

Growth of Ge thin films and islands on the Si(001) surface

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We study strained-layer growth of Ge on the Si(001) surface by means of an empirical potential that is further refined by fitting it to recent total-energy results for the stress and energies of various missing-dimer reconstructions of the Si(001) surface. The modified potential predicts the buckled dimer surface to be substantially lower in energy than the symmetric dimer surface. It is seen that the reconstruction of the GeSi surface, before the occurrence of islanding, has the missing-dimer-trench structure as observed in a number of scanning tunneling microscopy experiments. Our calculations provide direct support to the notion that islanding does indeed set in after layer-by-layer growth of three monolayers. We discuss the implications of our calculations for the growth of long thin islands of high aspect ratios as seen recently in Ag-on-Si(001) systems which has been attributed to elastic relaxation.

I. INTRODUCTION

There have been a number of recent experimental studies on the lattice mismatch ($\sim 4\%$) driven growth of thin Ge films on Si(100) substrates.¹⁻¹⁰ It is known that Ge grows in the Stranski-Krastanov (SK) mode, with islanding starting after layer-by-layer growth of up to three monolayers (ML).^{1-3,8-10} Scanning tunneling microscopy (STM) studies⁸⁻¹⁰ of the growth before islanding show the presence of missing-dimer (MD) defects.¹¹ Kohler *et al.*⁸ observed surfaces consisting of buckled dimers only, arranged in periodicities of about 2×8 on the third ML; sharp MD defect lines are seen perpendicular to "trench" structures running parallel to the dimer rows. Iwawaki, Tomitori, and Nishikawa⁹ also observed surfaces consisting of "patches" of buckled dimers bordered by MD defects; they report an average periodicity of about seven dimers long in the parallel direction and a width of from two to more than five dimers perpendicular to the dimer rows. Beyond three ML's three-dimensional islands are nucleated, which grow into the hut clusters that have been observed by Mo *et al.*⁴ These islands are bounded by (105) facets and have axes lying in the [100] directions. Hansson *et al.*⁶ used liquid-phase epitaxy to grow pseudomorphic $\text{Ge}_x\text{Si}_{1-x}$ on Si(100); this technique allows growth to occur close to thermodynamic equilibrium. They showed that the growth is also of the SK type but that the islands have the shape of truncated tetrahedral pyramids, with (111) facets as side faces; the island axes are along the [110] directions. Tersoff and Tromp⁷ studied the growth of Ag on Si(001) and observed that island shapes undergo a transition to long thin structures, which they attribute to elastic relaxation.

In this work, we investigate the growth of Ge thin films on Si(001) by means of empirical potentials that we have developed to study various Si and Si-Ge problems.¹² There have been recent total-energy calculations of dimer reconstruction which involve MD's on the Si(100) surface.¹³ In the next section we modify the potentials to take into account these results. The modifications make the buckled-dimer surface substantially lower in energy than one with symmetric dimers, which has not been seen

previously for empirical potentials. In Sec. III, we apply the potentials to the Ge-on-Si surface and show that we obtain results that are in close agreement with the reconstructions seen by Iwawaki, Tomitori, and Nishikawa⁹ and Kohler *et al.*⁸ In Sec. IV, we consider the tetrahedral islands seen by Hansson *et al.*,⁶ and show directly that indeed, islanding is favored after three ML's of layer-by-layer growth. We discuss the implications of our results for the formation of long islands of high aspect ratio as considered in the work of Tersoff and Tromp.⁷

II. MODIFICATION OF THE EMPIRICAL POTENTIAL

In previous work¹² we have used a potential of the form

$$V_{ij} = A e^{-\beta(r_{ij}-R_i)^\gamma} [e^{-\theta r_{ij}} - B_0 e^{-\lambda r_{ij}} G(\theta)/Z^{\alpha_1}], \quad (1)$$

