Stabilities of Single-Layer and Bilayer Steps on Si(001) Surfaces

D. J. Chadi
Xerox Palo Alto Research Center, Palo Alto, California 94304
(Received 15 June 1987)

The formation energies of single- and double-layer steps on Si(001) surfaces were calculated. For each case, two configurations with surface dimerization axes normal or parallel to the step edge were examined. Single-layer steps are found to have the lowest formation energy. Bilayer steps become energetically more favorable on surfaces misoriented towards [110] or $[\bar{1}10]$ axes where low- and high-energy single-layer steps are forced to alternate with each other.

PACS numbers: 68.35.Bs, 68.35.Md, 82.65.Dp

The structure of stepped Si(001) surfaces has come under intensive study recently because of its importance in the heteroepitaxy of III-V semiconductors, particularly GaAs, on Si.[1-5] An important and surprising recent development has been the stabilization of double-layer steps and the elimination of single-layer steps on this surface. As a result, a major potential problem in the growth of III-V compounds on Si, i.e., antiphase disorder, has been circumvented. The disappearance of single-layer steps shows up most clearly in low-energy electron-diffraction (LEED) experiments where the normal two-domain pattern is replaced by a single-domain 2×1 pattern.[5-10] A slight tilt of the surface normal from the (001) direction towards the [110] or $[\bar{1}10]$ azimuths is apparently crucial in the stabilization of double layers, although a single-domain pattern has been reported on a nominally flat surface.[5]

The main purpose of this paper is to address the question of the relative stabilities of single- and double-layer steps on Si(001) surfaces. The formation energies of four different step configurations, assuming various types of reconstructions at step edges, were determined through semiempirical tight-binding–based total-energy calculations.[11] The results are used to analyze the effects of surface misorientation towards [110] and [010] azimuths on step height distributions. As shown below, the calculations provide a simple explanation of why single-layer steps are more commonly seen on "normal" (001) surfaces while double-layer steps are more favorable on tilted surfaces.

Two distinct types each of single-layer (S) and double-layer (D) steps, labeled in the following by S_A, S_B, D_A, and D_B, were examined. The subscripts denote whether the dimerization direction on an upper terrace near a step is normal (A) or parallel (B) to the step edge. An example of each of the four different configurations is shown in Figs. 1(a)–1(d). Ordered step arrays in a slab geometry were used in the calculations. Steps on "flat" surfaces (where they alternately raise and lower the terrace height leading to a zero net inclination) as well as on surfaces tilted towards the [110] axis were studied. The advantage of the use of a flat surface is that a single type of step configuration, e.g., S_A, instead of an alternating sequence of S_A and S_B steps can be examined at a given time, allowing a determination of the formation energy for each type of step.

The calculations of the step formation energies were carried out in two stages. In the first stage the energy differences between single- and double-layer steps were determined by the use of high-index vicinal surfaces.

