability of an island

Having described the complexity brought into the Ge/Si system by intermixing, in the remaining of the paper we shall review some recent results showing that even under growth conditions where intermixing is negligible (indeed, if not stated otherwise, we shall assume $x = 1$), so that the system should display a *simple* behavior, surprising phenomena take place, as due to surface-energy effects. A simple model, ignoring dynamics but carefully quantifying total energy, will be used and compared with experiments.

Let us consider a WL made of N layers, and let us ask what is the difference in total energy ΔE between (a) a system where a volume V of Ge atoms is added and organized in the shape of an island, and (b) a system where the same extra-material V is added forcing a flat configuration (i.e. a partially covered $(N+1)$-th layer is created). The situation is sketched in Fig. 2. By considering volumetric (ΔE_V), surface (ΔE_S), and edge (ΔE_E) contributions [54,55], so that $\Delta E = \Delta E_V + \Delta E_S + \Delta E_E$, it is easy [28] to work out the explicit expressions for the three addenda, after neglecting step-energy terms associated with the 2D flat island representing the incomplete $N+1$ layer. In particular, the volumetric term can be

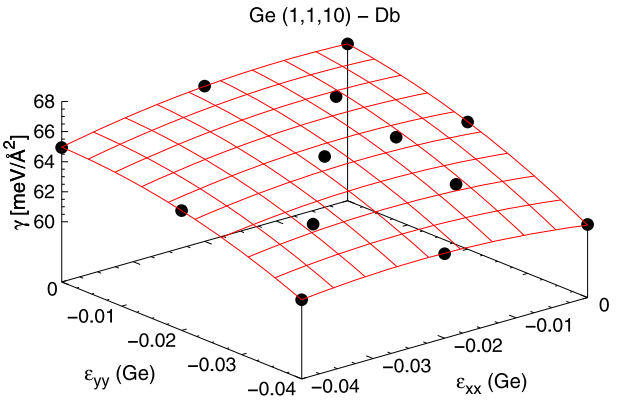

Fig. 3. From Ref. [27]. Behavior of the surface energy of Ge(1 1 10) as a function of uniaxial ϵ_{xx} and ϵ_{yy} applied strain. Color figure available on the web.

written as $E_V = V\,\Delta\rho_{\text{eff}}$, with

$$\Delta\rho_{\text{eff}} = (\rho_{\text{isl}} - \rho_{\text{WL}}) + \frac{\gamma_{\text{WL}}(N) - \gamma_{\text{WL}}(N+1)}{h_1} \tag{1}$$

where h_1 is the height of a single (001) ML, and ρ_{isl} ($< \rho_{\text{WL}}$) the elastic energy density of the island (including the effect on the Si substrate below [28]). It is clear that $\Delta\rho_{\text{eff}}$ accounts for both the extra relaxation provided by the island with respect to the WL and by the disadvantage of exposing a thinner WL in the configuration with the island (see Figs. 1, 2). While a reliable quantification of surface energies requires ab initio atomic-scale calculations, ρ_{isl} can be more easily extracted from continuum elasticity theory solved by Finite Element Methods (FEM). Some care is needed when mixing together the two into a single multiscale calculation [28]. The surface-term, accounting for the extra-surface exposed when replacing a flat configuration with a 3D one, reads:

$$\Delta E_S = S\gamma - A\gamma_{\text{WL}}(N) \tag{2}$$

where A is the WL area covered by the island, S the total surface exposed by the island, and γ represents the surface energy of the exposed facets of the island. Actually, γ is a complex quantity to be evaluated. Even considering the simple situation of an island exposing only one kind of facet, γ depends on the local strain [12]. An example of such dependence, as obtained by a set of ab initio calculations, is displayed in Fig. 3. Worst, for shallow islands it is necessary to include in γ also variations induced by the presence of the Si substrate, acting similarly to what discussed for the WL (the higher is the distance the lower is the surface energy, see Fig. 1). A detailed description of a procedure which allows to tackle all these contributions yielding island-facets surface energy is supplied in Ref. [27]. Finally, the edge term can be written as:

$$\Delta E_E = L\Gamma \tag{3}$$

where L is the total length of all edges (here considered all of the same kind, for sake of simplicity), and Γ the associated edge-energy (linear) density. In summary, the difference in total energy reads:

$$\Delta E = \left[V\,\Delta\rho_{\text{eff}} + S\gamma - A\gamma_{\text{WL}}(N) + L\Gamma\right] \tag{4}$$

