Growth of As overlayers on vicinal Si(100) surfaces

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(Received 29 January 1991; accepted 11 April 1991)

First-principles total-energy calculations are used to study the structure of As overlayers deposited on a stepped Si(100) surface. It is predicted that deposition of As at low substrate temperatures allows the As to grow directly on top of the Si surface, while growth at high temperatures results in a rearrangement of the surface as if the As replaced the original top Si layer. This result explains the sublattice orientation dilemma in GaAs-on-Si epitaxy.

It is experimentally observed that the adsorption of As on a stepped Si(100) surface can drastically rearrange the distribution of steps on the original surface.[1-4] These changes are controlled by different factors, like temperature, coverage of As, and the type and density of steps on the original surface. The change in morphology of the surface upon As deposition has important implications for the epitaxial growth of GaAs and related compounds on Si(100). Indeed, the adsorption of As is usually the first step in the growth process, and 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 a GaAs film grown on Si(100) can have two orientations related by a 90° rotation, depending on initial growth conditions.[5-8] This result, the so-called sublattice orientation dilemma,[5] can be naively understood by assuming that either As or Ga atoms form the first epilayer above the Si substrate, although bond strength and other theoretical arguments,[9] as well as experimental evidence,[10] suggest that selective wetting of the Si(100) surface by As or Ga cannot be achieved. Recent experiments by Becker, Klistner, and Vickers (BKV)[2] provide a clue towards the solution of this problem. Using scanning tunneling microscopy (STM) they observe that an As overlayer deposited on stepped Si(100) can have two configurations, related by a 90° rotation, depending on substrate temperature during the As deposition.

In this paper we use first-principles total-energy calculations to show that an As overlayer deposited on a vicinal Si(100) surface with double-layer steps can grow directly on top of the Si surface, or it can rearrange the surface as if the As replaced the top Si layer. The former leads to a metastable structure, while the latter results in a lower energy configuration. The final form of the surface depends on whether global equilibrium is attained. These two configurations of a stepped Si(100):As surface are related by a 90° rotation, but otherwise differ only in the type of steps present at the surface. We find that their difference in energy is related to the relaxation of surface stress by the steps at the expense of introducing bulk strain. These results explain the experiments of BKV, and show that the rearrangement of steps upon As adsorption controls the orientation of the final GaAs film. This brings into a coherent picture different experiments that appeared to be in contradiction, where both orientations of an As overlayer and a GaAs epitaxial film on Si(100) are observed.[1-8,14]

The Si(100)[11,12] and Si(100):As[2,13] surfaces both have a 2×1 reconstruction 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 new 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 2×1 Si(100) surface would then result in a Si(100):As surface with 1×2 surface periodicity. This $2\times1\rightarrow1\times2$ rotation in the orientation of the surface dimers was observed experimentally by Bringans *et al.*,[14] who used vicinal or off-axis surfaces with double-layer steps to obtain single-domain substrates. However, this picture for the adsorption of As seems to be inconsistent with the observations of BKV, and with the more recent experiments of Bringangs *et al.*[4] The STM images obtained by BKV show that the final orientation of the As dimers depends on the substrate temperature T_s during As deposition. For low values of T_s ($T_s\leqslant400$ °C), the reconstruction rotates from 2×1 to 1×2, as the simple picture described above would explain. However, at higher temperatures ($400\ °C\leqslant T_s\leqslant700$ °C) the surface reconstruction remains 2×1 after As adsorption, as if the As atoms replaced the top Si layer. For temperatures higher than ~700 °C mixtures of single, double and multilayer steps are observed.[2,3] For still higher temperatures, where the As coverage is a fraction of a monolayer, other surface morphologies result, with clean Si(100) facets and other not yet identified facets of the As-covered surface. In this latter case rotation of the As dimers under equilibrium adsorption conditions is also observed.[2] Here we will restrict ourselves to the case where both the starting Si(100) surface and the final Si(100):As surface have double-layer steps, and the As coverage is one full monolayer. This is the case of interest for heteroepitaxial crystal growth on Si(100). BKV speculated that the rearrangement of the surface upon As adsorption might be related to the strain induced by the dimerization of the surface and its interaction with surface steps. The calculations we present here show that the relaxation of surface stress at the steps is indeed the driving force.

