

***Ab Initio* Studies of the Diffusion Barriers at Single-Height Si(100) Steps**

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The binding sites and diffusion barriers for a Si adatom moving over a buckled Si(100) surface and single-height steps were calculated using *ab initio* methods. Surprisingly, the diffusion barriers may be sensitive to the local buckling of the dimers. The adatom binding energies and escape barriers at step edges depend strongly on the type of the step. The S_A step edge is a relatively poor sink for adatoms, while adatoms can be easily trapped at the S_B edge. These results explain the fast growth observed at the ends of the dimer rows.

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It has long been known that steps play a crucial role in the growth of semiconductor thin films [1]. At high temperatures, homoepitaxial growth takes place via the so-called “step flow” mechanism: Adatoms that have condensed on the flat terraces diffuse until they encounter a step edge, where they are more easily incorporated into the crystal. At intermediate temperatures, this mechanism is in competition with the nucleation, growth, and coalescence of two-dimensional islands. Growth at a step edge is determined by the rate at which adatoms can reach the step, either from the upper or from the lower terrace. In turn, these transition rates are governed by the activation energies for diffusive hops. The steps may introduce additional barriers at the edges. The origin of these barriers can be understood in terms of the specific geometry of the step edge. For example, consider the case of a close-packed surface with a step. An adatom approaching the step from the upper terrace must cross a region where it is relatively “far” away from the surface atoms, as it moves over the step edge. This is unfavorable and requires an additional activation energy. In contrast, atoms approaching from the lower terrace can always remain close to the substrate atoms, so that no additional barrier is expected. The presence or absence of such barriers has a crucial effect on the structures formed. Barriers at the steps determine the stability of step trains with respect to step bunching—the Schwoebel effect [2], and lead to an enhanced kinetic roughening of the surface [3]. The determination of the activation energies, along with the identification of the binding sites, is therefore an important problem in surface physics. In this Letter, we present the first such study of the Si(100) single-height steps, using *ab initio* methods.

The Si(100) surface is the most important surface for device applications. This surface reconstructs by forming dimers of (2×1) symmetry, which arrange themselves into parallel rows. It is now well established that at low temperatures the dimers buckle to form higher-order $p(2 \times 2)$ and $c(2 \times 4)$ reconstructions. The buckling is due to the transfer of an electron from the

lower to the upper atom of the dimer, which opens up a gap between the occupied and unoccupied states. At room temperatures and above, the buckled dimers oscillate in time and appear symmetric in scanning tunneling microscopy (STM) images [4]. Because of the structure of the bulk Si lattice, the orientation of the reconstruction is forced to alternate on terraces separated by single-height steps. The same orientation is, however, retained for terraces separated by double-height steps [5]. Following Chadi [6], S_A will denote the single-height steps with dimer rows on the upper terrace oriented parallel to the step edge, while S_B denotes a single-height step with the dimer rows on the upper terrace oriented perpendicular to the step edge. There are two types of S_B steps: with and without rebonded atoms on the lower ledge. Similarly, D_A and D_B will denote the corresponding double-height steps. To date, there has been considerable work on the energies of these steps [7], and the nature of the single- to double-height step transition [8].

Step flow takes place under nonequilibrium conditions of growth and evaporation. Theoretically, this problem has previously been addressed with classical molecular dynamics (MD) methods [9]. However, such studies rely on empirical potentials, whose accuracy is open to question, particularly when applied to problems where the energy differences may be subtle. Indeed, the optimal diffusion pathway on a flat Si(100) terrace, as predicted by *ab initio* [10] and classical MD simulations differ considerably [11]. Furthermore, recent total energy calculations show that there is considerable step-induced buckling of the dimers [12]. This is an electronic effect that is not reproduced by any of the classical models. All this underscores the need for a more accurate *ab initio* study of step flow on the Si(100) surface.

