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Critical layer thickness in Stranski–Krastanow growth of Ge on Si(001)

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Abstract

Using first-principles total energy calculations within density functional theory, we assess quantitatively the relative importance of different types of surface reconstructions in defining the critical layer thickness, h_c , for islanding in Stranski–Krastanow growth of Ge on Si(001). We show that, if the (2×1) reconstruction of the Si(001) substrate were assumed to be preserved at the growth front of the Ge overlayer, an underestimated h_c would be obtained. In contrast, proper inclusion of the dimer buckling and the appearance of the $(2 \times N)$ superstructure as the first strain-relieving mechanisms leads to delayed islanding, with h_c equal to the experimental value of 3–4 monolayers.

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Understanding and control of strain-induced heteroepitaxial growth is a central problem in fabrication of semiconductor and optoelectronic devices. Depending on the surface and interface energies, three elemental growth modes can be defined: layer-by-layer, island, and layer-by-layer followed by island [Stranski–Krastanow (SK)] growth [1]. The deposition of Ge on a Si(001)

surface is a prototypical model system for studying SK growth of lattice-mismatched semiconductors. The initial growth of Ge on Si(001) takes place in a layer-by-layer fashion. As the strain energy increases with the number of Ge layers, the system becomes unstable beyond certain critical film thickness, resulting in three-dimensional island formation. Experimental studies [2–4] have shown that Ge grows smoothly for about 3–4 layers before switching to the island growth mode.

Separately, on both clean Si(001) and Ge-covered Si(001) surfaces, various types of reconstruction have been observed [5–11]. On a clean Si(001) surface, the top-layer atoms dimerize and

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the dimers align to form dimer rows, resulting in a (2×1) reconstruction [5]. The dimers can also buckle and form various superstructures [6,7]. On a Ge-covered Si(001) surface, the strain associated with the lattice mismatch induces an additional “ $2 \times N$ missing dimer” reconstruction, with the value of N around 8–10 [8–10]. In this structure, every N th dimer along the dimer row direction is missing, allowing more room for the expansion of the strained Ge layer. The removal of the dimers creates extra dangling bonds which can be rebonded to the second-layer atoms [12] at the expense of local structural distortions (see Fig. 1). Several model studies of the energetics associated with the $2 \times N$ reconstruction at different coverages of Ge have been carried out, using both classical or tight-binding [13–17] as well as first-principles [18–20] based interaction potentials. More complex superstructure patterns corresponding to “ $M \times N$ ” reconstruction have also been observed recently at different growth conditions [11,15].

The physical origin of the wetting layer thickness has been the subject of active research in fundamental studies of SK growth [21–26]. In particular, a recent continuum model study has emphasized the importance of nonlinear elastic free energy and anisotropic surface tension in determining the critical thickness in generic heteroepitaxial growth systems [24]. For the specific system of Ge growth on Si(001), Tersoff has shown using the classical Keating model [27] that it is important to take into account the symmetric

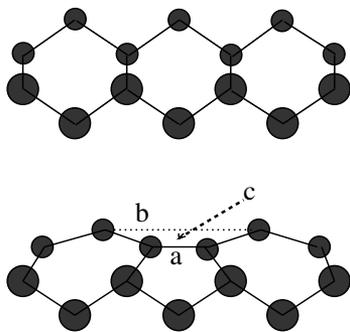


Fig. 1. Side views ([011] plane) of the perfect (001) surface (top) and the rebonded missing dimer structure (bottom).

dimerization in the (2×1) reconstruction when evaluating the critical thickness [21]. On the other hand, as described in the previous paragraph, it has been established both experimentally [8–10] and theoretically [5–7,19] that the dimers prefer to be buckled (or asymmetric), and there exists the $2 \times N$ -reconstruction at the growth front. It is therefore intriguing to investigate if the delicate nature of surface reconstruction at the growth front is important in defining the critical thickness for SK growth in this prototype system.

