

Adsorption of As on stepped Si(100): Resolution of the sublattice-orientation dilemma

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First-principles calculations are used to investigate the energetics of an As overlayer adsorbed on a stepped Si(100) surface. We show that the growth of As directly on top of the Si surface produces a metastable structure, while the replacement of the original top Si layer by As leads to a lower-energy configuration. In the latter case, the rearrangement of the surface is driven by the relaxation of stress by surface steps. This result explains the sublattice-orientation dilemma in GaAs-on-Si heteroepitaxy.

In epitaxial crystal growth the morphology of the starting surface, and its changes during the initial stages of growth, play a crucial role in determining the growth process itself. An interesting example of this is given by stepped Si(100) surfaces covered with As, the starting point for many systems of technological importance. Experimentally, it is observed that the adsorption of As on a stepped Si(100) surface can drastically rearrange the distribution of steps of the original surface.¹⁻⁴ These changes in surface morphology are controlled by different factors, including temperature, coverage of As, and the type and density of steps on the original surface. This has important consequences for the heteroepitaxial growth of GaAs and other related compounds on Si(100) substrates, where the first step in the growth process is the adsorption of As. The structure of the As-covered Si(100) surface [henceforth Si(100):As] determines many of the properties of the final epitaxial film.

In particular, it has been observed that GaAs grown epitaxially on Si(100) can have two orientations, related by a 90° rotation, with respect to the Si(100).⁵⁻⁸ This puzzling observation, the so-called sublattice-orientation (or allocation) dilemma,⁵ has not been understood. Naively, this could be explained if the first epilayer above the Si substrate could be selected to be a Ga or As layer. However, bond strength and other theoretical arguments,⁹ as well as experimental evidence,¹⁰ show this selective wetting of the Si(100) surface by As or Ga does not occur. A clue towards the solution of this problem is provided by recent experiments by Becker, Klitsner, and Vickers² (BKV). Using scanning tunneling microscopy (STM) they observe that an As overlayer grown on a stepped Si(100) surface can have two orientations, related by a 90° rotation, depending on growth temperature. More recent experiments confirm these observations.^{3,4}

In this paper we present results of theoretical calcula-

tions showing that As adsorbed on a vicinal Si(100) surface with double-layer steps either *can grow directly on top of the Si surface, or can rearrange the surface so as to replace the original top Si layer*. The former structure is metastable and results from growth at low temperatures. The latter has lower energy and occurs for growth at substrate temperatures where surface diffusion is activated. Replacing adsorption by substitution changes the sublattice of the diamond structure exposed at the surface, and corresponds to a 90° rotation of the crystal orientation about the surface normal. The resulting two configurations of the stepped Si(100):As surface are related by a 90° rotation, but otherwise differ only in the type of steps present at the surface. Their difference in energy, which we calculate from first principles, is related to the relaxation of stress at surface steps. This result explains the experiments of BKV, and shows that the rearrangement of steps upon As adsorption controls the orientation of an epitaxial GaAs film.

Both Si(100) (Refs. 11 and 12) and Si(100):As (Refs. 2 and 13) surfaces have 2×1 reconstructions where surface atoms (Si in the first case and As in the second) form dimers arranged in parallel rows. A simple picture for the adsorption of As on Si(100) is that the Si dimers break and As dimers are formed on top, perpendicular to the original Si dimers. This rotates the orientation of the surface dimers by 90°. A single-domain Si(100) 2×1 surface would result in a single-domain Si(100):As 1×2 surface. This 2×1 → 1×2 rotation was observed experimentally by Bringans *et al.*¹⁴ However, this picture could not explain the experiments of BKV nor other more recent experiments.^{3,4} The STM images obtained by BKV show that the orientation of the As dimers depends on the substrate temperature T_s during deposition. For low initial temperatures ($T_s \leq 400^\circ\text{C}$) the surface reconstruction rotates from 2×1 to 1×2, as the simple picture described

above would explain. However, at higher temperatures ($400^\circ\text{C} \leq T_s \leq 700^\circ\text{C}$) the surface reconstruction remains 2×1 after As adsorption, as if the As atoms *replaced* the top Si layer. BKV speculated that this might be related to the relaxation of stress at steps, and our calculations show that stress reduction is indeed the driving force for the rearrangement of the surface. For $T_s \geq 700^\circ\text{C}$, but below the temperature where As leaves the surface, mixtures of single-, double-, and multiple-layer steps are observed.^{2,4} Rotation of the As-dimers' orientation under different adsorption conditions is also observed when the coverage is less than one monolayer.³ The experimental picture has been very confusing, with different experiments in apparent contradiction.