The binding sites and diffusion pathways on the Si(100) surface were investigated with the *ab initio* method of Car and Parrinello [13]. This method combines local density theory with nonlocal pseudopotentials and computes both

the electronic structure and atomic forces. For both the flat and stepped structures, a repeated slab geometry of seven layers of Si separated by a vacuum region of equal thickness was used. The kinetic energy cutoff for the plane waves was 8 Ry. The two bottom layers were kept fixed at the ideal bulk sites, and the bottom layer was saturated with H atoms. The in-plane unit cell period was 6×4 , resulting in approximately 168 Si and 48 H atoms. Because of the large unit cell size, the summations over the Brillouin zone were approximated by the Γ point. The codes were highly parallel and run at a speed of 2.3 Gflops on four processors of a Cray C-90. To study the growth properties of the single-height Si(100) steps, an adatom was placed on the surface of a structure, which was then fully relaxed. The "adiabatic trajectory" method was then used to determine the diffusion barriers [14]. In this method, the adatom is pushed over the surface with a small, constant speed (e.g., the thermal speed at 300 K) in a given direction, while monitoring the total energy. Note that the adatom is constrained in one direction only: It is free to move in the directions perpendicular to the applied force, thereby enabling the adatom to find the optimum path. All other atoms are relaxed continuously in response to the adatom motion [15]. The adiabatic trajectory method represents a viable and realistic alternative to the costly point determination of the potential energy surface. Tests estimate that the errors induced by this procedure are less than 0.1 eV. The paths investigated were the most important ones for growth, as identified by previous molecular dynamics simulations [9].

We first discuss the diffusion of a Si adatom over the flat Si(100) surface. This problem was previously addressed using *ab initio* methods for the case of *symmetric* dimers [10]. The predicted motion is highly anisotropic, with fast diffusion taking place over top of the dimers (barrier ~ 0.60 eV) and slow diffusion across the dimer rows (barrier ~ 1.0 eV). Experiments based on the island density also point to faster diffusion along dimer rows [16].

We have re-examined this problem for the case of a *buckled* Si(100) surface, with both $c(2 \times 4)$ and $p(2 \times 2)$ reconstructions. While the results are in general agreement with that of the symmetric surface, there are differences resulting from the effect of the adatom on the local tilting of the dimers. As in the symmetric case, the global minimum of the two surfaces is situated between the dimers [site *M* in Fig. 1(a)]. The adsorption energy is 3.42 eV, which is 66% of the binding energy of a bulk Si atom. It must be noted, however, that LDA methods are known to overestimate the binding energies so that the absolute values must be treated with some caution. For both the buckled surfaces, important secondary minima for both $p(2 \times 2)$ and $c(2 \times 4)$ are found near sites *A*, *B*, and *C*, with binding energies smaller by 0.5, 0.7, and 0.1 eV, respectively, than the binding at the global minimum. Note that the binding at site *A*, which is next to an atom with empty states