For a fixed island shape, i.e. by considering self-similar evolution, then $E_S \propto V^{2/3}$ and $E_E \propto V^{1/3}$, where the proportionality coefficients are independent of the volume. While islands typically evolve by re-adjusting their shape during growth [14], so that self-similar evolution takes place only in limited volumetric ranges, the self-similar assumption is perfectly suited to answer to a key question: in which volumetric range is an island of shape S_1 more stable than another island of shape S_2 (where S_2 could also be the flat, WL configuration)? Notice that some general behavior can be easily extracted. For instance, if the WL is sufficiently thick (say, $N > 5$, see Fig. 1) so that γ_{WL} is well approximated by its limiting value, then in the large-V limit any 3D structure becomes stabler ($\Delta E < 0$) than the WL. Also, under the same limit, one predicts tendency towards maximizing R, therefore reaching the full-relaxation limit. More interesting, however, is to numerically investigate intermediate limits. Several examples can be found in the literature, and quite recently, a rather complete phase diagram for Ge/Si(001) has been presented and successfully compared with experiments [28].

Let us now consider a hut geometry. Huts were the very first Ge islands to be observed [1]. They display a rectangular base of area $L \times b$, where b (L) is the length of the short (large) side. More importantly, they are bound by four {105} facets, characterized by an inclination angle $\theta = 11.3°$ with respect to the flat (001) surface. A sketch is presented in Fig. 4. Now, let us suppose that $L \gg b$, as this case will be of direct relevance for describing the experimental results reported in the next section. Under these conditions, we shall call the huts *wires*. It is trivial [43] to show that Eq. (4) for a wire reads:

$$\Delta E = V\left[\Delta\rho_{\text{eff}} + \frac{4}{b\tan\theta}\Delta\gamma + \frac{4\Gamma}{b^2\tan\theta}\right] \tag{5}$$

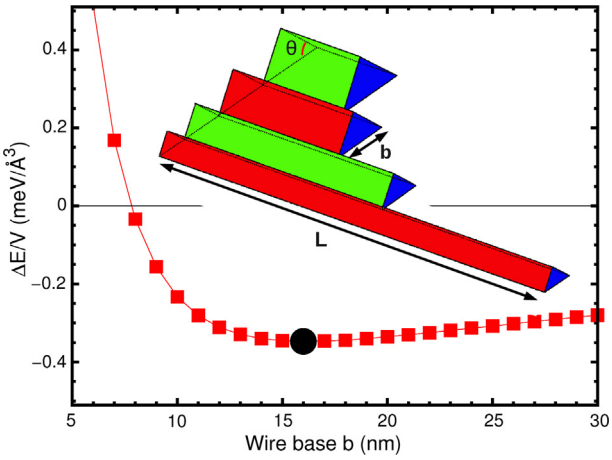

Fig. 4. From Ref. [56]. Energy difference (per unit volume) between a vertically-truncated wire and a WL configuration of the same volume at different wire bases b. The (black) point highlights the minimum-energy configuration. In the inset, the geometries of wires with different bases and length (but same volumes) are sketched. Color figure available on the web.