for the interaction between atoms i and j , where r_{ij} is the interatomic distance, the effective coordination number for atom i is $Z = \sum_j e^{-\beta(r_{ij}-R_i)^\gamma}$ summed over nearest neighbors, and R_i is their minimum distance from i ; $G(\theta) = 1 + \sum_{k \neq i,j} F(\Delta\theta_{jik})(\cos\eta\Delta\theta_{jik} - 1)$, where $\Delta\theta_{jik} = \theta_{jik} - \theta_i$, the function $F(\Delta\theta_{jik})$ is set to 1 and η , θ_1 , and θ_{jik} are the bond-bending constant, an equilibrium bond angle, and the angle between bonds ij, ik , respectively. In Table I are shown the energies obtained by Roberts and Needs¹³ for various dimer reconstructions of the Si(001) surface and also the surface stress calculated by Meade and Vanderbilt, as reported by Tersoff,¹³ for the relaxed symmetric dimer Si(100) 2×1 surface. We fit the stress and the energies of the $2 \times N$ MD surface with symmetric dimers for $N = 2$ and 4 by setting the function $F(\Delta\theta)$ thus

$$F(\Delta\theta) = \begin{cases} 1, & \Delta\theta < \theta_0 \\ e^{-\beta_0(\Delta\theta - \theta_0)^\gamma} + (1+C)/(C + e^{\beta_1(\Delta\theta - \theta_0)^\gamma}) - 1, & \Delta\theta > \theta_0, \end{cases} \quad (2)$$

TABLE I. Surface stress σ_{\parallel} and σ_{\perp} , parallel and perpendicular to dimer rows, in eV/(1×1 cell) for the ideal Si(001) symmetric dimer surface. Energies relative to that of the ideal surface, of the 2×2 and 2×4 MD surface with symmetric dimers, and of the ideal $p_{2\times 1}$ and $p_{2\times 2}$ buckled-dimer surfaces, in meV/cell.

	This work	Total-energy calculations ^a
σ_{\parallel}	-0.94	-0.9
σ_{\perp}	1.57	1.6
2×2 MD surface	265	275
2×4 MD surface	35.9	35
$p_{2\times 2}$ buckled-dimer surface	-33.3	-31
$p_{2\times 1}$ buckled-dimer surface	-36.0	-24

^aReference 13.

with the parameter values,

$$\beta_0 = 5.6854143143, \quad \gamma_0 = 1.1581515074,$$

$$\beta_1 = 6.1916694641, \quad \gamma_1 = 1.5241309404,$$

$\theta_0 = 12.5^\circ$, and $C = 2.6$. We show the results of the fit in Table I; the energies are referred to the energy of the ideal relaxed symmetric dimer surface. This potential, which is tuned only to the energies and stress of the symmetric dimer surface, gives energies for the ideal surface with buckled dimers, which are substantially lower than that for the symmetric dimer surface, in good agreement with the total-energy results. On the basis of their results for the 2×2 and 2×4 MD surfaces, Roberts and Needs¹³ suggest, in agreement with Pandey,¹¹ that the ground state of the Si(001) surface may be one consisting of an ordered array of missing dimers at periodicities higher than $N=4$. In Fig. 1, we plot the energies of the 2× N missing-dimer Si(001) surface. The minimum occurs at $N \sim 10$, but it is still about 10 meV/surface cell higher than the energy of the ideal surface with buckled dimers. The buckling of the dimers leads to substantial energy gains over the unbuckled surface, but this mechanism is restricted by the introduction of the MD's.

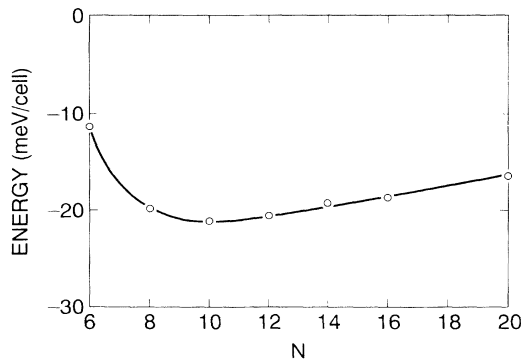


FIG. 1. Energy in meV/(1×1 surface cell), of the 2× N Si(001) missing-dimer surface relative to the energy of the symmetric dimer surface.