In this Letter, we present results from the first DFT study of the dependence of the critical thickness in SK growth of Ge on Si(100), on the specific forms of surface reconstruction at the growth front. We show that, if the (2×1) reconstruction of the Si(001) substrate were assumed to be preserved at the growth front of the Ge overlayer, an underestimated h_c would be obtained. In contrast, proper inclusion of the dimer buckling and the appearance of the $(2 \times N)$ superstructure as the first strain-relieving mechanisms leads to delayed three-dimensional islanding, with h_c equal to the experimental value of 3–4 monolayers.

The results reported here are obtained by performing ab initio total energy calculations using VASP [28,29] with ultrasoft pseudopotentials and local density approximation (LDA) [30,31]. A $(2 \times N)$ supercell has been used in the calculations, assuming, in accordance with experimental observations [10] and theoretical predictions [18], that the dimers are aligned in different dimer rows. The supercell contains n layers of Ge, $(10 - n)$ layers of Si, plus a 11 Å-thick vacuum layer. Each atomic layer has two rows of N atoms, except for the top layer, in which one dimer is missing in each dimer row. Atoms in the lowest two Si layers are fixed at their respective bulk positions, while the atoms in all other layers are allowed to fully relax. In calculating the physical properties of the 2×1 reconstructed surface, (6×12) \mathbf{k} points have been used in the surface Brillouin zone ensuring that the total energy is converged to have better than 1 meV accuracy. At every Ge coverage, the properties of the $2 \times N$ structure are calculated relative to the 2×1 structure. In these calculations, the same supercell, same plane wave cutoff (13 Ry), and same \mathbf{k} -point sampling (Γ point) have been used

for both the $2 \times N$ and 2×1 systems for maximal cancellation of errors.

The atoms in the uppermost Ge layer can form symmetric (2×1), asymmetric $b(2 \times 1)$, or alternating asymmetric dimer structures, $p(2 \times 2)$ and $c(4 \times 2)$. The asymmetric dimers are called buckled dimers. In the buckled dimers the dangling bonds are hybridized, involving partial charge transfer from the lower atom to the higher one belonging to the same dimer. We have found that at one monolayer Ge coverage, in agreement with previous results [19,18], the energy per dimer of the asymmetric dimer $b(2 \times 1)$ structure is lower than that of the symmetric one by 0.2 eV (see Table 1). The bond length of the asymmetric dimer is slightly shorter than the bond length of the symmetric one, and the tilting angle is about 18° . Furthermore, the alternating asymmetric dimer $p(2 \times 2)$ structure is found to be energetically the most favorable. The tilting angles and bond lengths of the dimers in the $p(2 \times 2)$ and $b(2 \times 1)$ structures are very similar. The calculated dimer length (2.49 Å) is in good agreement with the observed one (2.51 ± 0.01 Å) [32]. Although it has not been fully established experimentally [32,33], theoretical calculations [34] predict that the alternating asymmetric dimer configuration is the most stable structure at single monolayer Ge coverage. For $n \geq 2$ ML, the results shown in Table 1 indicate that the local structural properties of the dimers have weak substrate dependence, and hardly change with the Ge thickness. We have not investigated the properties of the $c(4 \times 2)$ -like alternating dimer reconstruction because it would

require much larger supercells. Nevertheless, the energetic properties of the $c(4 \times 2)$ and the $p(2 \times 2)$ structures are expected to be very similar [13] because the interaction between the dimers of different dimer rows is relatively small. Therefore, we will use the $p(2 \times 2)$ alternating asymmetric dimer reconstruction in assessing the physical factors influencing the critical thickness. Another aspect beyond the scope of the present study is the intermixing of Ge and Si at the interface [9,15,17] within the present first-principles scheme. This restriction implies that the conclusions reached here are more relevant to growth conditions where intermixing is not a dominant factor in strain relief, as in the case where the growth temperature is not high.