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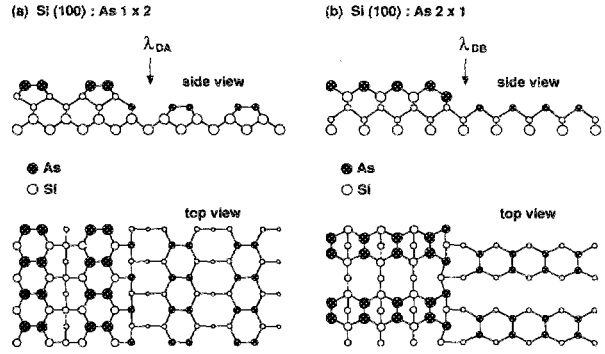

FIG. 1. Top and side views of double-layer steps on a Si(100):As surface. (a) Type DA steps: 1×2 surface with As dimers perpendicular to the step edge. (b) Type DB steps: 2×1 surface with As dimers parallel to the step edge. Solid and open circles represent As and Si atoms respectively. In side views circle sizes represent front and back $\{01\bar{1}\}$ planes, and in top views larger circles represent atoms closer to the surface. The nonuniform relaxation of atoms at the edge of type DB steps (see the text) is illustrated in the top view in (b).

We start by considering a vicinal or off-axis Si(100) surface misoriented towards the [011] direction, where the steps are double-layer high resulting in a single-domain 2×1 surface. The surface dimers on such a surface are oriented parallel to the step edge.[15,16] Double-layer steps where the dimers are perpendicular to the edges have much higher energy and are not observed. In principle, there are two types of double-layer steps on Si(100):As. Type DA steps, where the As dimers are perpendicular to the step [Fig. 1(a)], and type DB steps where the As dimers are parallel to the step [Fig. 1(b)]. Their energies (per unit length) will be denoted λ_{DA} and λ_{DB}, respectively. The reconstruction of the surface is 1×2 with DA steps, and 2×1 with DB steps. Note that the DA and DB steps shown in Fig. 1 have a simple edge termination. The Si atoms have fourfold coordination and the As atoms have threefold coordination with a doubly occupied lone-pair orbital. This is the same bonding configuration that passivates the Si(100):As surface.[13] (Other possible step reconstructions were considered, but were found to have higher energies; they will be discussed later.)

To determine the relative stability of the 1×2 and 2×1 configurations of the off-axis Si(100):As surface, the energy difference of stepped surfaces with DA and with DB steps is calculated. We calculate total-energies from first-principles within the framework of Density Functional Theory in the local density approximation, using norm-conserving pseudopotentials.[17] The calculations are implemented using a plane-wave basis with a cut-off energy of 8 Ryd, pseudopotentials that are nonlocal in momentum space, and one k point in the surface Brillouin zone. Surfaces are represented by a slab geometry with a periodic array of steps and terraces. At their thinnest point the slabs we used have ten layers, and the width of the terraces is 4.5 surface lattice constants or more. To relax electronic and ionic coordinates in the geometries studied, which included unit cells with up to 120 atoms, we use a recently developed conjugate gradient method.[18,19]

The calculated energy difference between DA and DB steps on Si(100):As is

$$\lambda_{DA}-\lambda_{DB}=200\ \text{meV}/a\ (\pm20), \tag{1}$$

where $a=3.80$ Å is the unit length along the step[20] (the calculated cubic lattice constant of Si, with the same approximations, is 5.38 Å). This represents a large energy difference for surface steps. Indeed, a step energy difference of ~100 meV/a is large enough to favor double-layer steps over single-layer steps on vicinal Si(100) surfaces with misorientations larger than $\sim2°$.[15,21] An inspection of the geometries of DA and DB steps (Fig. 1) reveals no obvious electronic origin for the large energy difference in Eq. (1). In both structures Si and As atoms have their ideal bonding configuration. Also, there is no particular atom or bond whose relaxation or rehybridization might explain this result.

We find that the large energy difference between DA and DB steps is related to the relaxation of surface stress. The dimer reconstruction results in a large tensile surface stress, both parallel and perpendicular to the surface As dimers.[22,23] This stress is caused by the tendency of the As surface atoms to form 90° bond angles. The presence of steps gives the surface the freedom to partially relax the tensile stress by contracting the surface area in the region near the steps. This change in surface area is made at the expense of introducing bulk strain. To investigate this behavior for DA and DB steps, we plot in Fig. 2 the width of a terraces between two neighboring steps for the relaxed configuration. We plot the changes in terrace width layer by layer, starting

