Diffusion Mechanism of Si Adatoms on a Double-Layer Stepped Si(001) Surface

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Using the \textit{ab initio} molecular dynamics approach we investigate the diffusion mechanism of Si adatoms on a rebonded and a nonrebonded double-layer stepped Si(001) surface. The rebonded $D_B$ step shows two Schwoebel barriers, whereas the nonrebonded step reveals a single barrier. This is due to the severe tensile strain on the surface layers parallel to the dimer row near the rebonded step edge. Adatom-step interaction is more favorable on a nonrebonded step than on a rebonded one near the ascending step. Several pathways for diffusion of an ad-dimer to the rebonded step edge from an upper terrace are examined. We find that the exchange and crossing-over processes are favored over the rolling-over process.

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The structure of a stepped Si(001) surface has been studied intensively, not only because of its technological importance in the homo- and heteroepitaxial processes, but also because of the rich variety of structures that it exhibits [1–3]. A flat Si(001) surface is known to reconstruct with an asymmetric dimer. Slightly miscut surfaces lead to the formation of steps and are of technologically great interest for the possibility that they offer to allow regular crystal growth. The steps can be single (S) or double (D) layered, and the dimer row of an upper terrace can align either parallel (A) or perpendicular (B) to the step edge [4]. The structure and the diffusion mechanism on a monolayer step have been experimentally studied by scanning tunneling microscope (STM) measurements [5–10] and by various theoretical models [11–15]. The double-layer stepped surface can be generated when the miscut angle is greater than 2° or when half a monolayer of Si atoms is deposited on a single layered step [5]. Additional interest in the $D_B$ step is generated by the fact that Ge islands on Si(001) surfaces form with \{311\} facets, which can be described as a succession of $D_B$ steps [16,17]. Yet, in spite of its technological relevance, the local structure of the $D_B$ step is little known. Even less understood is the issue on the kinetics at the $D_B$ step, which is crucial for the growth mechanism.

It is well known that an adatom at the edge of a step has to overcome an additional energy barrier, called Schwoebel barrier ($E_S$), before joining the step edge [18]. $E_S$ has been intensively studied on metal surfaces by experiments [19,20]. In contrast, $E_F$ is much less known in the semiconductor surfaces, and the diffusion mechanism is far from being clearly understood.

In this Letter, we make a stride in this direction by using \textit{ab initio} molecular dynamics (MD). Specifically, we study the $D_B$ structure obtained by cutting the Si(001) surface with a plane misoriented by 9° in the [110] direction. Two types of steps, rebonded and nonrebonded ones, have been suggested [4]. The former has lower energy and leads to larger atomic relaxation near the step edge. We find that $E_S$ is rather different in two cases. In particular, $E_S$ exhibits a complex two humped structure in the rebonded step, as a consequence of large surface relaxation. We also study the migration mechanism of step propagation by moving a dimer across the step edge along different pathways, and we are able to discard a number of possible mechanisms.

In this calculation the surface is simulated by periodically repeated slabs of Si atoms in which six atomic layers are included, with the bottom surface terminated by hydrogens and the top surface followed by a vacuum region of 8 Å. We have chosen a triclinic supercell with lattice vectors $\hat{a}$ ($\sqrt{2}$, 0, 0), $\hat{b}$ ($-\sqrt{2}/4$, $9\sqrt{2}/4$, 1/2), and $\hat{c}$ ($\sqrt{2}/4$, $-\sqrt{2}/4$, 3/2) in units of the lattice constant of bulk Si. This cell includes 54 Si atoms and 18 H atoms. In this way, the number of layers at upper and lower terraces is kept equivalent in order to prevent any unnecessary effects on both terraces. This unusual periodic boundary condition is necessary to simulate the $D_B$ with a limited number of atoms. The cell dimension is $l = 17.278$ Å in the [110] direction. Given that the step height is $h = 2.715$ Å we get a possible misorientation angle of $\gamma = \tan^{-1}(h/l) = 9°$.

Our calculations have been performed using the Car-Parrinello approach [21]. The interaction between ionic cores and valence electrons was described by a fully nonlocal pseudopotential with $s$-only nonlocality. We used a plane-wave basis set with a typical cutoff kinetic energy of 8 Ry and Bloch functions only at the $\Gamma$ point in the surface Brillouin zone of the supercell. We started from an ideally (unreconstructed) stepped Si(001) surface. In addition to the terminating H atoms, we kept fixed two Si layers at the bottom. In order to test the convergence of the cutoff we estimated the energy difference between transient pathways to be approximately 0.1 eV with larger cutoff [22]. We first searched for the electron energy...
minimization using a steepest descent approach. In order
to move ions we used the fast relaxation scheme where the
ion is accelerated only when the velocity and the
force have the same direction. The remaining forces
on the surface atoms were less than $5.0 \times 10^{-7}$ Ry/Å
in optimized geometries. The energy was converged to
$0.5 \times 10^{-5}$ Ry.