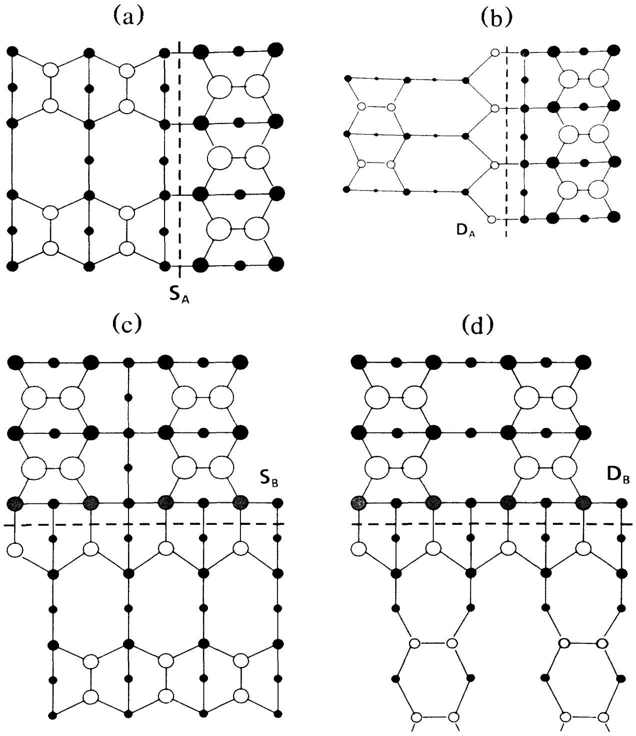

FIG. 1. (a)–(d) Top views of S_A, D_A, S_B, and D_B steps, respectively. The dimerization direction of the topmost atoms shown in Figs. 1–3 is along the $[\bar{1}10]$ direction. The dashed lines, which run parallel to $[\bar{1}10]$ or [110] axes, indicate the step positions. Open circles denote atoms with dangling bonds. Edge atoms (shaded circles) in (b)–(d) are rebonded, i.e., they form dimerlike bonds with lower terrace atoms. Larger circles are used for upper-terrace atoms. Only some sublayer atoms are shown for the sake of clarity. The figures are not drawn to scale. *All the dimers are asymmetric.*

Ordered step arrays on (001) surfaces inclined towards either the [110] or [$\bar{1}$10] axes give rise to high-index ($\bar{1}1n$) or ($11n$) surfaces. Vicinal (1,1,15) and ($\bar{1}$,1,15) surfaces with a tilt angle of 5.4° were used to examine the relative stabilities of double-layer D_A, D_B and single-layer S_A+S_B steps and to test various types of atomic reconstructions at the edge. The use of the same unit-cell dimensions and numbers of atomic planes in the slab calculations has the advantage of minimizing systematic errors[12] in the comparison of energies. The energy differences per unit length λ between single- and double-layer steps are calculated to be

$$\lambda(D_A)-[\lambda(S_A)+\lambda(S_B)]=+(0.38\ \mathrm{eV})/a, \tag{1}$$

and

$$\lambda(D_B)-[\lambda(S_A)+\lambda(S_B)]=-(0.11\ \mathrm{eV})/a, \tag{2}$$

where $a\simeq 3.85$ Å is the 1×1 surface lattice constant. These results also show that the double-layer step configuration D_A is significantly higher in energy than D_B. For each step the atomic structure shown in Fig. 1 is found to lead to the lowest formation energy. The atomic structures for S_B, D_A, and D_B steps involve a "rebonding" of the second-layer edge atoms (shaded circles), resulting in a dimerlike configuration. Simpler "nonbonded" edge structures such as that shown in Fig. 2 were also examined.

In the second part of the calculations, the formation energies $\lambda(S_A)$ and $\lambda(D_B)$ were individually determined by the consideration of ordered step arrays on "flat" (001) surfaces with 2×5 and 6×2 periodicities. The energies of the stepped surfaces were compared with those of the corresponding "ideally" dimerized surfaces with no steps to obtain the formation energies. The results from the two sets of calculations on vicinal and flat surfaces were then combined to evaluate the formation energies of all four types of steps. Since the atomic relaxations on (001) surfaces extend deeply into the bulk, at least four atomic planes were allowed to relax. A high degree of convergence towards the minimum-energy configuration was found to be important in the energy comparisons. For each surface over 100 iterations in a Hellmann-Feynman force-reduction process[11] were used in the optimization of atomic coordinates. The final results for the formation energies per unit length for the four types of steps shown in Fig. 1 are given by

$$\begin{aligned}\lambda(S_A)&\simeq(0.01\pm0.01\ \mathrm{eV})/a,\\ \lambda(S_B)&\simeq(0.15\pm0.03\ \mathrm{eV})/a,\end{aligned} \tag{3}$$

and

$$\begin{aligned}\lambda(D_A)&\simeq(0.54\pm0.10\ \mathrm{eV})/a,\\ \lambda(D_B)&\simeq(0.05\pm0.02\ \mathrm{eV})/a.\end{aligned} \tag{4}$$

The formation energies are relative to that of a fully relaxed Si(001) surface with an asymmetric dimer reconstruction.[13] The results of the calculations for each type of step are discussed in more detail below.