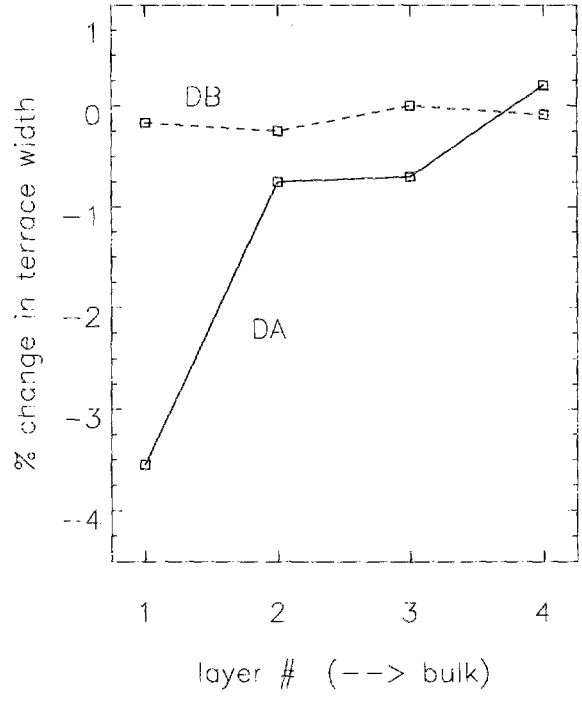

FIG. 2. Terrace width (percentage change with respect to the bulk value) of a stepped Si(100):As surface, given layer-by-layer, as a function of penetration into the bulk. Layer no. 1 denotes the first layer of Si atoms below the As surface dimers. Solid line: 1×2 surface with DA steps (As dimers perpendicular to step edge). Dashed line: 2×1 surface with DB steps (As dimers parallel to step edge).

from the first layer of Si atoms below the As surface dimers. DA steps exhibit the expected behavior for a surface under tension. The first layer of Si atoms contracts by a large percentage, $\sim 3.5\%$, and the change in terrace width from the ideal bulk value decays to zero by the fourth layer. Most of the layer contraction can be accounted for within a region of $2a$ from the step edge on the upper terrace. The As dimers, which are perpendicular to the step edge, are $\sim 2\%$ shorter than their value calculated on a flat Si(100):As surface.

The response of the surface with DB steps to the tensile surface stress is different. The strength of this tensile stress is approximately the same in the directions parallel and perpendicular to the dimers[22] (the large energy difference in Eq. (1) is consistent with this). Nevertheless, Fig. 2 shows that instead of the expected surface contraction, the terraces retain a width close to the ideal bulk value. However, even though there is no uniform contraction, the atomic relaxations suggest that the DB steps have efficiently reduced the stress at the surface. Although we have not directly calculated the stress remaining on this surface (such calculations for stepped surfaces with large unit cells are beyond current capabilities), the lack of strain in the subsurface gives evidence of this. On the Si(100):As surface the strain fields generated by the surface stress displace the atoms below the dimers from their ideal bulk positions. Atoms in the third and fourth layer are shifted down below the dimers, and up between dimers. This distortion is further enhanced in a surface with DA steps. However, in surfaces with DB steps these subsurface atoms are much closer to their ideal bulk-like positions. The lack of strain in the subsurface near DB steps is consistent with the reduction of surface stress.

Microscopically, a DB step has a $2\times$ unit cell along its edge. The two atoms in the unit cell at the edge of the step have a different bonding configuration with respect to the lower terrace [see Fig. 1(b), top view]. One of the edge atoms is at the beginning of a row of dimers, while the other is located between two rows of dimers. The step undergoes an undulatory relaxation where the second of these edge atoms contracts further than the first, as illustrated in Fig. 1(b). This nonuniform contraction of DB steps reduces the tensile surface stress in the region near the steps, but introduces a minimum of bulk strain. On the other hand, the edge atoms on the DA steps all have the same bonding configuration, and the relaxation is uniform. We checked this by using also a $2\times$ unit cell for DA steps to allow for any possible distortions. Fig. 2 then shows that the energy difference in Eq. (1) is related to the relative efficiency of DA and DB steps to reduce surface stress at the expense of bulk strain.

In Fig. 3 we show rebonded-edge reconstructions of both DA and DB type steps. These are similar to the reconstructions of steps on clean Si(100) considered by Chadi.[15] In that case, the rebonded edge reduces the density of dangling bonds at the surface. This however does not occur for Si(100):As, where there are no dangling bonds. There is no driving force for having a rebonded edge on steps on the As terminated surface. Furthermore, the rebonded edge leads to a stretched Si–As bond (2.58 Å) which limits the ability of the step to contract in response to the tensile surface stress. The calculated energies of the rebonded-edge steps are approximately 1 eV/a higher than the energy of the simple-edge steps shown in Fig. 1. Note that for DA steps, where the As dimers are perpendicular to the step, the simple-edge termination [Fig. 1(a)] requires terraces with even number of lattice sites, whereas the rebonded-edge termination [Fig. 3(a)] requires an odd number. If the substrate temperature during As deposition is low enough that surface diffusion is completely frozen, DA steps with a rebonded edge may occur on terraces that originally had an odd number of lattice sites, even though these steps have higher energy than DA steps with a simple edge. In the case of DB steps, the lower energy simple-edge termination can be accommodated on terraces with an even or odd number of lattice sites.

