# Kinetic Role of a Surfactant in Island Formation

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Diffusion in the presence of a surfactant on islands is investigated using *ab initio* molecular dynamics. We introduce a double layer step on the Si(001) surface that emulates the {311} facet of an island and show how the diffusion barrier varies with introduction of an Sb surfactant at the step edge. In contrast with the role of surfactants on a flat surface, where diffusion of adatoms is suppressed by site exchange, we find that the surfactant significantly reduces the Schwoebel barrier near the step edge such that island formation is severely suppressed and thus layer-by-layer growth is promoted. We show that the surfactant favors the step edge site and is replaced by adatoms via a pushing-out mechanism, thus repeating the step growth until the island is flattened.

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Fabrication of quantum electronic devices requires in general atomic layer-by-layer growth for high quality devices. One may reduce the growth temperature to suppress diffusion of surface adatoms and thus prohibit island formation. However, this causes less crystalline structure [1] and sometimes dislocations [2]. One alternative is to introduce a surfactant, for instance, group V materials such as As, Sb, and Bi during Ge/Si growth. The surfactant lowers the surface free energy and thus reduces the Ge segregation in Ge/Si growth [3]. For instance, the surface free energy of the As/Ge/Si system is lower than that of the Ge/As/Si system by 1.7 eV/dimer. The site-exchange mechanism has been suggested both experimentally [3] and theoretically [4] in order to explain the suppression of Ge segregation by a surfactant. The presence of a surfactant in the front growing *flat* surface suppresses diffusion of surface adatoms using the site-exchange mechanism, prohibiting island formation. (Hereafter we call the suppression of an adatomic diffusion on a *flat* surface type-I diffusion.)

On the other hand, it was shown that the island growth rate induced by the strain on the Ge/Si(100) system is faster than the suppression rate of islands by a surfactant, and therefore the islands are grown first and subsequently the island "smoothing out" and island coalescence with a highly twinned structure occur [5]. It was also shown that postgrowth annealing in Sb drastically flattens the {311} facets of Ge islands [6]. It seems that the presence of a surfactant on an *island* enhances diffusion down to the lower terrace such that islands are flattened (hereafter called type-II diffusion). This observation seems to be contradictory to type-I diffusion where the surfactant suppresses diffusion of adatoms on a flat surface. However, this behavior has not clearly been understood yet. This phenomenon involves not only the energetics but also the kinetics on the island. A reliable calculation is required to understand type-II diffusion.

In this Letter, we investigate the effect of a surfactant on an island using *ab initio* molecular dynamics (MD) calculations. The Sb favors the site at the step edge. This drastically reduces the diffusion barrier near the step edge, enhancing anisotropic diffusion along the dimer row at the upper terrace. The islands are flattened via a pushing-out mechanism rather than a rolling-over mechanism, such that the Sb atoms are always pushed out to the step edge until the islands coalesce with each other.

In this calculation we introduce a rebonded double layer step ($D_B$) on the Si(001) surface to emulate the {311} facet of the island which is composed of consecutively rebonded $D_B$ steps [7]. Therefore we expect that the diffusion phenomenon on the $D_B$ step is similar to that on islands with experimentally observed {311} facets. We choose a triclinic cell with lattice vectors $\vec{a}$ ($\sqrt{2}$, 0, 0), $\vec{b}$ ($-\sqrt{2}/4$, $9\sqrt{2}/4$, $1/2$), and $\vec{c}$ ($\sqrt{2}/4$, $-\sqrt{2}/4$, $3/2$) in units of a lattice constant to have a smaller supercell. In this way we choose 54 Si atoms where the bottom layer is saturated by 18 H atoms. The number of layers of the upper and lower terraces is kept equivalent to prevent any unnecessary effects on both terraces. A detailed description of this structure can be found elsewhere [8].

We adopt in this calculation the Car-Parrinello *ab initio* MD approach [9]. We use a plane-wave basis set with a kinetic energy cutoff of 8 Ry and Bloch functions only at the $\Gamma$ point of the supercell surface Brillouin zone. The interaction between ionic cores and valence electrons is described by a fully nonlocal pseudopotential with $sp$ nonlocality. We fix the two bottom Si and H layers to prevent any spurious forces. We first search for the electron energy minimization using a steepest decent approach. Ions are moved by a fast relaxation scheme [8]. The energy and forces are converged to $0.5 \times 10^{-5}$ Ry and 0.005 Ry/Å, respectively.

We first search for the stable Sb site at the stepped surface. Two Si atoms on the surface are replaced by Sb atoms. Figure 1 shows possible sites of an Sb dimer. The rebonded site in Fig. 1(a) is taken as the reference energy. The Sb atoms at the rebonded step edge increase

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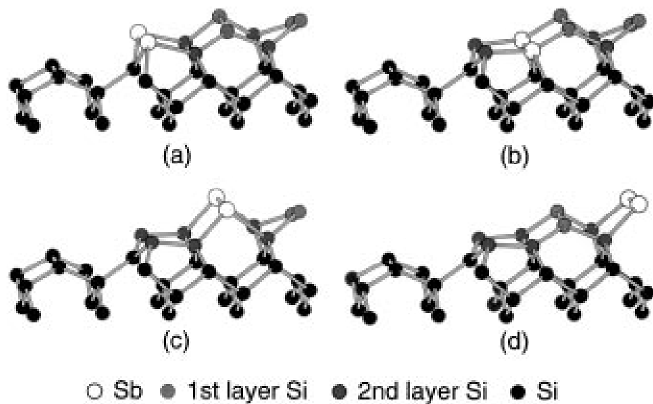