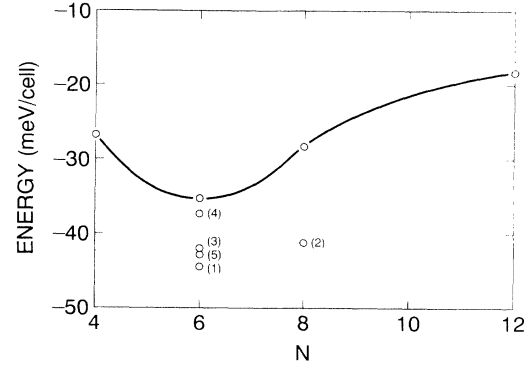


FIG. 2. Energy in meV/cell of the 2× N Ge₃Si missing-dimer surface referred to the energy of the ideal buckled-dimer surface. Numbered points give energies of surfaces with the “missing-dimer-trench” configurations of Table II.

III. RESULTS ON Ge-Si MD SURFACE

We consider now the Ge-on-Si surface. With three ML's of Ge on the Si substrate (Ge₃Si), we obtain the stress of the ideal surface with symmetric dimers to be $\sigma_{\perp} = -2.0$ eV/(1×1 cell) and $\sigma_{\parallel} = -0.71$ eV/(1×1 cell). This surface shows strong compression in both directions; it may be favorable to introduce MD's also in the two directions. The buckled-dimer surface is lower in energy than that of the surface with symmetric dimers by 29.4 meV/cell. In Fig. 2, we plot the energy of the 2× N missing-dimer surface against N , with the energy of the buckled-dimer surface as zero. Unlike the pure Si surface, the missing-dimer surface here is much more stable than the ideal buckled-dimer surface. The minimum occurs at $N=6$, which is consistent with experimental results^{8,9} and comparable to the value of eight obtained by Tersoff.¹⁵ Consider now a surface with a step of single atomic height of the S_A (Ref. 15) type with dimers on the upper and lower terraces (Fig. 3). The surface stress results above indicate that it may be even more energetically favorable to form MD's on both terraces. We list in Table II the energies of configurations given by N , M , and $M1$, where M is the number of dimer rows of the upper

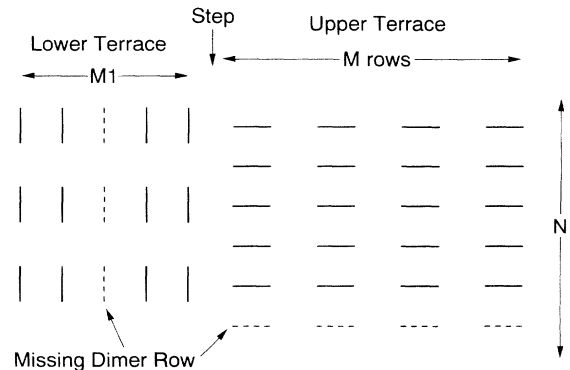


FIG. 3. A schematic of a S_A stepped surface with missing-dimer configurations on the upper and lower terraces given by N , M , and $M1$.

TABLE II. Energies of stepped surfaces with a range of MD configurations as shown in Fig. 3.

	Configurations			Energy (meV/cell)	
	<i>N</i>	<i>M</i>	<i>M1</i>		
Lower terrace MD's only		2	4	4	-24.2
MD's on both terraces	(1)	6	4	5	-44.5
	(2)	8	4	5	-41.3
	(3)	6	4	7	-42.1
	(4)	6	4	3	-37.4
	(5)	6	6	5	-42.9

terrace and *N* is the length of each of these rows; *M1* is the length of the dimer rows on the lower terrace. Even with MD's *only* on the lower terrace, there is a large energy gain over the ideal buckled surface for a typical configuration. With MD's on both terraces, the most energetically favorable configurations have energies of about -40 meV/cell, some 8-10 meV/cell lower than the energy of the surface with MD's only on the upper terrace, as seen in Fig. 3. Our results are consistent with the size and distribution of the "patches" seen by Iwawaki, Tomitori, and Nishikawa.⁹

In Fig. 4(a), we plot the energy needed to add an *n*th Ge layer to a Ge_{n-1}Si substrate, with MD's spaced *N* = 6 unit cells apart. The plot with no MD's is similar, except that for *n* = 2, the energy is +2 meV/cell [Fig. 4(b)]. The energy of the surface (with MD's) is lowered when the