Figure 1(a) shows the rebonded $D_B$ step which is ob-
tained by relaxing an ideally stepped surface where each
terrace reveals the

tained by relaxing an ideally stepped surface where each
terrace. Because of the periodic boundary con-
dition, the $d_3$ dimer is a neighbor of $d_1$. The buckling
($\Delta z$) and bond length of dimers ($d_2$ and $d_3$) close to the
edge are much reduced from values in the $p(2 \times 2)$ sur-
face. The effect on $d_1$, which sits on the middle of the
terrace, is smaller and the $\Delta z = 0.52$ Å is closer to the
value of 0.69 Å in the flat Si(001) surface [23]. We ex-
pect that for smaller miscut angles and therefore larger ter-
races, the buckling in the middle of the terrace is 0.69 Å,
as in the $p(2 \times 2)$ flat surface. In the step region re-
bonding leads to bond lengths of 2.43 and 2.45 Å. This
amounts to a 4% strain relative to the bulk value. The
total energy gain associated with the formation of

In order to generate the nonrebonded $D_B$ step, we add
two more atoms near the rebonded step edge as shown in
Fig. 1(b). Buckling in this surface is closer to the ideal
one with $d_1$, already equal to the flat surface value of
0.69 Å [23,24]. It is interesting to examine the bond angle
distortion near the step edge. The bond angle $\alpha$ which is
close to the down atom of the dimer $d_4$ is 87°, whereas
the $\beta$ which is close to the up atom of the dimer $d_1$ is
120°, as a consequence of the dehybridization from $sp^2$ to
$sp^2 + p$, similarly to what has been observed in defective

[25] and an ideally dimerized [26] Si(001) surfaces, and
even in amorphous Si network [27].

The kinetics on an ideally dimerized Si(001) surface is
governed by an anisotropic diffusion at moderate tempera-
tures [28–30]. However, the kinetics near the step edge
will be different from that on an ideally dimerized surface.
In order to understand the diffusion process of Si adatom
on the $D_B$ step, we calculate the diffusion barrier near the
step edge. Figure 2 shows the potential profile and the cor-
responding top views near the rebonded and nonrebonded
step edges for a diffusing Si adatom. In this calculation,
we keep the $y$ ([110]) coordinate of the adatom fixed and
fully relax the rest atoms relative to all other degrees of
freedom, except the two Si layers and H layer at the bot-
tom as usual. The potential profile near the step edge is
quite different from that of an ideally dimerized surface.
For instance, the local minimum $H$, which is located at the
center of two dimers for an ideal surface, is shifted to $H_1'$
and $H_2'$ near the step edge. The local barrier $D$, which is
located at the middle of the dimer atoms for an ideal surface
[28], is also shifted to $D'$ close to the $H$'. These unusual
shifts are due to the rebonded step edge which has stretched
dimers of $d_1$ and $d_2$ to the left, as shown in Fig. 2. The poten-
tial profile of the lower terrace, where such distortions
are absent, does not reveal a significant change. As the
Si adatom passes through the middle of dimers of $d_1$ and

![FIG. 1. The fully relaxed geometries of (a) the rebonded and
(b) the nonrebonded $D_B$ steps. The values in parentheses are
the bucklings of the dimer. All lengths are in units of Å.](image)

![FIG. 2. The potential profiles and the corresponding pathways
(top view). The circles (squares) indicate the energies of the
rebonded (nonrebonded) structures. The lengths along [110]
and [110] directions are in units of Å. The $E_{B1}$ and $E_{B2}$ are
the first and the second Schwoebel barrier, respectively. The
$E_{ES}$ is defined with respect to the diffusion barrier of the flat
surface.](image)
$d_2$, the buckling disappears due to the charge transfer from the adatom to the down atom of the dimer. Another local minimum ($H_0^2$) exists to the left of the dimer $d_2$ and has the similar origin. The height of the barrier is reached out at point $B$ where the adatom can make only weak bonds (2.64 and 2.56 Å) with sublayer atoms and involves larger angular distortions.

The surface activation barrier $E_{SD}$ at the edge of the lower terrace is 0.25 eV, slightly lower than that (0.35 eV) of the ideal $p(2 \times 2)$ surface. However, the shape of the potential profile is very similar to that of the ideal surface. We note here that two local minima ($H_0^1$ and $H_0^2$) appear at the upper terrace near the rebonded step edge. This gives rise to the unusual appearance of two Schwoebel barriers of energy $E_{S1}$ (0.3 eV) and $E_{S2}$ (0.65 eV). Total barrier height of 0.95 eV will dominate the kinetic rate and is considerably larger than typical values of $\sim$0.1–0.2 eV on metal surfaces [20]. (This is not surprising, given the fact that here a distortion of covalent bonds is involved.) This large Schwoebel barrier will delay the step-adatom reaction from an upper terrace. Having in mind future applications to heteroepitaxial growth we have calculated the potential profile for a Ge adatom. The results are similar to the diffusion of a Si adatom, although the Schwoebel barrier height is reduced to 0.63 eV.

