Binding and diffusion of a Si adatom around the type A step on Si(001) c(4×2)

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The results of a simulation are described, using a density functional method, of the diffusion of adatoms on a flat Si(001)$c(4\times2)$ surface and around one type of surface step (the S_A step). These indicate that there is a moderate additional energy barrier (0.2 ± 0.1 eV) to cross the S_A step as compared to the energy for diffusion on a flat surface. The dimer-top lattice site on the lower terrace adjacent to the step edge is stabilized (by 0.15 ± 0.1 eV) with respect to the flat surface result although the most stable binding sites near the step are unaffected. This behavior can be understood based on the disruption of dimer tilt near the step. The results suggest that adatoms are more likely to stop on lattice sites at the S_A step edge than on lattice sites on the open surface. This may affect the relative dimer formation rate near the step with respect to the behavior on the flat surface even in the absence of a clear change in binding energy. The effect of the S_A step terrace edge on adatom behavior is very short ranged and weak. This is consistent with the relatively small strain field and lack of change in dangling bond density associated with the step edge. © *1995 American Institute of Physics.*

Microelectronic device applications require increasingly short range changes in the properties of their constituent materials, in some cases over distances of one atomic layer. Great progress in forming such abrupt junctions has been achieved. However, further progress will require a more detailed understanding of atom dynamics. Of the technologically important materials and surfaces, Si(001)2×1 is by far the most widely used. Studies of Si(001)2×1 have given an excellent picture of the static surface.[1–4] However, to understand adatom dynamics it is necessary to follow the motion of individual adatoms as they diffuse. Unfortunately, to date it has been impossible to observe the motion of single adatoms directly. To study these indirectly, computer simulations based on the Monte Carlo[5–7] or molecular statics,[7–10] approaches have been developed. Both experimental and theoretical studies of the structure of Si(001)2×1 grown by molecular beam epitaxy (MBE) suggest that under many conditions the morphology is dominated by attachment of atoms to the two predominant types of surface steps (S_A and bonded S_B[11]). For example, step-evolution analysis[7] and Monte Carlo (MC) simulations[6,7] suggested that the S_A step may present no significant barrier to adatom diffusion and may bind adatoms weakly relative to positions on the free surface. Furthermore, it was suggested[6] that the morphology of surfaces during growth is primarily determined by the interaction of adatoms with S_A steps.

In this letter, we present a fundamental study of the motion of Si adatoms around S_A steps on Si(001) based on

density functional theory using an approach developed by Sankey and co-workers and described in detail elsewhere.[12–14] The calculation was carried out under the local density approximation and used nonlocal, norm-conserving pseudopotentials and a pseudoatomic wave function basis set that eliminates the requirement of artificial (e.g., normal to the surface) periodic boundary conditions. While the method does not provide a self-consistent solution of the density functional equations for the system, the results have been shown to provide an excellent description of a variety of systems including Si surface reconstructions.[15–17]

The simulation cell used here consisted of six layers of 16 Si atoms each for a total of 96 Si atoms, as shown in Fig. 1, with periodic boundary conditions on the (110), ($\bar{1}\bar{1}0$), ($1\bar{1}0$), and ($\bar{1}10$) faces. The atoms on the lower ($00\bar{1}$) face of the slab were fixed on their bulk lattices sites and the dangling bonds on the lower surface were passivated by 32 hydrogen atoms. The (001) surface was free to reconstruct. The lowest energy reconstruction for a flat surface was found to be the $c(4\times2)$, a modified 2×1 structure with tilted dimers, as shown schematically in Fig. 1. Surface steps were generated by placing an extra half monolayer of Si atoms on the substrate and allowing the new structure to relax. The total energy was calculated and minimized using a quenching method.[14] The total energies were estimated to be accurate to better than ±0.06 eV relative to each other. The energy values for minimum energy binding sites and minimum energy diffusion paths presented below are estimated to be accurate to ±0.1 eV and to be limited primarily by the density of mesh points calculated to obtain the surface map. The energy