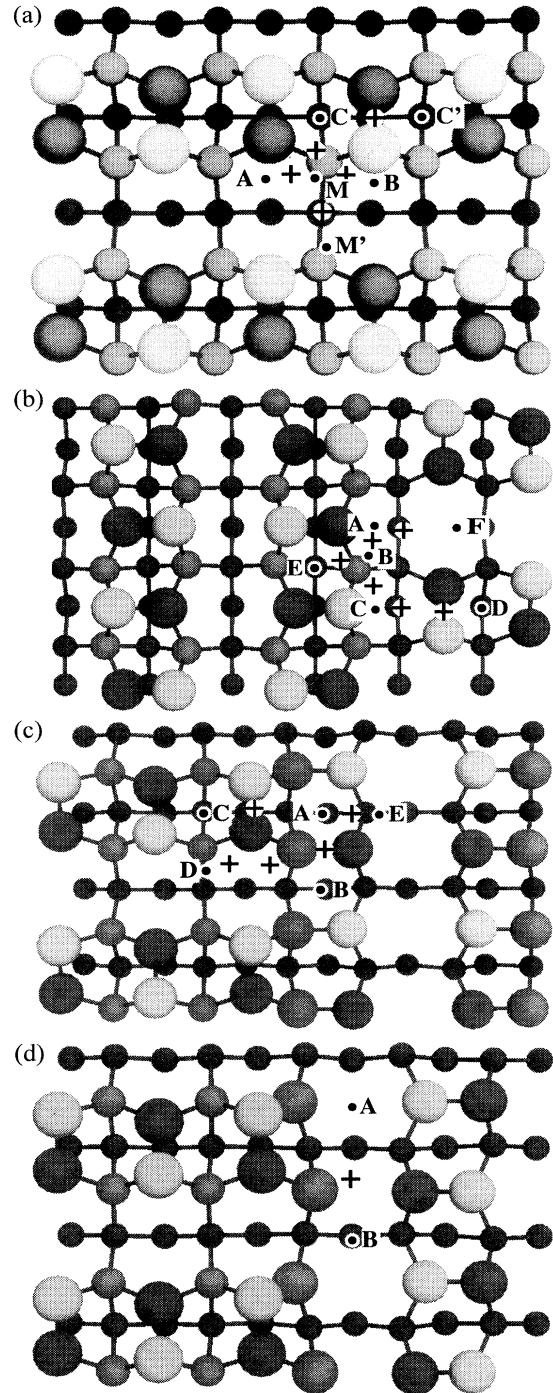


FIG. 1. Top view of (a) Si(100) surface with $p(2 \times 2)$ reconstruction; (b) S_A step edge; (c) rebonded S_B step edge; and (d) nonrebonded S_B edge. In the case of (a) the labels (*A*, *B*, *C*, etc.) indicate the approximate positions of the minima discussed in the text. The shading is such that lighter atoms indicate the "up" atom of a buckled dimer. The crosses give the approximate positions of the saddle points.

(the "down" atom of a dimer) is stronger than at site *B*, where the adatom is next to an "up" atom of a dimer.

Diffusion over the buckled Si(100) surface is still highly anisotropic. To move over top of the dimers ($M \rightarrow C \rightarrow C'$) the intervening barriers are 0.7 and 0.55 eV. To move across the valley separating dimer rows, $M \rightarrow M'$, the barrier is 0.95 eV. However, the barriers for motion in the channel separating the dimer rows are quite sensitive to the local tilting of the dimers, with a lower barrier being encountered if one moves past a down dimer. Thus, on the $p(2 \times 2)$ surface, the barrier is 0.75 eV for $M \rightarrow A$ and 1.1 eV for $M \rightarrow B$. This difference is quite substantial, indicating that the buckling of the dimers can have important effects on the diffusion barriers. A barrier of 0.75 eV is encountered for an adatom moving down the channel separating the dimer rows on a $c(2 \times 4)$ surface. Again, here the tilt of the dimers follows the motion of the adatom.

The anisotropy in the diffusion barriers for the different directions sets up natural diffusion pathways for step flow on the Si(100) surface. Thus, in the absence of any additional barriers and under the conditions of a constant external flux, one can expect the rate at which adatoms reach the S_A step edge from the lower terrace to be higher than the rate with which they come in from the upper terrace. The opposite will be true for the S_B step edge.

Figure 1(b) shows the structure of the S_A step, with the terraces having $c(2 \times 4)$ reconstructions [12]. Note that the geometry of the S_A step edge simply resembles that of a dimer row, as seen from the channel separating the dimer rows. There are three main binding sites (A , B , and C) at the lower step edge. Sites A and C are located in front of a down and an up atom of a buckled dimer, respectively. The corresponding binding energies are 0.35 and 0.6 eV less than that of the global minimum on the flat surface. Again, this difference is understood in terms of an enhanced bonding between the adatom and the empty states of the lower atom of a buckled dimer. The location of site B corresponds closely to that of a global minimum on the flat Si(100) surface, and indeed, the binding energies are essentially the same. Since the binding energy at the S_A step is close to that of the flat surface, we expect the S_A step to be a weak sink.

Motion at the S_A step resembles the motion of adatoms inside the channel separating the dimer rows. For $C \rightarrow B$, the activation energy required for a hop is 0.64 (1.25 eV for a reverse hop) and 0.6 eV for $B \rightarrow A$ (0.24 eV for the reverse path). For this path, in moving past a downwardly tilted dimer versus an upwardly tilted dimer, the activation energies differ by about 0.6 eV. This difference makes motion along the S_A step possible. Although the stability of the dimer buckling is enhanced at the step edges, the dimers will still oscillate at high temperatures on a time scale of picoseconds, so that the effective barrier to hopping will be considerably less than the relatively large 1.25 eV low temperature barrier. As the adatom moves past the step edge, we find that dimer can rotate and change its tilt. The energy cost for the rotation

is estimated by the difference between the energy of a uniformly buckled (2×1) surface and the energy of a $c(2 \times 4)$ or $p(2 \times 2)$ surface. This is 0.13 eV per dimer.