The single-layer step S_A [Fig. 1(a)] comes out to have, by far, the lowest formation energy because it is the only step which does not lead to large strains or to extra dangling bonds. It only causes a rotation of the dimerization axis by 90°. The formation energy is primarily the excess elastic strain energy associated with this rotation, which turns out to be small making it likely to occur on well-aligned (001) surfaces where two or more such steps can occur consecutively. Each step alternately raises or lowers the terrace height by one interplanar lattice spacing, so that on the average, the surface remains untilted. A preference for S_A steps should lead to smaller mean terrace widths along the dimerization direction than normal to it. For a tilted surface it is *not* possible to have only S_A steps. If such a step does occur then an S_B step is unavoidable across some boundary between terraces. It is primarily this feature which makes the elimination of single-layer steps from the annealed (001) surface possible. Scanning-tunneling-microscopy studies[14] of Si(001) and[15] Ge(001) surfaces reveal both S_A and S_B types of monatomic steps. The predicted low energy for S_A steps is consistent with the result of a recent analysis of reflection-high-energy electron-diffraction oscillations in Si which indicates that the preferred direction for island formation during growth is perpendicular to the dimerization axis of the topmost atomic layer.[16]

For each of the remaining types of steps several types of atomic reconstruction at the step edges were considered and the atomic coordinates were fully optimized. The "rebonded edge" atomic configurations for S_B, D_A, and D_B steps shown in Figs. 1(b)–1(d) were compared with simpler edge structures with no rebonding, as shown

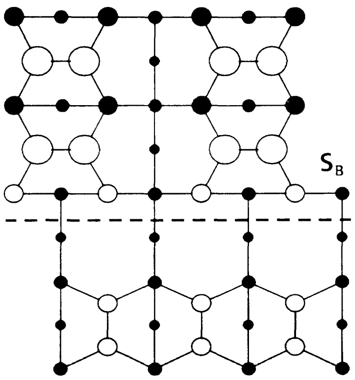

FIG. 2. Top view of a simple "nonbonded" edge geometry for S_B. Open circles denote atoms with dangling bonds. This structure is characterized by having a dangling bond on each second-layer edge atom and is not as energetically favorable as the "rebonded" atomic configuration in Fig. 1(c). A similar result was found for nonbonded D_A and D_B steps.

for S_B in Fig. 2, for example. These structures are found to be energetically less favorable by at least (0.16 ± 0.02 eV)/a than the corresponding rebonded structures in Fig. 1 despite bond-length strains of as large as 5% at the edge for the latter. For S_B-type steps in Si, scanning tunneling microscopy has provided evidence for both the rebonded [Fig. 1(c)] and simple (Fig. 2) edge configurations.[14] Since D_B and S_B have nearly the same optimal atomic configurations at the step edge [Figs. 1(c)–1(d)], the formation energy difference $\lambda(S_B)-\lambda(D_B)$ should be insensitive to the precise geometry at the step edge and is calculated to be nearly (0.1 eV)/a for the structures tested.

The orientation and stability of bilayer over monatomic steps on surfaces misoriented by a few degrees off the (001) axis towards the [110] direction are properly explained by Eqs. (1) and (2). The high energy of D_A relative to D_B steps is consistent with experimental observations[6-10] that when double-layer steps occur on annealed surfaces, they are always of the D_B-type orientation [Fig. 1(d)] with the surface dimerization axis parallel to the step edge. For surfaces tilted towards the [110] axis, the greater stability of bilayer D_B steps as compared with monatomic steps is consistent with Eq. (2). On such a misoriented surface it is not possible to have only the low-energy S_A-type single-layer step; instead, S_A and S_B steps have to alternate with each other. For a given tilt angle one can have either an S_A and an S_B step or a single D_B step per unit cell.[17] In this case Eq. (2) shows that the latter structure is energetically preferable. This is the same conclusion as that reached by Aspnes and Ihm[1] on the basis of a similar total-energy calculation. The energy difference in Eq. (2) is a factor of 2.5 larger than theirs because of the use of different atomic configurations at the step edge.[17] The high energy for D_A steps is also critical in stabilizing double-layer steps. If $\lambda(D_A)$ were as small as $\lambda(D_B)$ then a *mixture* of single- and double-layer steps, nearly degenerate energetically with double-layer D_B steps, could easily occur.