where $\Delta\gamma = \sec\theta\gamma_{\rm hut} - \gamma_{\rm WL}(N)$, and $\gamma_{\rm hut}$ is the surface energy density of the huts' facets. Notice that if Eq. (4) described the stability of an island of assigned shape as a function of volume, Eq. (5) describes instead a set of possible islands, characterized at any fixed V by different b and L values, as we are not imposing a fixed lateral b/L aspect ratio. This makes it possible to look for an ideal, energy-lowering island at each volume. By taking the derivative of Eq. (5) with respect to b at fixed V and equating it to zero, one finds a *magic* base minimizing the wire energy with respect to zero: $b_{\rm min} = 2\Gamma/(-\Delta\gamma)$, provided that $\Delta\gamma < 0$ (actually, in Eq. (5) we have not considered some further dependencies on b, which can be safely neglected in typical cases of interest [43]). Now, $\Delta\gamma < 0$ only if the {105} surface energy is lower than the {001}, which might sound awkward. Instead, several theoretical investigations based on ab initio calculations [27,57–59] pointed out that the {105} is a particularly favored orientation for growing strained Ge. By considering its peculiar rebonded-step reconstruction [60,61], indeed, it has been shown that the surface energy of Ge{105} is strongly stabilized under the compressive conditions felt by Ge on Si(001). The most recent available calculation [27] leaves little doubt: as anticipated by Fig. 1, {105} is a better orientation with respect to {001} for compressively strained Ge. Notice that for sufficiently large N values, so that $\Delta\rho_{\rm eff} \sim \rho_{\rm is} - \rho_{\rm WL} < 0$, the edge energy Γ is the only term opposing wire formation.

So, for 1D Ge nanostructures involving solely {105} facets there exists a magic base. Even better, it is volume-independent. This means that once a wire reaches the $b_{\rm min}$ value on its short side, it will display a strong tendency towards increasing its volume by simply elongating and, as a consequence, keeping the same height. This is a totally different evolution with respect to the above-described self-similar case.

Let us now introduce some experimental results confirming the theoretical prediction of a magic wire base b, followed by a more quantitative comparison with theory. Before, we find it relevant to recall that the major stability of {105} influences in a similar way also the energetics of {105} pyramids, leading to magic bases also for those kind of islands [28]. Their quick transformation into differently-shaped islands exposing other facets, however, makes it harder to appreciate the effect [28].

4. Micron-long Ge wires on Si(001)

In Fig. 5, taken from Ref. [56], clear evidence of Ge wires grown on Si(001) is given. Such surprising structures were grown by MBE. In a first stage, 4.4 ML of Ge were deposited, with a growth rate of 0.04 ML/s at a substrate temperature of 570 °C. The deposited Ge amount was chosen in order to be slightly smaller than the critical thickness of 4.5 ML for the formation of usual huts clusters [1,17,62]. After Ge deposition, the substrate temperature was kept at 560 °C for different time durations. During this in situ annealing, 3D islands appear and evolve into long wires via anisotropic growth along either the [100] or the [010] crystallographic direction, as shown in Fig. 5. The length of the wires turned out to be a few hundreds of nanometers after 1 h annealing, while reaching the micrometer scale in 3 h. Actually, we stress again that length is the only parameters distinguishing a *wire* from a *hut*, the former being the first example of a one-dimensional structure extending on the micron length by pure self-assembly of Ge/Si(001). The peculiar growth procedure, leading to island formation during annealing only, and using a long annealing time at a temperature lower than the growth one, proved to be key in producing such surprising results, which had escaped from more than twenty years of research on Ge/Si(001). Reducing island nucleation probability, carefully controlling the rate of adatoms creation from the WL and their mobility, and freezing Si/Ge intermixing appear to be the key ingredients needed to obtain the isolated long wires depicted in Fig. 5. Always in Ref. [56], a statistical analysis of the wires was supplied, revealing an average height of 1.86 nm (i.e. a short base $b = 18.6$ nm), with an extremely small standard deviation (of the order of 0.1 nm). The theory introduced in the previous section offers a solid interpretation of the findings. After plugging into Eq. (5) the values of the surface energies