We have also investigated the effect of the removal of a dimer on the geometrical structure and on the relaxation of the surface using the (2×8) reconstruction as an example. The missing dimer leads to substantial relaxation of the neighboring atoms. These distortions strongly depend on the Ge layer thickness (see Table 2) due to the large difference in the Ge–Ge and Ge–Si bond strengths. By increasing the number of Ge layers the distance between the first and second layer at the missing dimer location decreases to 0.45 Å from its bulk value of 1.35 Å. At the same time, the distance between the atoms next to the missing dimer (a and b in Fig. 1) increases. Table 2 lists the distances for the case of (2×8) reconstruction; the other $(2 \times N)$ reconstructions with N different from 8 have very similar tendency but with somewhat different magnitudes of relaxation.

Table 1

Structural and energetic properties of Ge dimers at the growth front of an Ge overlayer of varying thickness on Si(001), without considering the missing dimer reconstruction

Structure	Coverage	l_d (Å)	ϕ (deg)	E_d (eV)
(2×1)	1 ML	2.45	0	0
(2×1)	2 or more ML	2.48	0	0
$b(2 \times 1)$	1 ML	2.43	18	0.22
$b(2 \times 1)$	2 or more ML	2.44	19.4	0.41
$p(2 \times 2)$	1 ML	2.54	19.3	0.32
$p(2 \times 2)$	2 or more ML	2.54	21.4	0.48

l_d is the dimer bond length, ϕ is the buckling angle, and E_d is the dimer energy with respect to the symmetric (2×1) structure. The calculated bulk lattice constant is 5.39 Å for Si and 5.63 Å for Ge, in good agreement with the experimental values of 5.43 and 5.65 Å, respectively.

Table 2
Some geometrical properties of the rebonded missing dimer (2×8) structure

<i>n</i>	<i>b</i>	<i>a</i>	<i>c</i>
1	6.72	2.45	0.78
2	6.91	2.55	0.66
3	7.00	2.57	0.52
4	7.02	2.57	0.49
5	7.04	2.57	0.45

See Fig. 1 for definition of *a*, *b*, and *c*. All the distances are in Å, *n* is the number of Ge monolayers.

These results show that the lattice distortion and thus the strain relief is strongly influenced by the number of Ge monolayers and the missing dimers.

To determine the equilibrium film thickness, following Tersoff [21], we define the lower limit of the island formation energy to be equal to the energy per atom of the bulk unstrained Ge, $E_1 = \mu_{Ge}$. If the energy required per atom, E_n , is smaller than E_1 , then layer by layer growth is energetically favorable. Realizing that the three-dimensional islands are not strain free, we define the upper limit of the island formation energy by the energy per atom of the biaxially strained bulk Ge, $E_u = \mu'_{Ge}$. This upper bound is calculated by constraining the Ge lattice constant parallel to the surface to be equal to the Si lattice constant, but allowing relaxation in the perpendicular direction. In reality the energy per atom in the partially relaxed islands, E_i , should be intermediate between E_1 and E_u , $E_1 < E_i < E_u$. Three-dimensional island formation starts when the partially relaxed quantum dots have lower chemical potential than the atoms in the strained layer, $E_i < E_n$. In the intermediate region $E_1 < E_n < E_i$, where the films are not stable anymore and the quantum dots are not stable yet, various other mechanisms may appear depending on the growth conditions [35,36].

The energy of the Ge atoms in the $Ge_nSi(001)$ film terminated by symmetric dimers [(2×1) reconstruction] is plotted against the Ge layer thickness in Fig. 2. The figure shows that, if the (2×1) reconstruction of the Si(100) substrate would be preserved at the growth front of the Ge layer, island formation would be preferred after the first monolayer. The figure also shows that the asymmetric p(2×2) buckled reconstruction delays