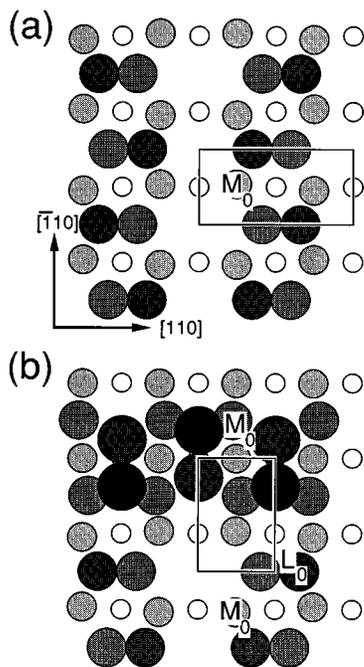[a)]Electronic mail: rocket@tux1.cso.uiuc,edu

FIG. 1. A schematic diagram of the top view of the simulation cells of (a) the flat surface and (b) the type A step. The rectangles indicate the areas calculated in the surface maps. For the flat surface the minimum energy position is labeled M_0 while the lattice site stabilized by the type A step edge is marked L_0.

FIG. 2. The energy map for a Si adatom on a Si(001)$c(4\times2)$ surface. The contours are labeled in eV relative to the minimum binding energy sites (M_0) and the contour interval is 0.4 eV. Dashed lines indicate contours with energies of ≤ 0.8 eV while solid lines represent contours of higher energies.

map contour interval is 0.4 eV which is the minimum useful interval for the density of calculated surface points. A few simulations of larger unit cells were conducted as a check of the energy and position of atoms used in the 96 atom cells. The atoms in the normal cell area were not found to change position or energy significantly as the cell size was increased.

Minimum energy barriers for adatom motion adsorption energies and sites were found by a mapping strategy using an adatom as a probe. To construct an energy map, a substrate containing two S_A surface steps was generated (see Fig. 1) and the residual forces were reduced to <0.1 eV/Å. An adatom was then introduced onto a grid of sites on the surface and the forces were again minimized with the constraint that the adatom was only allowed to move along [001] during the relaxation. The total energy of the simulated volume was recorded for each grid site and these energies were collected to yield the energy map.

An energy map for a flat Si(001)$c(4\times2)$ surface was calculated first to provide reference energies and diffusion behaviors for comparison with the stepped surface studies. The results are shown in Fig. 2. The surface examined is similar to one modeled by Brocks, Kelly, and Car[18] using the Car–Parinello method[19] but included tilted dimers as in calculations by Boguslawski *et al.*[20] Unlike the results for the flat surface, the adatom did not travel exclusively along the dimer top sites from one twofold fault site (position M_0 in Fig. 1) to the next when the dimers were tilted. The adatom could also diffuse through the interdimer channel around the downward ends of the tiled dimers. This path has an approximately equivalent, to within 0.15±0.10 eV, diffusion activation energy relative to the path along the dimer top sites. This path was not available for diffusion around the high end of
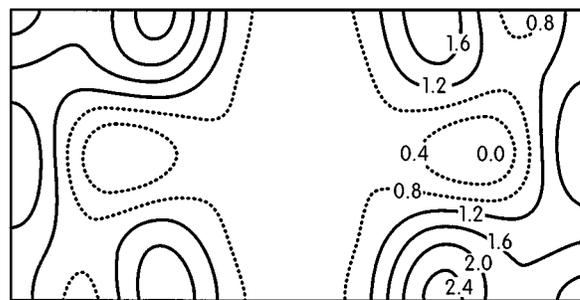
the tilted dimers indicating that continuous diffusion along the long bridge sites between dimer rows is not possible. A moderate additional energy barrier (~0.4 eV) for crossing the channel via the long bridge site between down ends of the dimers was observed in agreement with previous calculations[18,20] and with relative diffusion rates obtained experimentally.[4] We note that dimer tilts probably change rapidly (fractions of microseconds) to give the average untilted appearance of the surface in STM images. In this case, defects associated with changes in the tilt orientation may permit more rapid diffusion along the channel and from one side of the channel to the other than is implied by the energy map in Fig. 2.

The behavior of diffusion adatoms around the S_A surface step was found to match well with the flat surface behavior away from the step but was modified at the step edge. The calculated energy map for the area around the step edge is shown in Fig. 3. This figure was constructed by calculating the energy contours in the area shown in Fig. 1 and extending the map with flat surface results both above and below the edge to reduce interpolation errors in the contour generating program. Only the area simulated for the step is shown. The area adjacent to the map shown in Fig. 3 covering the upwardly tilted side of the dimer on the lower terrace was not calculated to save computing time. It is anticipated that the energy barrier for motion would be much higher in this region analogous to the results in Fig. 2 for the flat surface.
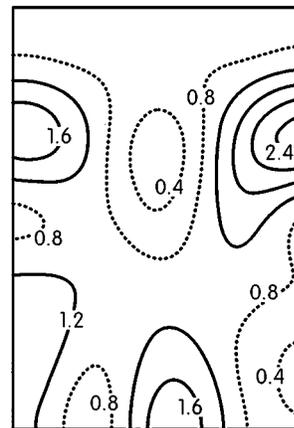

FIG. 3. The energy map for a Si adatom around the type A step on the Si(001) surface with tilted dimers (see Fig. 1). The contours are as in Fig. 2.