A missing dimer row on a (001) surface gives rise to a structure equivalent to two side-by-side D_B steps with unbonded edge atoms (similar to the situation for S_B shown in Fig. 2) running parallel to each other. Total-energy calculations with 4×4 unit cells show a repulsive step-step interaction of (0.13 eV)/a in this case as compared with the situation on (1,1,15) surface where they are well separated.

So far only results for steps oriented purely along [110] or [$\bar{1}$10] azimuths have been discussed. An interesting question is the degree to which the results change when the step edge runs in a direction intermediate between these two axes. The analysis presented below suggests that a bilayer step distribution may also be maintained on these surfaces for a relatively large range of step directions.

A simple way for the surface to accommodate a rotation of the step edge away from the [$\bar{1}$10] and towards the [110] direction is through the introduction of kinks (e.g., see Fig. 3) which change the propagation direction of the step. If only single-layer steps occur everywhere then they will be of types S_A and S_B as before. However, if the steps are bilayer in height then both D_B and the energetically unfavorable D_A steps are bound to occur. Figure 3 shows that exactly the same type of atomic reconstructions discussed above [Figs. 1(a) and 1(d)] can extend all the way across a kink. The relative lateral ordering of the dimers on the top and bottom terraces shown in Fig. 3, sometimes denoted[4] as R_+, is the one actually observed experimentally. An alternative orientation R_- where the lower dimers are shifted to the left by a 1×1 lattice constant gives rise to a higher dangling-bond density and is not energetically favorable. The two configurations are energetically equivalent in the absence of kinks and LEED patterns provide evidence for both orientations.[4,7] The fact that a kink does not introduce any major new bonding features at step edges suggests that the formation energy of a structure like that in Fig. 3 can be deduced from that of the constituent steps derived earlier. For a step edge propagating at an angle $0<\Phi<\frac{1}{4}\pi$ away from the [$\bar{1}$10] and towards the [110] direction the formation energies per unit length, λ_S and λ_D, for single- and double-layer steps are given by

$$\lambda_S=[\lambda(S_A)+\lambda(S_B)][1+\tan\Phi]\cos\Phi, \qquad (5)$$

and

$$\lambda_D=[\lambda(D_B)+\lambda(D_A)\tan\Phi]\cos\Phi. \qquad (6)$$

The above expressions represent an *average* of the ener-

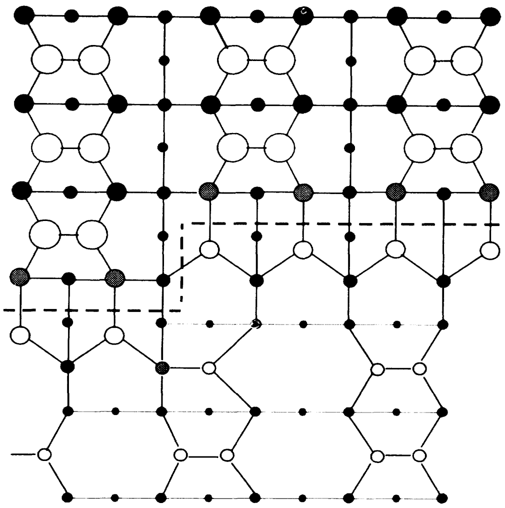

FIG. 3. Top view of a stepped surface with kinks. The atomic reconstructions at the kink are similar to those for bilayer D_A and D_B steps discussed in Figs. 1(b) and 1(d).

gies (per unit length) of the steps along the edges. For $\Phi=0$, the difference $\lambda_D-\lambda_S$ is the same as that given by Eq. (2). The above approximations are good in a low-kink-density regime, i.e., when the step lengths in the [110] and [$\bar{1}$10] directions are sufficiently long that the excess strain energy associated with kinks is much smaller than that arising from steps. Within this approximation, double-layer steps will be energetically more favorable than monatomic steps when

$$\tan\Phi < \frac{\lambda(S_A)+\lambda(S_B)-\lambda(D_B)}{\lambda(D_A)-\lambda(S_A)-\lambda(S_B)}. \qquad (7)$$