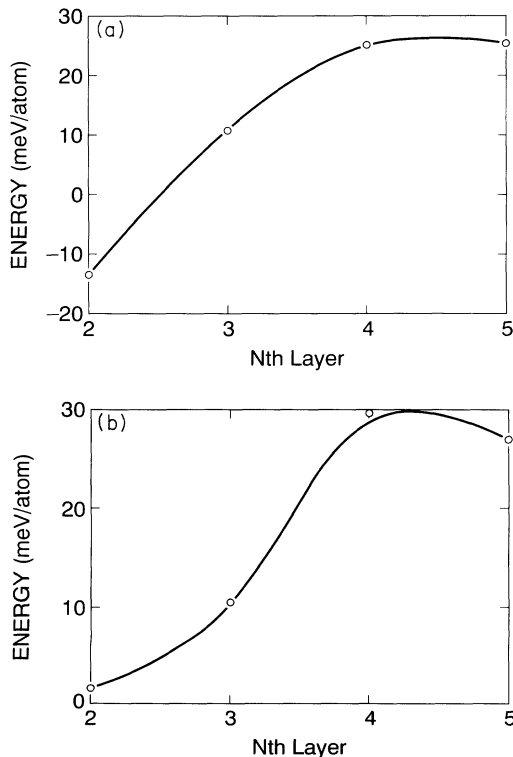


FIG. 4. (a) The energy to add a further layer of Ge atoms to a Ge_{n-1}Si substrate, with missing dimers set six unit cells apart. (b) Shows the same plot, but without MD's.

second layer is added. The addition of the fourth- or higher-order layer increases energy by a constant amount of about 25 meV/atom, which is almost the elastic energy (28 meV/atom) of bulk Ge biaxially strained to match the Si substrate [Fig. 4(b)]. The addition of the third layer costs 10.8 meV/atom, less than half that of the higher layers, and is clearly related to the observation that islanding begins after the third layer. These results show that a minimum of two layers will wet the Si(001) surface. Calculations in the next section will show that the third layer, because of its substantially lower-energy cost than that of subsequent layers, will also wet the surface.

IV. ISLANDS

In this section, we consider the growth of Ge islands on Si(100). Hansson *et al.*,⁶ in a recent experiment, were able to grow $\text{Ge}_{0.85}\text{Si}_{0.15}$ islands on Si(100) at conditions close to thermodynamic equilibrium, by means of liquid-phase epitaxy. They observed islands shaped like tetrahedral pyramids, truncated at the top, with side faces of [111] facets. These square islands have bases of average width $w \approx 50$ nm and *all* have a constant height (*h*) to width ratio $h/w \approx 0.5$. If we assume simple scaling with the square of the mismatch, the corresponding width for pure Ge islands would be about 36 nm. For convenience, we will now take *s* and *t* to be the sides of an island, measured at midheight, in units of the side of a [001] surface cell (SC) (3.84 Å), and *h* to be the number of layers in the [001] direction. In terms of these units, the height to width ratio above becomes $h/s \approx 2$.

Tersoff and Tromp⁷ have obtained the energy per unit volume, E/V , of a coherently strained island as

$$\frac{E}{V} = 2\Gamma(s^{-1} + t^{-1}) - 2ch \left\{ s^{-1} \ln \left[\frac{s}{\phi h} \right] + t^{-1} \ln \left[\frac{t}{\phi h} \right] \right\}, \quad (3)$$

where Γ and *c* are constants related to surface energies and elastic moduli, respectively, and $\phi = e^{-1.5} \cot(\theta)/2\sqrt{2}$, θ being the angle of inclination of the side faces to the substrate. (3) has been taken to second order in h/s and h/t .