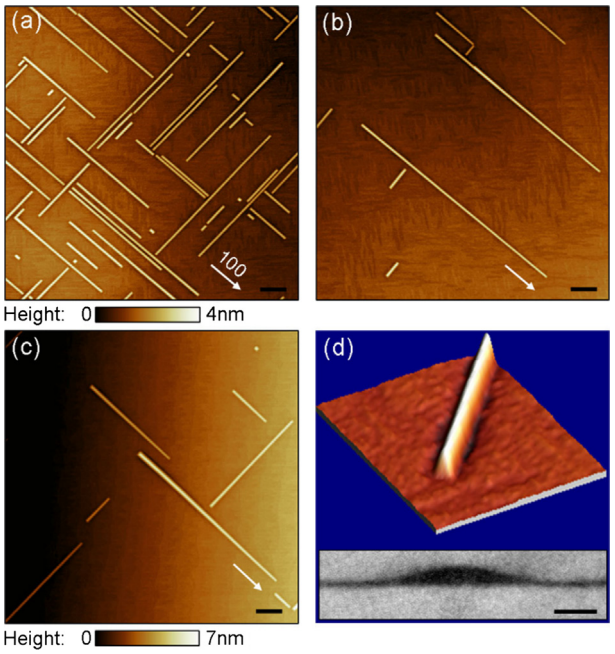

Fig. 5. From Ref. [56]. AFM images of long Ge {105} wires on Si(001) substrate created upon deposition of 4.4 ML of Ge after 12-h annealing. In panel (c), a substrate with a larger miscut angle was used [56], so that some wire tapering is visible. The black scale bar corresponds to 200 nm. In panel (d), a cross-sectional TEM of a Si-capped wire is shown, together with an AFM image of an isolated wire. Color figure available on the web.

(only {105} and {001} are involved in this case), as obtained from first-principle calculations [27] and the elastic relaxation term (computed via FEM calculations [27]), we are left with only one unknown parameter, the edge energy Γ. This was taken from Ref. [56], where a value of $\Gamma = 370$ meV/Å was inferred by a comparison between theory and experiments on a similar system (Ge ripples on Si(1 1 10), see next section for a further discussion on the Γ value).

Once Γ is determined, we can attempt a quantitative comparison between theory and experiments, using the results of Fig. 4. Theory predicts a preferred base $b = 16.3$ nm within 15% of the experimental value. We find this agreement excellent, taking into account the simplicity of the model which does not take into account any intermixing (but see discussion in [56]), and neglects fluctuations around minimum-energy configurations.

Beside the direct comparison between measured and predicted size, and perhaps more importantly from a general point of view, the prediction per se of a magic base is nicely confirmed by the homogeneity in size dimensions, as well as the by the noticeable length of the wires (see previous section).

Once again, we emphasize that the observed behavior is due mainly to surface-energy lowering, strain relaxation yielding a driving force for wires' formation one order of magnitude smaller under typical conditions (see Supplemental Material in Ref. [56]). This makes the present predictions qualitatively different from previous ones [63].

5. {105} ripples and WL faceting on Si(1 1 10)

In this section we shall discuss results concerning Ge deposition on Si(1 1 10). We recall that growth on vicinal Si(001) surfaces has been the object of several investigations (see, e.g., [9,64,65,11]). Here, however, we shall solely focus on a recent experiment which allows for a better understanding of the results discussed in the previous section. A few months before Ge wires on Si(001) were reported [56], somewhat similar structures were revealed and analyzed on Si(1 1 10) [66], under more standard growth conditions (i.e. continuous deposition). Results at different Ge coverage, as obtained by MBE deposition at $T = 550\,^{\circ}$C, are displayed in Fig. 6. Before analyzing them, we shall recall some features of the (1 1 10) orientations. As nicely discussed and demonstrated in [67], the shape of a 3D island can be tailored by changing the substrate orientation, so that the evolution of families (huts, pyramids, domes) of islands when increasingly departing from the (001) substrate orientation can be predicted. The four closing facets of a hut, in particular, while conserving their {105} orientations, give raise to progressively (i.e. with increasing miscut angle) elongated angles, until the (1 1 10) orientation ($\sim 8^{\circ}$ miscut) is reached, and one is left with (virtually) infinitely long structures [11,68,64], called ripples. Fig. 6a shows such structures while developing. At variance with wires on Si(001), ripples can only extend in one dimension. And, their extension is favored by kinetics. Indeed, the Si(1 1 10) surface is ideally made of double steps only, the ripple long direction being always perpendicular to surface dimers, i.e. parallel to the fast diffusion direction on Si(001) terraces [68]. With this respect, the presence per se of long Ge ripples on Si(1 1 10) is less surprising than on Si(001). But in view of the results discussed in the previous section, we can now rule out that the peculiarities of the (1 1 10) orientations play a key role in the appearance of long 1D structures. A very intriguing result is however shown in Fig. 6. As the Ge coverages exceeds