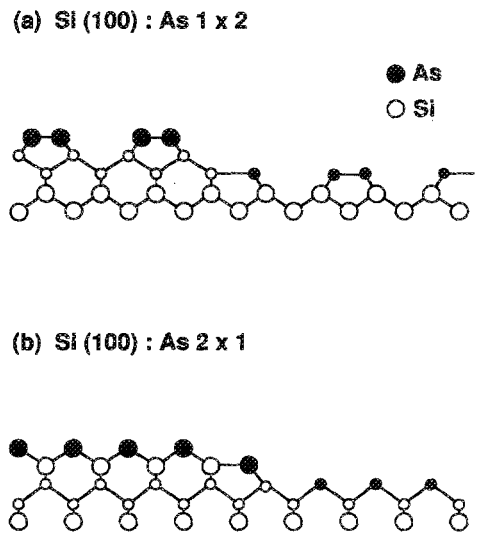

FIG. 3. Side view of (a) DA and (b) DB double-layer steps on Si(100):As with rebonded-edge termination.

Our calculations show that a double-stepped Si(100) 1×2 surface with DA steps is a metastable configuration of the surface. This is the structure that results from growing As directly on top of the Si surface. This surface can be obtained by growing at low substrate temperatures, when the As dimers cap the surface and freeze any surface mobility. On the other hand, if the substrate temperature is high enough to activate surface diffusion during the deposition of As, the surface can reach its lower energy configuration with DB steps. This change of the surface requires large mass transport across the surface, and it may happen that the conversion of DA to DB steps is not always complete. It is also possible that the crossover temperature between the growth of the stable and the metastable configurations depends on the intensity of As flux, and on whether As_2 or As_4 gas sources are used. We note however that similar large rearrangements of the surface have been observed when As is deposited on Si(100) surfaces with single-layer steps.[1] In principle, the surface should change from the metastable to the stable configuration by annealing. However, as the substrate temperature is raised the As begins to leave the surface and mixtures of steps of different heights are formed,[2,3] and also the As coverage falls below one monolayer.[3] This precludes the transition from the metastable 1×2 to the lower energy 2×1 double-stepped surface.

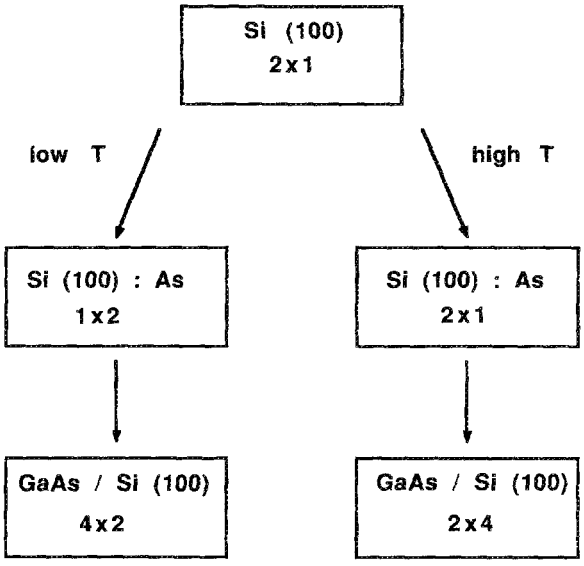

FIG. 4. Orientation of the surface dimers with respect to the Si(100) 2×1 substrate in the Si(100)→Si(100):As→GaAs/Si(100) growth process. The 2×4 and 4×2 periodicities of the GaAs film refer to the orientation of As surface dimers for the "2×4" As-terminated surface.

To summarize, we have shown that Si(100):As surface with double-layer steps has a stable and a metastable configuration. The former has DA type steps, and is obtained by initiating growth at low substrate temperatures. The latter has DB type steps and results from growth at higher temperatures. The orientation of the As surface dimers on these two configurations is related by 90°. This determines the sequence of orientations of the As surface dimers in the epitaxial growth of GaAs on double-stepped vicinal Si(100) surfaces, depending on initial growth temperature. The predicted orientation of the As dimers at different stages of the growth process is shown in Fig. 4. This figure explains the sublattice orientation dilemma in GaAs-on-Si epitaxy.

We acknowledge many useful and stimulating discussions with D. E. Aspnes, R. D. Meade, and G. W. Turner. This work was supported in part by the U.S. Joint Services Electronics Program Contract No. DAAL-03-86-K-0002, and the Office of Naval Research Contract No. N00014-86-K-0158.

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