The use of the energy differences given in Eqs. (1) and (2) in Eq. (7) gives an upper limit of $\Phi_{\max}=16°$. The excess strain energy associated with kinks will tend to depress $\Phi_{\max}$; however, the possibility that a high-energy D_A step can break into an S_A and an S_B step should tend to increase it. A careful investigation of step-step interactions is necessary before $\Phi_{\max}$ can be more accurately determined. Nakayama, Tanishiro, and Takayanagi[4] have recently demonstrated by transmission electron diffraction and microscopy that the step heights do indeed remain bilayer for $\Phi<20°$ and become monolayer for larger angles. They show that if kinks were energetically favorable, then $\Phi_{\max}$ should be smaller than 26° on purely geometrical arguments. At this angle, kinks will occur every one lattice constant along the [110] and every *two* lattice constants along the [$\bar{1}$10] axis. In this high-kink-density regime, angles larger than 26° would interfere with dimer formation and would be naturally prohibited.

In summary, the formation energies of single and bilayer atomic-height steps on flat and misoriented Si(001) surfaces were calculated. Single-layer S_A-type steps are calculated to have the lowest formation energy. Two-layer D_B steps are found to be energetically favored over single-layer S_A+S_B steps. The calculated step energies lead to predictions of step and kink configurations in good agreement with all presently available experimental data.

I would like to thank Dr. D. K. Biegelsen, Dr. R. D. Bringans, and Dr. R. M. Martin for useful discussions and comments. This work is supported in part by the U.S. Office of Naval Research through Contract No. N00014-82-C-0244.

---

[1] D. E. Aspnes and J. Ihm, Phys. Rev. Lett. **57**, 3054 (1986).

[2] H. Kroemer, in *Heteroepitaxy on Silicon,* edited by J. C. C. Fan and J. M. Poate, MRS Symposia Proceedings Vol. 67 (Materials Research Society, Pittsburgh, 1986), p. 3.

[3] D. Saloner, J. A. Martin, M. C. Trinigides, D. E. Savage, C. E. Aumann, and M. G. Lagally, J. Appl. Phys. **61**, 2884 (1987); R. J. Fischer, N. C. Chand, W. F. Knopp, H. Morkoc, L. P. Erickson, and R. Youngman, Appl. Phys. Lett. **47**, 397 (1985).

[4] T. Nakayma, Y. Tanishiro, and K. Takayanagi, Jpn. J. Appl. Phys. Pt. 2 **26**, L280 (1987).

[5] S. Sakamoto and G. Hashiguchi, Jpn. J. Appl. Phys. Pt. 2 **25**, L78 (1986).

[6] M. Henzler and J. Clabes, Jpn. J. Appl. Phys. Suppl. Pt. 2 **2**, 389 (1974).

[7] R. Kaplan, Surf. Sci. **93**, 145 (1980).

[8] B. Z. Olshanetsky and V. I. Mashanov, Surf. Sci. **111**, 414 (1981).

[9] R. D. Bringans, R. I. G. Uhrberg, M. A. Olmstead, and R. Z. Bachrach, Phys. Rev. B **34**, 7447 (1986).

[10] Y. J. Chabal and K. Ragavachari, Phys. Rev. Lett. **53**, 282 (1984).

[11] D. J. Chadi, Phys. Rev. B **29**, 785 (1984).

[12] For example, errors arising from the use of different Brillouin-zone sampling points in the energy summations or from different atomic relaxations when inequivalent unit cells are used.

[13] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979).

[14] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986); R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985).

[15] J. A. Kubby, J. E. Griffith, R. S. Becker, and J. S. Vickers, to be published.

[16] T. Kawamura, T. Natori, T. Sakamoto, and P. A. Maksym, Surf. Sci. **181**, L171 (1987).

[17] For D_B, the rebonded geometry shown in Fig. 1(d) was calculated to have an energy lower by (0.3 eV)/a than the π-bonded-chain type of reconstruction suggested by Ihm and Aspnes (Ref. 1). The primary reasons for this are related to the strain energy associated with dimerized, *fourfold coordinated* atoms, directly under the π-bonded chains, the nonoptimal nature of the π-bonding interaction between the nearest-neighbor dangling bonds at the step edge as compared to that on the Si(111)-2×1 surface, and a higher dangling-bond density.