Following the experimental results of Hansson *et al.*,⁶ we consider, in our simulations, two-dimensional islands of side *s*, side faces of [111] facets and height *h*, equivalent to letting *t* go to infinity in Eq. (3). The islands are set on three Ge layers and a 24-layer Si (Ge_3Si) substrate of planar (*x, y*) dimensions $2 \times L$. Periodic boundary conditions are applied in the *x* and *y* axes, parallel to the [110] directions. Increasing the substrate thickness to 36 layers does not change our results in any significant way. In order to be able to compare energies of islands of different sizes, we need to relate the energies to that of a substrate with a given coverage. For an island of size $2M$ atoms, an appropriate energy to calculate is that of the configuration made up of this island on a substrate of specific length $L = M$, so that when the atoms of the island are spread over this substrate, it is covered with exactly one more ML. Our calculations show that island-island elastic interactions are negligible. This is con-

sistent with the results of Rickman and Srolovitz,¹⁶ that island interactions go as $1/d^3$, where d is the separation between islands. In Fig. 5(a), we show a plot of E/V (measured relative to the Ge_4Si MD surface energy) against s , while keeping h/s constant at 2 as suggested by the experimental results above and by our simulations below. On the terrace, MD defects are set six SC units apart, in accordance with our results on the MD surface. Simulations with islands also show that six is optimal. In our plot, we have assumed that the side faces have adatoms; total-energy calculations by Vanderbilt¹⁷ on [111] adatom surfaces of Si show that adatoms reduce surface energies from 0.28 eV (upper curve) to 0.47 eV (lower curve) per [111] surface cell. In Fig. 5(b) we show the results of the lower curve of Fig. 5(a), plotted against $1/s$. Results for islands on Ge_2Si surfaces show similar $1/s$ behavior, but the energies are less favorable than that of the Ge_3Si surface as shown by the upper line in Fig. 5(b). Our results directly support the STM observations of Kohler *et al.*⁸ and Iwawaki, Tomitori, and Nishikawa,⁹ and are in agreement with the calculations of Tersoff,¹⁴ that the growth of Ge on Si(100) is layer-by-layer for three monolayers; islanding sets in after that. Our results show the linear $1/s$ behavior of Eq. (3) when the ratio h/s is kept constant.

In Fig. 6(a) we show a plot of island energy E/V , in meV/atom, against $h \ln(s/\phi h)/s$ keeping s constant at 16 SC units. For simplicity, our simulations for this figure

do not include adatom or missing-dimer contributions for they only shift the curve vertically by a constant amount. Here the energy is referred to that of a Ge_3Si surface without MD's. Our results deviate substantially from the linear behavior (dashed line) expected from Eq. (3). Luryi and Suhir¹⁸ have also considered the elastic energy of islands on lattice-mismatched materials and concluded that it should decay exponentially with h/s . In Fig. 6(b), we have plotted this energy against $[1 - \exp(-\alpha h/s)] \ln(s/\phi h)$, with $\alpha = 0.585\pi$. We have also carried out calculations for $s = 64$ and obtained results which scale essentially as $H = h/s$. Note that, as a result of this exponential decay, the energy surface as a function of h, s (and t) is relatively "flat;" the energy changes by less than 1.2 meV, in going from $H = 1$ to $H = 4$ (the maximum value), and by a similar amount if s is increased substantially (see Fig. 5). We fitted our results to the expression

$$E/V = 2\Gamma s^{-1} - 2c/\alpha [1 - \exp(-\alpha h/s)] \ln(s/\phi h), \quad (4)$$

and obtained $\Gamma = 29.8$ and $c = 5.786$. Equation (4) has a minimum, for constant s , at $H \approx 2$ [compared with $H \sim 6.6$ for Eq. (3)], for all s values. This is consistent with the experimental findings of Hansson *et al.*⁶ However, both Eqs. (3) and (4) have no strict minimum in energy although the experiments show the existence of stable optimal island sizes. In the case of Eq. (4), though, the flatness of the energy surface shows the possibility of