We start by considering a single-domain Si(100) 2×1 surface, as typically used in growth experiments. These are obtained by using double-layer-stepped vicinal surfaces misoriented towards the [011] direction. Here we will restrict ourselves to the case where both the starting Si(100) and the final Si(100):As surfaces are double-layer stepped and the As coverage is one complete monolayer. These are the conditions relevant to typical growth conditions. On the clean Si(100) surface the Si dimers are parallel to the step edges.^{15,16} Double-layer steps with dimers perpendicular to the edge have much higher energy and are not observed. In principle, there are two types of double-layer steps on the Si(100):As surface. Type *A* where the As dimers are perpendicular to the step edge [Fig. 1(a)], and type *B* where the As dimers are parallel to the edges [Fig. 1(b)]. The reconstruction of the surface is 1×2 with type-*A* steps, and 2×1 with type-*B* steps. Figure 1 shows steps with a simple edge termination, where Si atoms are fourfold coordinated and As atoms are threefold coordinated with a doubly occupied lone-pair orbital. This is the same bonding configuration that passivates the flat Si(100):As surface. Other step reconstruction we considered, discussed later, were found to have higher energies.

To determine the relative stability of the 1×2 and 2×1 stepped Si(100):As surfaces, we compare the energies of

surfaces with type-*A* and type-*B* steps, respectively. We calculate total energies from first principles within the framework of density-functional theory in the local-density approximation, using norm-conserving pseudopotentials.¹⁷ We use a plane-wave basis with a cutoff energy of 8 Ry, pseudopotentials that are nonlocal in momentum space, and one \mathbf{k} point in the surface Brillouin zone for band-structure integrations. Surfaces are represented with slabs having a periodic array of steps and terraces. We used slabs with ten layers at their thinnest point, and with a separation between steps of 4.5 surface lattice constants (9° surface misorientation) or more. To relax electronic and ionic coordinates in the geometries studied, which include unit cells with up to 120 atoms, we used a recently developed conjugate-gradient method.¹⁸

The calculated energy difference between type-*A* and type-*B* steps of Si(100):As is

$$\lambda_A - \lambda_B = (200 \pm 20) \text{ meV}/a, \quad (1)$$

where λ_A and λ_B are the energies of type-*A* and type-*B* steps, respectively, and $a = 3.80 \text{ \AA}$ is the unit length along the step.¹⁹ This energy difference is large enough to change the surface from one step configuration to the other. Indeed, an energy difference of $\sim 110 \text{ meV}/a$ between single- and double-layer steps on vicinal Si(100) surfaces [for a surface misorientation larger than $\sim 3\text{--}4^\circ$ (Refs. 15 and 20)] drives the surface to have a majority of double-layer steps. It should be noted that the calculated step energies represent step-formation plus step-step-interaction energies, and the large size of these systems makes it prohibitive to increase the separation between steps and systematically separate these two contributions. However, it is assumed that the latter is approximately eliminated from the problem by taking energy differences between stepped surfaces, and that this difference does not change significantly with larger step separations.

An inspection of Fig. 1 shows no obvious electronic origin for the large energy difference between type-*A* and type-*B* steps. In both cases the Si and As atoms have ideal bonding configurations, and there is no particular atom or