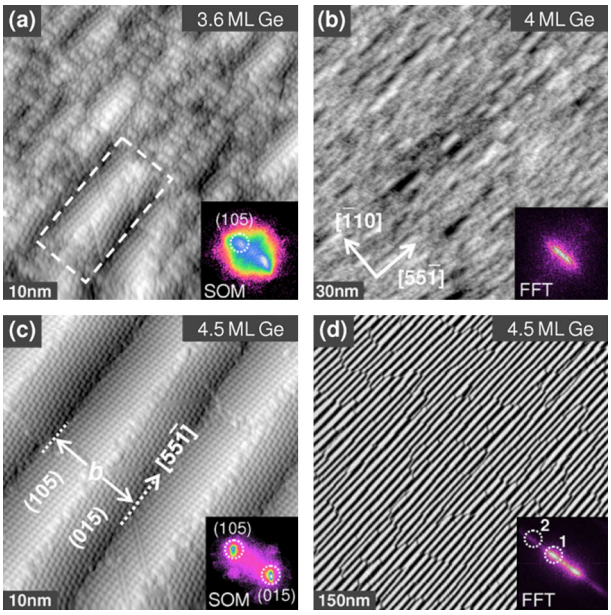

Fig. 6. From Ref. [66]. STM images of Si(1 1 10) samples showing the fast evolution towards seamless faceting of {105} ripples for different Ge coverages, at a growth temperature of 550 °C. Color figure available on the web.

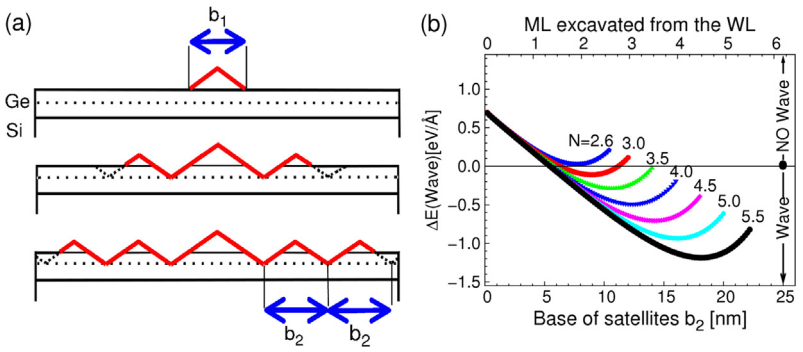

Fig. 7. From Ref. [66]. (a) Sketch of our wave model, envisioned to explain the dynamic path leading to coherent faceting. (b) Energetics of the wave model for different initial WL thicknesses. Color figure available on the web.

∼4 ML, a perfectly ordered structure made of parallel ripples is observed, leading to faceting of Ge/Si(1 1 10). Uniformity in ripples dimensions is remarkable [66].

Unfortunately, the process seems to be very fast, and no experimental information on the intermediate states connecting the collection of isolated pre-ripples (panel a) and full faceting (panels c and d) is available. What happens in between? In Ref. [66] we proposed the following picture. An isolated ripple tends to quickly elongate in one direction for the above-recalled kinetic reasons and because surface-energy lowering leads to selection of a magic base, followed by elongation. The latter point has been already discussed in the previous section, the main difference between wires on Si(001) and ripples on Si(1 1 10) stemming in the WL orientation. As the surface energy of the latter is higher on Si(1 1 10) (see Fig. 1), replacing the WL with {105} is even more convenient than on (001). This leads to a prediction of ripples' formation at lower coverages on Si(1 1 10), as it can be inferred by comparing Ref. [56] and Ref. [66]. In both references, the same value $\Gamma = 370$ meV/Å was used for the edge energy, as determined in [66] by a comparison between experimentally and theoretically estimated critical WL thicknesses needed to stabilize ripples. While this value exceeds by more than one order of magnitude previous theoretical estimates of the edge energy of two adjacent {105} facets [69], the sealing region has been shown to be very disordered and to typically extend by some ∼2 nm [56]. If such edge energy is transformed into an equivalent sealing-surface energy, the value appears as much more reasonable [56].