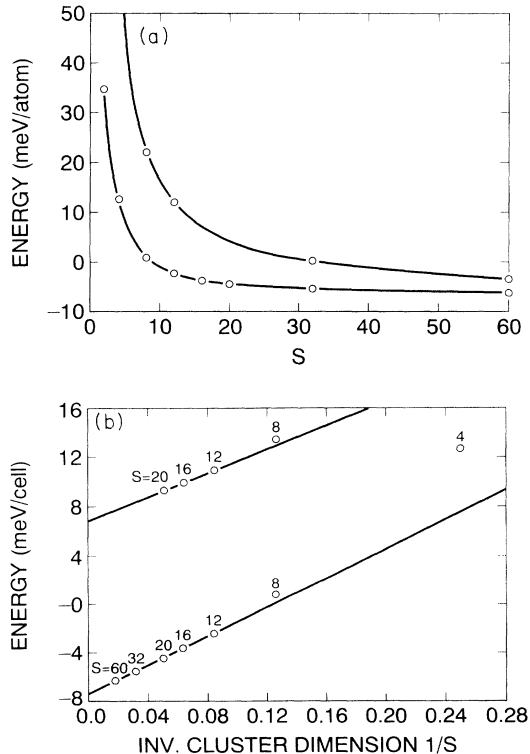


FIG. 5. (a) Island energy in meV/atom, plotted against side s in SC units while keeping the ratio h/s constant. The upper and lower curves correspond to [111] adatom reconstruction energies of 0.28 and 0.47 eV per [111] surface cell, respectively. (b) Shows energies for the lower curve plotted against $1/s$.

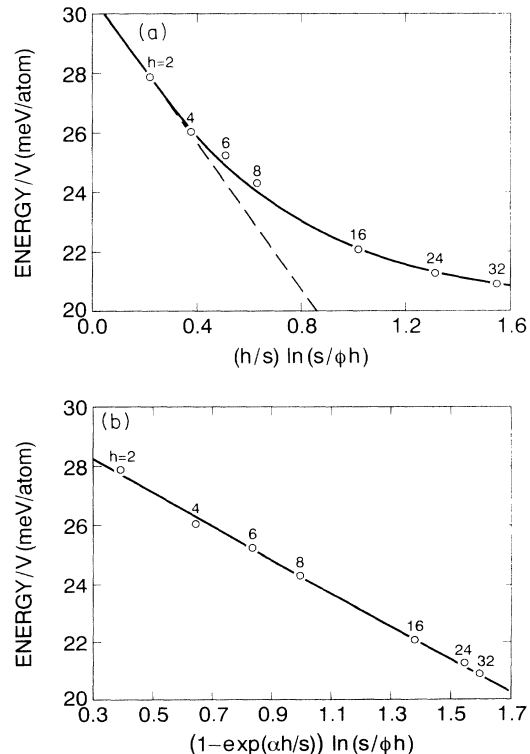


FIG. 6. (a) Island energy, in meV atom, plotted against $(h/s)\ln(s/\phi h)$, while keeping s constant at 16 surface-cell units. Dashed line shows the linear behavior expected from Eq. (3). (b) Shows the same island energy plotted against $[1 - \exp(-\alpha h/s)] \ln(s/\phi h)$.

a free-energy minimum if configurational entropy is taken into account; the free energy should show a minimum when $H \sim 2$. For Eq. (2), the “steepness” of the energy surface [Fig. 6(a)] makes a free-energy minimum much less likely.

Tersoff and Tromp⁷ discussed the growth of Ag islands on Si(100), as an illustration of the importance of strain in island growth; there is a large lattice mismatch of 6%. They observed islands, initially compact, grow into shapes of large aspect ratios, $a = t/s$, with some a 's greater than 50. They showed that when the height h is kept fixed, Eq. (3) indicates that the optimal shape of an island of a given size, $A = st$, has an ever-increasing aspect ratio beyond a certain value of A . However, there is no *a priori* reason to choose any particular value of h to keep fixed. It seems more appropriate to consider the optimal shape for a given size $V = hst$, allowing all variables h , s , and t to vary. Under these conditions, both Eq. (3) and the extension of Eq. (4) to three-dimensional islands give the optimal shape with aspect ratio $a = 1$ for all sizes. We consider the implications of keeping h constant. We calculate the aspect ratio of the island shape, which minimizes the energy of islands of size $V = 16 \times 10^6$ atoms, while keeping h fixed at a given value. In Fig. 7(a) we show a plot of this energy versus aspect ratio; in the figure, $f = h/h_m$, where h_m is the height of the island, which has the lowest energy of islands of this size. The particular value of V is not important since f and a behave as “reduced” variables. We see