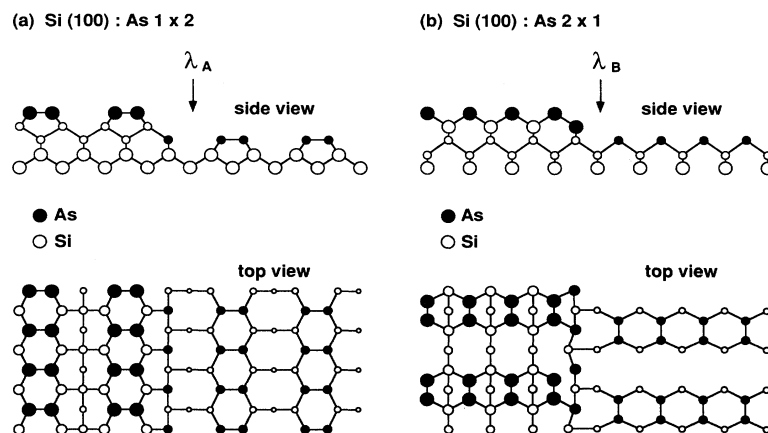


FIG. 1. Top and side views of double-layer steps on Si(100):As surfaces. (a) Type-*A* steps: As dimers perpendicular to the step edge. (b) Type-*B* steps: As dimers parallel to the step edge (edge relaxation is illustrated in the top view, see text). Larger circles on top views represent atoms closer to the surface. The two circle sizes on side views represent front and back $\{01\bar{1}\}$ planes.

bond whose relaxation or rehybridization might explain this result. We find that the energy difference is related to the relaxation of surface stress. The Si(100):As surface is under a large tensile stress, both parallel and perpendicular to the As dimers,^{21,22} that results from the tendency of the As atoms to form 90° bond angles and pull themselves up from the surface. This stress introduces a torque on surface steps, which allows a lateral contraction of the surface in the region near the steps, at the expense of introducing bulk strain.

Figure 2 shows the response of type-*A* and type-*B* steps to the tensile surface stress. Type-*A* steps lead to a large lateral contraction. This contraction is ~3.5% for the first layer of Si atoms, most of it within two lattice constants from the step edge (see inset in Fig. 2), and decays to zero deeper into the bulk. Similar but smaller (~0.7%) lateral contractions have been measured on trenches on As-terminated Ge(111) surfaces.²³ The surface As dimers, perpendicular to the step edge, are ~2% shorter than their calculated value on a flat Si(100):As surface. The relaxation type-*B* steps is different, even though the strength the tensile stress is calculated to be approximately equal both parallel and perpendicular to the surface dimers²¹ [the large energy difference in Eq. (1) is consistent with this]. Figure 2 shows that type-*B* steps undergo almost no contraction. Still, the relaxed coordinates suggest that the surface stress has been significantly reduced. Although we have not directly calculated the stress remaining on the stepped surface (such calculations are beyond current capabilities), the lack of strain in the subsurface of type-*B* steps provides evidence of a reduced surface stress. On flat Si(100):As subsurface strain forces a displacement of atoms from their ideal bulk positions. Atoms in the third and fourth layers that are underneath surface dimers shift up, and subsurface atoms

that are between dimer rows shift down. For type-*A* steps this distortion is further enhanced. On the other hand, for type-*B* steps the relaxed positions of the subsurface atoms are close to their ideal bulk value. This lack of strain in the subsurface for type-*B* steps is consistent with the reduction of surface stress.

Microscopically, type-*B* steps have a 2× periodicity along its edge, with two edge atoms per unit cell that are not equivalent [see Fig. 1(b), top view]. One is at the center of a row of dimers on the lower terrace, and the other is located between two of the dimer rows. The relaxation of the step is not uniform, with the second of these edge atoms contracting further than the first. This nonuniform contraction efficiently reduces the stress in the region near the edge, but introduces a minimum of bulk strain. On the other hand, the edge atoms on the type-*A* steps are equivalent and the contraction of the step is uniform. (We also used a 2× geometry for type-*A* steps to allow any possible relaxation.) Thus the energy difference in Eq. (1) is explained by the relative efficiency of type-*A* and type-*B* steps to reduce the tensile surface stress at the expense of bulk strain.

We have also considered reconstructions of both type-*A* and type-*B* steps with a rebonded edge, similar to those proposed by Chadi¹⁵ for steps on clean Si(100). In that case, a rebonded edge reduces the density of surface dangling bonds. On Si(100):As there are no dangling bonds and there is no driving force beyond the simple edge terminations of Fig. 1. Furthermore, a rebonded edge results in a stretched Si-As bond (2.58 Å) reducing the ability of the surface to contract. Our calculations show that for the rebonded edge terminations, type-*B* steps are lower in energy than type-*A* steps by 170 ± 20 meV/*a*, compared with the 200 ± 20 meV/*a* difference for the simple edge terminations of Fig. 1. Also, the rebonded edge reconstructions are each higher in energy than their simple edge versions by a value of order 1 eV/*a*, consistent with some observations.²