Hence, it is likely that the adatom would avoid this part of the surface unless another adatom or atom cluster was already present nearby.

Several observations may be made from the energy map shown in Fig. 3. First, the behavior is very similar to that of a flat surface except in the immediate vicinity of the step edge where only minor changes were found. These appear as essentially interpolations between the two flat surface results. Specifically, all numerical energy values calculated were within 0.15 eV of the flat surface values at all points calculated on the stepped surface except at the exact step edge, an area ~0.5 surface lattice constants wide. Some variations in energies with respect to the flat surface can be explained, in part, by slight shifts in the adatom positions with respect to the calculation mesh points which result from the presence of the step. These variations were shown to be negligible by calculations at the corrected sites. The individual calculated energy values near but not exactly at the step edge are barely altered by the presence of the step. On the upper terrace the energy values averaged 0.04 eV lower along sites on the dimer top of the step edge dimer row and averaged 0.07 eV lower along a line from the downward-tilted side of the dimer row to the long-bridge site in the channel of the lower terrace as compared with flat surface values. This indicates that the dimers near both sides of the step were slightly destabilized, consistent with the disruption of the strain field associated with dimer buckling near the step. While on average sites along the top of the dimer row of the upper terrace were slightly more favorable than on the flat surface, the minimum binding energy sites (M_0) along the upper step edge were essentially unchanged in energy. The absence of change in the M_0 site binding energy is not surprising since there is little change in the coordination of the atoms contributing to binding at this site.

Diffusion pathways very similar to the flat surface results extend on the lower terrace right up to the step edge. The binding energy of the dimer top site on the lower terrace adjacent to the step edge is increased slightly indicating a weak binding of the adatom there. The diffusion channel around the downwardly tilted atom of the dimer in the lower terrace ends in a binding site between the dangling bond of the dimer and the long bridge site at the channel center. The energy of this site is slightly lower than the corresponding site on the flat surface but the site is still 0.3 eV higher in energy than the minima of the flat surface. The dimer top site for adatoms along the lower edge of the terrace, while more stable than the corresponding flat surface sites by ~0.15 eV, is 0.25 eV above the most favorable sites on the flat surface (the M_0 sites). These changes are only barely above the confidence level estimated for the calculation indicating a very weak attraction of a single adatom to the step edge.

Because the dangling bonds of the dimer row that give rise to binding at the twofold fault sites are exposed along the S_A step edge, it is not surprising to find that adatoms approaching the step from below find it relatively easy to access them, as indicated by the low barrier to motion across the step edge (~0.2 eV in the current calculation). Once in these sites, the relatively weak perturbation of the surface by the step makes motion on the upper side of the terrace essentially equivalent to motion on a flat surface.

The conclusions that can be drawn from these results for adatom diffusion around the S_A step are as follows. (1) There is a moderate additional energy barrier to motion across the S_A step as compared with diffusion on the flat surface (0.2 $\pm$0.1 eV). (2) The dimer-top lattice site on the lower terrace adjacent to the step edge is stabilized with respect to the flat surface result indicating a weak binding of the adatom to the step edge below the step. This is proposed to result from disruption of the $c(4\times2)$ dimer tilt structure of the flat surface. More importantly, the site is a lattice site rather than a twofold fault site. This suggests that when adatoms diffuse to a step edge they are more likely to reside on lattice sites than is likely on the open surface. Transition of adatoms from the fault sites to the lattice sites would presumably be more likely at the step edge. This may account for the relatively rare observed formation of dimers on the flat surface compared with the behavior suggested by Monte Carlo simulations. (3) Adatoms are not bound to the step from above. (4) The effect of the S_A step terrace edge on adatom behavior is very short ranged (>0.2 eV effects are limited to one half surface lattice constant) and very weak. This is consistent with the relatively small strain field and lack of change in dangling bond density associated with the step edge.

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