Once an elongated ripple is created, we can envision the mechanism behind full faceting, once again driven by surface-energy minimization. As we know that it is energetically convenient for the system to get rid of the highly-energetic (1 1 10) WL orientation, a possibility is to extend the {105} facets in the WL, as sketched in Fig. 7a. The process creates satellite ripples that trigger the formation of additional satellites in a wave-like fashion. Notice that once the first pair of satellites is created, all further-generation satellites have the same base, so that the process could indeed lead to a very ordered array

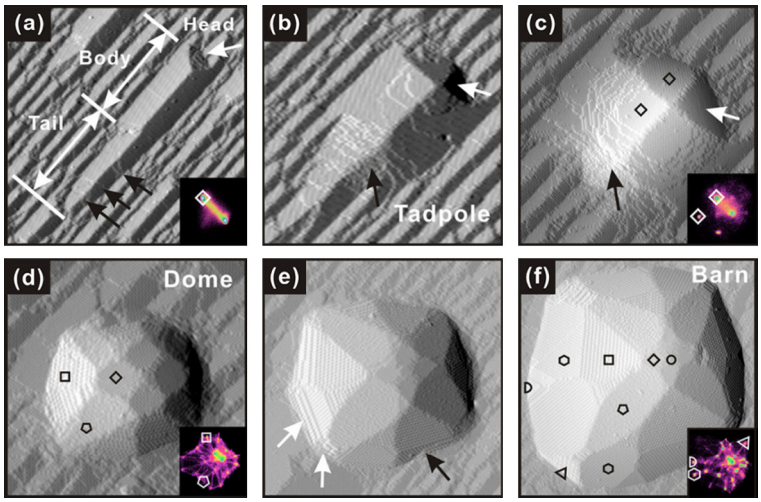

Fig. 8. From Ref. [71]. (a–e) 100 nm × 100 nm high-resolution STM images of the path leading to the evolution from a pure Ge tadpole into a dome and a barn 3D island on the Si(1 1 10) surface. 5.5 MLs of Ge are deposited at a substrate temperature of 600 °C. Color figure available on the web.

of ripples, similarly to the experimental situation depicted in Fig. 6. In Fig. 7b, the energetics of the process (taking place at constant Ge volume) is quantified, for different initial WL thicknesses. Beyond a critical thickness, the wave mechanism is energetically favored. And, at the experimental $N = 4.5$ ML value, a preferred base $b \sim 15$ nm of the ripple structure is predicted. Notice that the model does not predict full excavation down to the Si substrate. As at the $N = 4.5$ ML minimum, it is energetically favorable to leave some ∼1 ML Ge underneath the ripples. Both the predicted base value (see Fig. 6) and the residual WL thickness [66] turned out to be in good agreement with the experiments. Notice that such wave mechanism does not involve long-range transport of material (which would be hard to envision in the slow-diffusion direction, perpendicular to the ripples), as the Ge adatoms needed to form adjacent satellites are created directly at the ripple side while the excavation process leading to the extension of the lateral {105} facets takes place. The compressive stress field present at any island base edges [12] is likely to facilitate the process. As presented in Ref. [66], the wave model was an educated guess, corroborated by the final agreement between theory and experiments. Very recent results, however, demonstrated that the same mechanism takes place also on Si(001). Better, the propagation of the wave leading to lateral wire replication was imaged while taking place, exploiting the slower pace at which the process takes place on Si(001) [70].