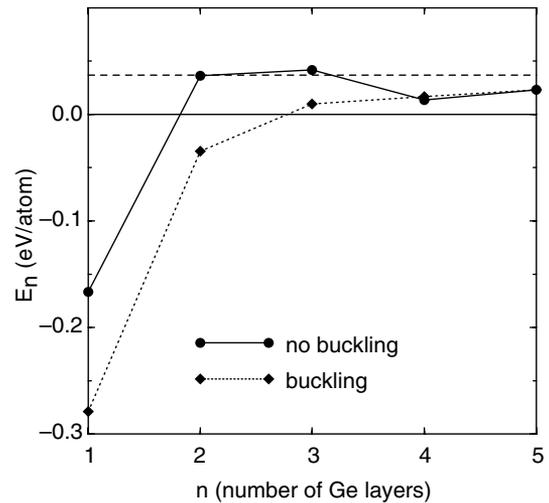


Fig. 2. Energy per atom E_n to add an n th layer of Ge on a Si(001) substrate. The reference energy is $E_1 = \mu_{Ge}$. The top Ge layer is terminated by a (2×1) dimer reconstruction. The dashed line is the chemical potential, E_u , when the lattice constant of Ge parallel to the surface is equal to the Si lattice constant, but relaxation is allowed in the perpendicular direction.

the island formation. In the case of buckled dimer reconstruction, island formation is preferred after two monolayers of Ge, but the critical thickness is still lower than the experimentally observed values of 3–4 layers. These results show that, within the accuracy of the present first-principles calculations, neither the inclusion of the symmetric 2×1 reconstruction alone nor proper consideration of dimer buckling is sufficient to result in the quantitatively correct critical thickness for SK growth of Ge on Si(001).

We next examine the effect of the 2×*N* reconstruction. The surface energy of a surface unit cell of the (2×*N*) superstructure is given by

$$\Omega_{Ge}(N, n) = \frac{(E_{total} - m_{Ge}\mu_{Ge} - m_{Si}\mu_{Si} - 2N\Omega_{Si})}{2(N-1)}, \quad (1)$$

where the chemical potentials μ_{Si} and μ_{Ge} are the energies per atom in the bulk equilibrium Si and Ge crystals, respectively, m_{Ge} and m_{Si} are the numbers of Ge and Si atoms, respectively, Ω_{Si} is the surface energy of the Si at the bottom of the slab, and E_{total} is the energy of the (2×*N*) reconstructed $Ge_nSi(100)$ system in the supercell. The

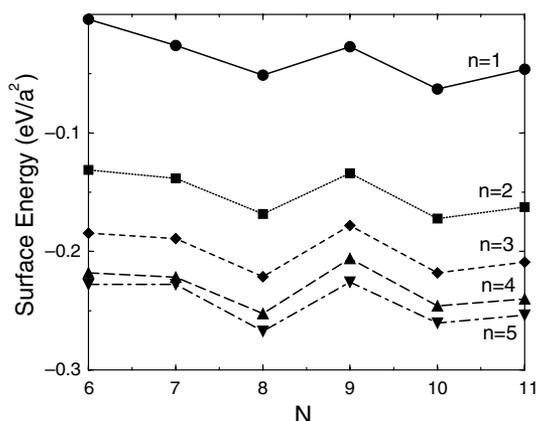


Fig. 3. Surface energy of the $(2 \times N)$ reconstructed $\text{Ge}_n\text{Si}(001)$ surfaces, relative to that for an ideal (2×1) reconstructed surface, plotted versus the period N (a is the lattice constant of the bulk Si).

calculated surface energy of the $(2 \times N)$ $\text{Ge}_n\text{Si}(100)$ surface relative to the ideal (2×1) one is presented in Fig. 3. The results show that removal of dimers in the top Ge Layer always leads to a more stable structure. The (2×8) reconstruction is found to be the most stable structure for $n = 3, 4, 5$ monolayers. In the case of $n = 1$ and 2 monolayers of Ge the (2×10) structure is the lowest in energy. The predicted $N = 8$ and $N = 10$ values are in good agreement with the experimental observations which show that the value of N is around 8–10 [9]. A Keating model [27] calculation which assumed $n = 3$ monolayer of Ge on the Si(001) substrate also predicts the $N = 8$ periodicity to be the energetically most favorable configuration [16]. The surface energy in Fig. 3 oscillates, higher for odd N , lower for even N . The physical reason for such oscillations is attributed to the different structural relaxations of the surface layers when different (odd or even) numbers of dimers are trapped between two missing dimer lines. Similar oscillation has also been found in classical molecular dynamics simulations of the system [22].