Adatoms can easily escape from the S_A step edge onto the lower terrace. Relatively small barriers of 0.35 and 0.60 eV are needed for jumps to positions between the dimer rows ($A \rightarrow F$) and overtop of the dimer rows ($C \rightarrow D$). The reverse motions require activation energies of 0.4 and 1.25 eV, respectively. Thus adatoms approaching the S_A step from the top of the dimers of the lower terrace have a good chance of being reflected. For atoms to escape onto the upper terrace ($B \rightarrow E$), the barrier is 0.85 eV. As an alternate pathway for movement onto the upper terrace, we have studied the replacement mechanism shown in Fig. 2. Here an adatom in front of a dimer on the lower terrace approaches a dimer directly and pushes itself over. This requires an energy of 1.2 eV if the adatom pushes a downwardly tilted dimer atom and 1.45 eV for an upwardly tilted dimer atom. In summary, because the binding at the S_A step is relatively weak and the barriers for adatoms to escape are low, we expect this step to be an inefficient sink.

The growth properties of the S_A step are to be contrasted with those of the rebonded S_B step [Fig. 1(c)]. At the S_B step edge, there are several local minima where the binding is significantly stronger than on the flat surface. Thus the potential energy well at sites A , B , and E are 0.35, 0.15, and 1.0 eV deeper than the global minimum on the flat surface [Fig. 1(c)]. The S_B step edge therefore acts as a strong sink for adatoms.

Most of the adatoms will reach the S_B step edge from the upper terrace. Adatoms coming into the step edge from over the top of the dimer rows of the upper terrace cross a barrier of 0.85 eV, while a barrier of only 0.70 eV is encountered if the adatom comes in from the channel separating the dimer rows [17]. An activation energy of more than 1.00 eV is required for adatoms to enter from the lower terrace. To escape onto the upper terrace

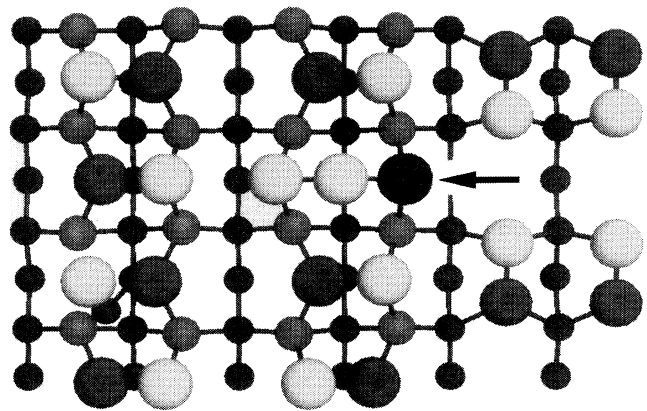


FIG. 2. Atomic configuration as an adatom approaches the S_A step edge from the lower terrace. The adatom and its path of approach is marked by the arrow.

requires 1.1 eV for the hop $A \rightarrow C$ and 0.7 eV for the hop $B \rightarrow D$. In contrast to the S_A step edge, the activation barrier for adatoms to escape from the S_B step edge is thus significantly higher, so that the adatoms are effectively localized at the S_B step edge.

Facilitating the growth at the S_B step edge is a relatively low activation barrier for diffusion over the top of the rebonded dimer atoms. We compute this to be 0.5 eV, so that adatoms will be able to find each other fairly rapidly and nucleate a kink site leading to a much rougher step edge. In contrast to diffusion at the S_A step edge, the adatom seems to have little effect on the tilting of the dimers at the S_B edge. This is due to the fact that the optimum path over the top of the rebonded atoms is relatively far away from the dimers at the upper step edge. Growth at a rebonded S_B step edge leads to a nonrebonded step edge [Fig. 1(d)]. Each atom terminating this edge has a dangling bond. Surprisingly, the minimum at this step edge (along path $A \rightarrow B$) is only slightly deeper (~ 0.10 eV) than the global minimum on the flat terrace. This result differs substantially from that obtained with classical MD simulations, where a deep potential energy well was observed. The barrier for diffusion along the nonrebonded S_B step edge is 0.65 eV.

That growth at the rebonded S_B step edge is much faster than at the S_A step edge has been confirmed by a number of experimental studies [18]. It also explains the highly asymmetric shapes of islands [19] that form on the flat Si(100) surface: fast diffusion directs the adatoms to the edges of the islands that resemble the S_A step edge. From there, adatoms are directed to the ends of the dimer rows by either moving alongside the edge of the island or over the top of the dimer rows. At the end of a dimer row the stronger binding localizes the atoms until another adatom comes along and growth of the dimer string can occur.