We now discuss the implications of these results to growth experiments. Our calculations show that the Si(100):As 1×2 surface with type-*A* steps is a metastable structure. This surface results from the growth of As directly on top of the initial Si surface. Experimentally, it is obtained by depositing As at low substrate temperatures, where the As overlayer caps the surface and freezes any surface mobility. However, if the temperature is high enough during As deposition to activate surface diffusion, the surface can then reach the lower-energy configuration with type-*B* steps. This explains the surprising observations of BKV. We note that this change in step type requires a large rearrangement of the surface, but similar step redistributions requiring mass transport across the surface have been observed when the initial Si surface has single-layer steps.^{1,3} The transformation from type-*A* to type-*B* steps may occur through other intermediate step configurations, including single-layer steps, and a complete conversion may not occur because of the large amount of mass transport required. This may further depend on the flux of As, and on whether As₂ or As₄ gas sources are used. Also, if surface diffusion is completely frozen, or defects pin the edges of steps, type-*A* steps with

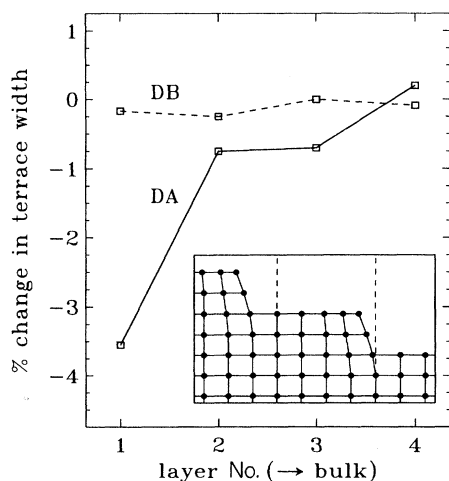


FIG. 2. Layer-by-layer lateral contraction for a surface with type-*A* (solid line) and type-*B* (dashed line) steps as a function of penetrate into the bulk. Layer No. 1 denotes the first layer of Si atoms below the surface As dimers. Inset: Schematic representation of lateral contraction for a surface under tensile stress, defined with respect to the ideal terrace width shown by the vertical dashed lines.

a rebonded edge may occur on terraces that originally had an odd number of lattice sites, and both types of type-*A* steps may appear on the low-temperature surface.² In principle, the surface with type-*B* steps ought to be reached from the surface with type-*A* steps upon annealing. However, As begins to leave the surface before this change occurs, and mixtures of steps with different heights are then observed.²⁻⁴

It should be noted that since the driving force for the rotation of the As surface dimers is the difference in energy between type-*A* and type-*B* steps, as the surface misorientation becomes smaller and the density of steps decreases, the energy gain by step rearrangement diminishes. On nearly flat surfaces only the $2 \times 1 \rightarrow 1 \times 2$ change in orientation of Si to As surface dimers should be observed.

For the heteroepitaxial growth of GaAs on Si(100), our results predict the sequence of orientations of the Si and then As surface dimers in the growth process $\text{Si}(100) \rightarrow \text{Si}(100):\text{As} \rightarrow \text{GaAs}/\text{Si}(100)$. For low initial substrate temperatures, the predicted sequence is $2 \times 1 \rightarrow 1 \times 2 \rightarrow 4 \times 2$, and for high initial temperatures the sequence is $2 \times 1 \rightarrow 2 \times 1 \rightarrow 2 \times 4$. The final orientation of the GaAs epilayer depends on whether the equilibrium Si(100):As

surface is attained, illustrating the interplay between kinetics and energetics in epitaxial crystal growth. This results explains the sublattice orientation dilemma, and brings into a coherent picture experiments that seemed to be in contradiction. Also, type-*A* and type-*B* steps on Si(100):As may promote different nucleation channels for growth,²⁴ leading to epitaxial films with different characteristics.

Finally, it would be interesting to repeat these investigations for adsorbates other than As. In a recent experiment²⁵ with Sb only a $2 \times 1 \rightarrow 1 \times 2$ rotation was observed, although the range of surface temperatures investigated was not large. Sb dimers have longer bonds than As dimers, and therefore the stress on this surface and the driving force for step rearrangement may be smaller than on the As-covered surface.

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