We also calculate the potential profile of the nonrebonded step edge, as shown in Fig. 2(a). Unlike the complicated potential profile of the rebonded step, the nonrebonded step reveals a relatively simple potential profile. One notes that the dimers of the upper terrace near the nonrebonded step edge are not stretched at all to the left. Thus the potential profile at $H$ and $D$ is very similar to that of the ideal surface, and only one Schwoebel barrier appears. The height of $E_S$ in the nonrebonded step is similar to that in the rebonded one. We find the step-adatom interaction near the ascending step to be stronger in the nonrebonded step due to the larger diffusion barrier (2.0 eV) than that (1.6 eV) in the rebonded one. This may cause the instability that leads to the mound formation [31]. The energy to remove the adatom to the lower terrace from the step sink is 0.65 eV, whereas the step sinks occur in different positions for both types of steps, in good contrast with the experimental value of 1.3 eV in the single-layer step [7].

We now study the diffusion mechanism of an ad-dimer at the upper terrace of the rebonded $D_B$ step. At moderate temperature and a high flow rate during the molecular beam epitaxial growth, a single adatom may easily diffuse to the step edge and thus have high probability to form a dimer [32] before reaching the step sink. Therefore, it is worthwhile to investigate the ad-dimer diffusion mechanism. We generate the potential energy profile, as before, by using a constraint minimization method.

The adsorption energy of the ad-dimer placed parallel to the surface dimer on the dimer row, as shown in Fig. 3 [step (i) of path I], is 3.2 eV/atom, revealing relatively strong adsorption [33]. We first look at diffusion pathways of the ad-dimer along the parallel axis to the $x$ direction. This is achieved by constraining the ad-dimer to have the same $y$ coordinates. We searched for paths I–III as described in Fig. 3(a). Although allowed to relax in the $x$ direction by our constraints, the ad-dimer did not exhibit a tendency to dissociate even in the energetically most unfavorable configurations [34]. We also tried the ad-dimer to roll aside in the trough as shown in path II, giving relatively lower activation barrier. In this case, one of the ad-dimers was stabilized by having more neighbors with subsurface atoms as shown in step (iv). We then tried an exchange (or pushing-out) pathway where the ad-dimer pushes out the surface dimer at the edge as shown in path III. Since less bond breaking is involved in this pathway, the energy cost is less too. The potential profile in Fig. 3(b) shows that path III is the most likely.
We also tried a different configuration in which we aligned the ad-dimer along the direction of the dimer row. The constraint here was to fix the y coordinate at one (front) of the ad-dimer. No bond breaking of the ad-dimer was observed. The energy of step (i) in path IV is larger by 0.02 eV than step (i) in path I, comparable to the energy difference of 0.01 eV on a flat surface [15]. This energy difference is indistinguishable within the accuracy limit of our calculations. In this case, rotation of the ad-dimer is allowed, but no rotation was observed due to the existence of the rotational barrier. Rotation from one to another configuration requires the barrier of 0.7 eV as observed on a flat surface by the STM measurements [9]. Therefore, we expect this rotation to occur at moderate temperature, and thus path IV may appear to be competitive with path III. It is also observed that absorption energies are very similar to each other for the ad-dimer located both parallel and perpendicular to the direction of the dimer row, and therefore both pathways have to be considered in a description of the ad-dimer diffusion on this surface. The diffusion barriers of the exchange and crossing-over processes are 1.55 and 1.74 eV on DB step, respectively, in good contrast with the diffusion barrier (1.45 eV) of an ad-dimer diffusing along the dimer row on a flat surface [14]. This may suggest that the diffusion of an ad-dimer does not require a large Schwoebel barrier at the step edge unlike the diffusion of a single adatom.

In summary, we have studied the diffusion mechanism on the $D_B$ step on the Si(001) surface using the ab initio MD method. We have discussed the equilibrium structures of the rebonded and the nonrebonded steps in detail. We have found that the rebonded step reveals double $E_S$ (0.95 eV), whereas the nonrebonded step shows a single barrier with similar barrier height. The difference is due to the severe tensile strain on surface layers near the rebonded step edge. The detailed pathways of various diffusion processes of a dimer have been examined. We found that the exchange and the crossing-over processes are favored over the rolling-over process.

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[17] Use of larger kinetic energy cutoff (10 Ry) changed the total energy of the system by 0.4 eV/atom, and the changes of the bond length were negligible compared to those with smaller cutoff (8 Ry). The relevant quantity is rather the energy difference between transient pathways of adatom, which was estimated to be 0.08 eV. We have also done the convergence test for the number of layers and the vacuum size, resulting in bond length changes to be less than 1%.
[29] The binding energy of an isolated Si$_2$ dimer is 2.4 eV, stable enough to sustain a dimer at moderate growth temperature.