One has to be cautious when comparing the energies of surface structures having different stoichiometries. To minimize the errors caused by comparing systems with different numbers of Ge atoms, we have calculated the surface energy of the

$2 \times N$ reconstructed Ge film relative to the ideal 2×1 surface as suggested by Tersoff [21]. Alternative approaches to handle this delicate issue have also been proposed [20,14]. In [20] the reconstructions of different periodicity have been compared by using the energy change per Ge dimer in going from a perfect layer to a $2 \times N$ reconstructed one. This energy change is given by

$$\xi(N) = \frac{E_f(N) + E_m}{N - 1}. \quad (2)$$

Here, $E_f(N)$ is the formation energy of the fully relaxed missing dimers in the top layers with $2 \times N$ reconstruction (defined as the energy of the relaxed $2 \times N$ surface relative to the perfect 2×1 surface). E_m is the energy of the Ge dimer in the 2×1 reconstruction (calculated as the difference per Ge dimer between a system with 2×1 reconstruction and a system obtained by removing the top Ge layer and relaxing the system with 2×1 reconstruction). To cross check our predictions of the energetically most favorable structures, we have analyzed our calculations using this approach as well. The results of the two different analyses are in good qualitative agreement. Our calculations using this approach also agree very well with the results presented in [20] for the single monolayer case.

Fig. 4 shows that the $(2 \times N)$ reconstruction further delays the formation of three-dimensional islands up to a critical film thickness of 3–4 monolayers. The behavior of the chemical potential difference is very similar for all the cases where $N = 5$ –11, exceeding its bulk value at about 3–4 monolayers. The predicted critical film thickness is in good agreement with the experimental observations [2–4]. We note that, if the calculation is restricted to symmetric dimers but the $2 \times N$ symmetry is included, then three-dimensional island formation becomes favorable earlier, after only two monolayers. This finding, together with that shown in Fig. 2, clearly demonstrate that both the buckling and the missing dimer reconstruction are important in quantitative determination of the critical thickness.

In summary, the physical factors determining the critical thickness in Stranski–Krastanow growth of Ge on Si(001) have been investigated using total energy calculations within density

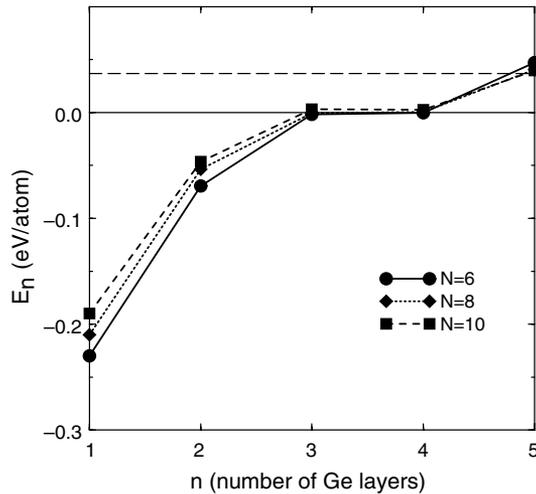


Fig. 4. Energy per atom, E_n , needed to add an n th layer of Ge on a Si(001) substrate. The reference energy is $E_1 = \mu_{\text{Ge}}$. The top Ge layer is terminated by a $(2 \times N)$ dimer reconstruction.

functional theory. We have shown that the effects of both the $(2 \times N)$ reconstruction and dimer buckling at the growth front have to be taken into account in order to determine h_c accurately. If the growth front is assumed to preserve the (2×1) reconstruction of the Si(001) substrate, the resulting h_c is lower than what has been observed experimentally. But with a proper inclusion of the $(2 \times N)$ reconstruction and dimer buckling as the first stress-relieving mechanism, three-dimensional islanding is delayed just to the experimental value of 3–4 monolayers.

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