In summary, using *ab initio* simulations we have investigated the motion of an adatom over the flat Si(100) surface with both $p(2 \times 2)$ and $c(2 \times 4)$ reconstructions, as well as near the S_A and rebonded S_B steps. Surprisingly, the activation energies for the diffusive hops may be strongly influenced by the tilt of the dimers. The diffusion over the flat Si(100) surface is anisotropic, with fast diffusion taking place over the top of the dimers. Because of this anisotropy, most adatoms reach the S_A ledge from the lower terrace. In fact, there exists a pathway in which the adatom can approach the step edge without encountering any addition barriers. The S_A step edge is shown to be a weak sink for adatoms both due to the binding energies being comparable to that on the flat surface and low escape barriers. Movement to the higher terrace by a replacement mechanism is energetically unfavorable. Adatoms preferentially approach the S_B step edge from the upper terrace, encountering small additional barriers to cross the edge. This step edge is a strong sink, due to the substantial binding energy for the adatoms. Diffusion along both step edges may be faster than on the flat surface.

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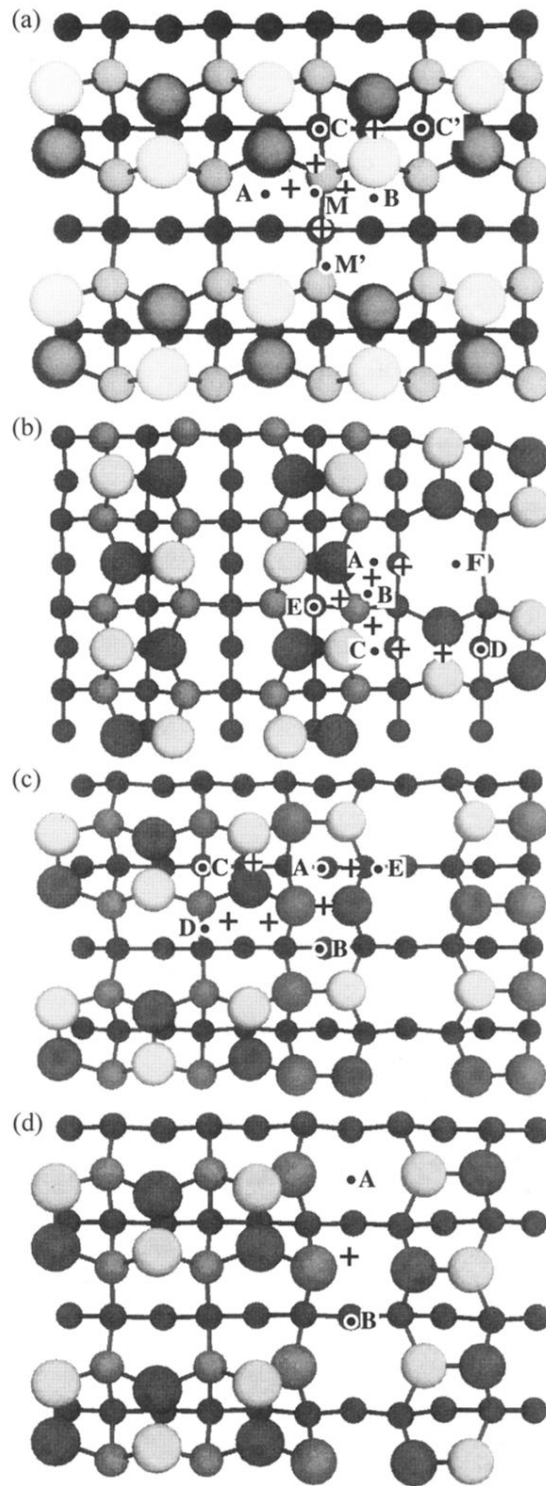


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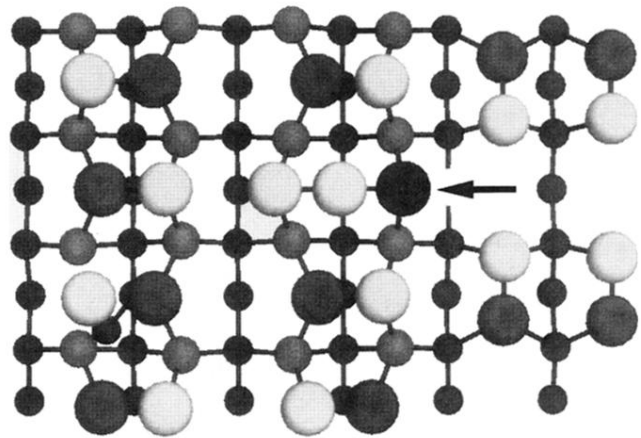


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