6. Back to Stranski–Krastanow growth

As it is evident from Eq. (5), once a wire (or, a ripple) with optimal base is formed, its elongation keeps on yielding a fixed energy gain (with respect to the WL configuration) with increasing length and, therefore, V. For sake of simplicity, let us consider a sufficient WL thickness, so that variations in surface energies with N are negligible, and the full term under square brackets in Eq. (5) is simply a number C_{1D}. If we now consider the alternative configuration where the same V is arranged into a 3D island, at large enough V values the energy gain for this island (see Eq. (4)) is simply given by $\rho_{is} - \rho_{WL} \equiv C_{3D}$. As discussed in the Introduction, C_{3D} depends on the island aspect ratio R. For small R values ($R \to 0$), $|C_{1D}| > |C_{3D}|$, meaning that once an optimal 1D structure is formed, no transition to (small-R) 3D islands is predicted. But there might be large enough R values leading to a switch of the relative energies at large enough V. And, this is the case for our system. Indeed, in Ref. [56] it was observed that the strain relaxation guaranteed by a typical dome island is sufficient to make such 3D structure more stable than a wire at sufficiently large V values. However, a quantitative estimate of the wire length $\tilde{L}$ at which the transformation to dome becomes energy-driven yielded $\tilde{L} \sim 0.6$ μm. Now, once such a long wire is formed, re-arranging its material into a 3D morphology requires a major transformation, so that 1D structures are likely to persist also beyond their thermodynamic stability limit, unless the system finds a convenient low-energy path leading to 1D symmetry breaking. This is what happens on Si(1 1 10). Once complete faceting, described in the previous section, is achieved, further deposition triggers tapering of some ripples. In Fig. 8a, the existence of a short “tail” on one side and of a large “head” on the other is evident. The head of such a “tadpole” structure progressively grows while the tail shrinks. Already at the evolution stage depicted in Fig. 8b, the breaking of the initial 1D symmetry is evident. As a true, nicely relaxed 3D structure is created, atoms composing the tail quickly migrate towards the other end, attracted by the lower elastic chemical potential, until a dome (or an even steeper barn) island is formed. Notice that although the dome displayed in Fig. 8 (see also [72]) strongly resembles the corresponding ones seen on Si(001), the path leading to its formation is totally different [73].

7. Conclusions and perspectives

The popular picture of Ge islands being formed on Si(001) as a result of strain relaxation counterbalanced by a surface-energy cost does not hold when dealing with structures solely made of {105} facets. The peculiar stability of such a vicinal under compression leads to a very characteristic behavior. Noticeably, magic sizes exist, as mainly determined by a balance between surface-energy gain and edge-energy costs. Here we reviewed some recent experimental findings which strongly corroborates this view, as demonstrated by successful comparison with interpretative models. By suitably tuning the growth conditions, our experimental colleagues in Dresden [56,70] and Linz [66,71] were able to grow micron-long wires on Si(001) and of ripples on Si(1 1 10). The latter case is peculiar, as ripples quickly self-organize, leading to a perfectly faceted WL, before usual SK growth sets in. A collective wave mechanism was proposed to explain faceting, where a single isolated 1D structure creates equally-sized satellites. A compelling evidence of such process was given very recently [70], where the wave mechanism led to orthogonal intersecting bundles of wires, self-tessellating the surface. Research on similar 1D structures grown on vicinal surface with miscut angles between the here explored extremes (0° and 8°) is likely to provide a set of complex self-organization patterns between the two extremes (orthogonal bundles vs. perfect faceting).

Some aspects of growth still need for a clarification. For several years, huts on Si(001) were simply regarded as kinetic intermediates caused by limited atomic mobility at low growth temperatures. However our results show that, provided they can reach their preferred base (short size), they provide a major lowering of the system energy. The initial formation of {105} huts vs. {105} pyramid, however, escapes from our modeling which is limited to high long/short side ratios. Careful atomic-scale evaluation of 3D edge energies, as well as investigation of the stability of small atomic clusters, with this respect, appear as crucial ingredients to shed light on the very initial stages of growth. Actually, experimental proof of the delicate role played by few-atom configurations was recently given [62,74]. The lack of an atomic-scale description is not the only limitation of the theoretical approach exploited in this work. While appealing in the demonstrated possibility of providing quantitative estimates directly comparable with the experimental data, being based on local thermodynamics it cannot predict any relevant kinetic effect. Moreover, its extension to heavily intermixed Ge/Si systems is far to be straightforward. This limits the portion of the growth-parameter space which can be sampled. To go beyond, the use of Kinetic Monte Carlo approaches and/or continuum model appears to be the only possibility.

We are confident that further experimental research on the here-introduced 1D Ge/Si nanostructure will lead to interesting applications. In view of their exceptionally small and self-defined cross section, for instance, isolated Ge wires on Si(001) hold promise for the realization of hole systems with exotic properties and provide a new development route for silicon-based nanoelectronics.

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