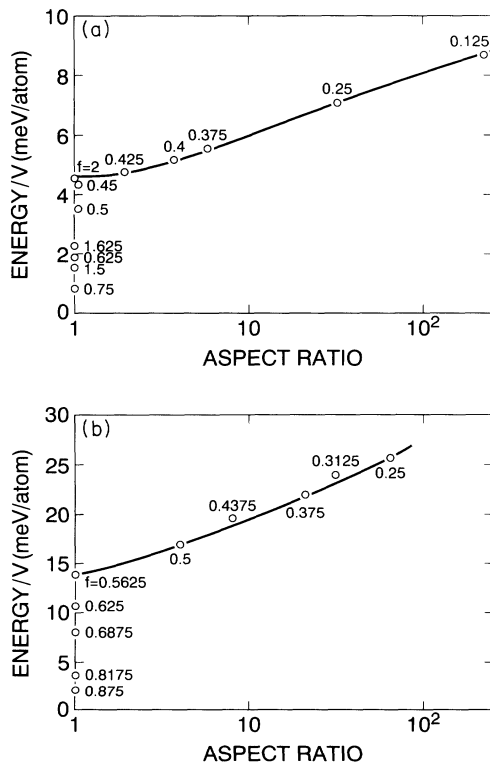


FIG. 7. (a) Plot of the energy of islands of size $V = 16 \times 10^6$ atoms, minimized while keeping the height h fixed at values given by $f = h/h_m$, where h_m is the height of the island of this size with the lowest energy. (b) shows the corresponding plot for Eq. (3).

that it costs a substantial amount of energy to maintain an aspect ratio of 50, as observed experimentally,⁷ where $f \sim 0.2$ and that this energy remains high, even when the aspect ratio is ~ 1 at $f \sim 0.5$. These results make it difficult to account for the elongated islands seen experimentally,⁷ on the basis of energetics of strain relaxation alone. The range of values of f for which the ratio is not 1 is small. There is no energy barrier in the energy surface that can prevent growth along the minimum energy path and so drive growth of long islands in a kinetically driven process. The conclusions remain the same even if we use Eq. (3). The corresponding plot [Fig. 7(b)] would map into that of Fig. 7(a), except that h_m is the maximum value of h and that the energies for a particular value of aspect ratio is approximately three times larger.

Hansson *et al.*⁶ also observed the introduction of the misfit dislocation under islands of a critical height h_c of about 30 nm. Using standard dislocation theory,¹⁹ and the considerations of Luryi and Suhir¹⁸ for elastic relaxation of islands, they calculated the critical island height to be about 15 nm; they attributed the discrepancy to a kinetic barrier to the formation of the misfit dislocation. Another possible explanation is that the presence of MD's on the terrace on which the island is set reduces the effective surface strain for the island and should increase the critical island height.

V. CONCLUSIONS

Our calculations show that dimer buckling substantially reduces the energies of both the Si(001) and the Ge-on-Si surfaces over the unbuckled-dimer surface. This is in agreement with the STM observations of Wolkow²⁰ and total-energy calculations¹³ for the Si surface. While Pandey¹¹ and Roberts and Needs¹³ argue that the Si MD surface would be more stable than the ideal dimer surface, our results show that this is not so; the presence of MD's restrict dimer buckling and reduce the corresponding gain. However, MD's do stabilize the GeSi surface; in particular, for the $2 \times N$ MD Ge_3Si surface, the minimum energy is attained at $N \sim 6$. We find the “MD-trench”⁸ or “patch”⁹ structure to have an even lower energy over a comparatively broad spread of configurations given by N , M , and $M1$, in agreement with STM observations.^{8,9} The calculations here give direct support to experimental observations that islanding is more favorable after three Ge ML's have been laid down. It is seen that elastic relaxation of the islands agrees, essentially, with classical elasticity calculations, even down to clusters of a few hundred atoms. There is no strict energy minimum; island energy decreases monotonically and slowly with size. But because of the flatness of the energy surface, we expect a free-energy minimum; the results indicate that at thermodynamic equilibrium, the ratio h/s to be about 2 as seen in experiments.⁶ We feel that high-aspect ratios seen in Ag islands grown on Si(001) (Ref. 7) cannot be attributed just to a general elastic relaxation mechanism.

ACKNOWLEDGMENT

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