FIG. 1. Various sites for an Sb dimer on the $D_B$ step. (a) is taken as a reference energy.

slightly the symmetry of the Si dimer at the step edge. The Sb atoms do not favor the subsurface sites as shown in Fig. 1(b), increasing the total energy by 2.48 eV. Substitution of an Si dimer by an Sb dimer at the step edge lowers the energy by 0.63 eV although the next Si dimer site is also favorable with a similar energy gain of 0.57 eV. The energy difference between Figs. 1(b) and 1(c) is 3.11 eV, as compared to the energy difference of 3.5 eV/dimer between Si/Sb/Ge/Si and Sb/Si/Ge/Si on flat surfaces. The Sb dimer bond length in Fig. 1(c) is 2.98 Å with an asymmetry of 0.21 Å. This is comparable with the previously calculated value of 2.94 Å on the flat surface [10]. The Si-Sb bond length ranges from 2.71 to 2.82 Å in Fig. 1(c), which is slightly larger than the values of pseudopotential calculations [10]. We conclude that the Sb dimer favors the site at the step edge.

In order to investigate the kinetics of Si adatoms on a stepped surface we calculate the potential surface with and without the presence of an Sb dimer at the step edge. We use a single Si adatom and move it along the top of the dimer row. The kinetics of a dimerized flat Si(001) surface is governed by anisotropic diffusion [11,12]. We accordingly move the Si adatom along the dimer row. We fix the $y$ ([110]) direction and relax the $x$ and $z$ directions of an adatom. The substrate atoms are fully relaxed simultaneously. Once we determine the minimum energy for the given $y$ value of an adatom, we move it to the next point and repeat the same calculation. Figure 2 shows the total energy variation along the $y$ direction. The dotted and solid lines indicate the diffusion barriers without and with the Sb dimer at the step edge, respectively, as shown in Fig. 2(a). The dimerized Si surface without the presence of the Sb dimer shows two additional (Schwoebel) barriers with a diffusion barrier of 0.93 eV whereas with the presence of the Sb dimer it shows a single Schwoebel barrier of 2.1 eV, increasing the barrier height significantly. The diffusion barrier with the presence of the Sb dimer at the step edge is increased because of the weak bonding of Sb to the Si atoms in the subsurface as the Si adatom

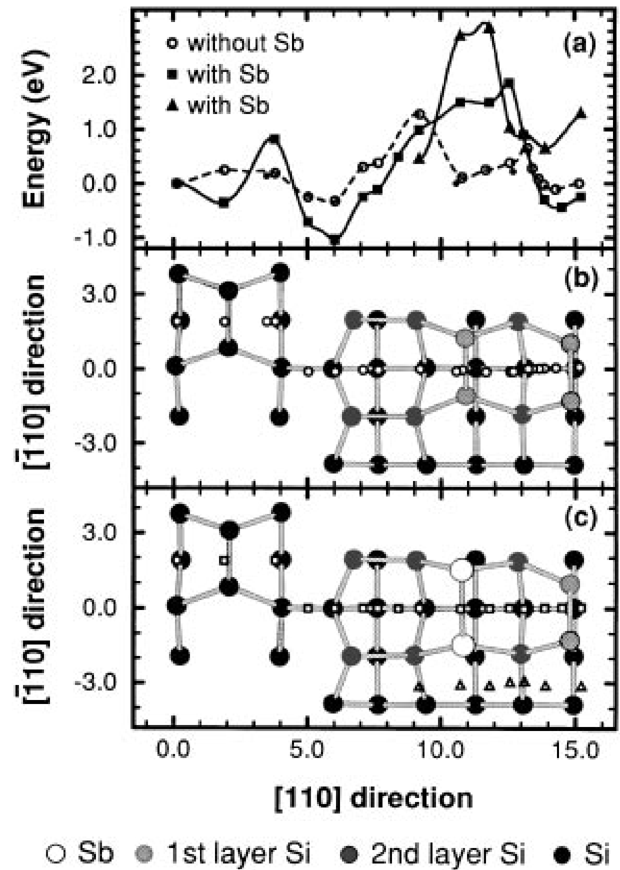


FIG. 2. Total energy variation and reaction pathways along the top of the dimer row. The circles (squares) indicate (a) the total energy variations without (with) Sb dimer at the step edge, and (b),(c) the corresponding top views of the pathways on top of a dimer along the [110] direction. The triangles in (c) represent the pathway along the trough between two dimer rows. The filled circles in (a) indicate the energy without constraints given in the text.

approaches the Sb dimer. We note that the presence of Sb at the step edge of the upper terrace creates an additional barrier at the lower terrace by about 0.62 eV, as compared to that without the Sb dimer. This suppresses the incorporation of a single adatom in the ascending step. Although an additional barrier at the lower terrace is also suggested in previous work [13], an increase of the barrier for a single Si adatom to diffuse along the dimer row near the step edge at the upper terrace is not expected. We have also tested diffusion along the trough between the dimer rows as shown in Fig. 2(c). The diffusion barrier height in the presence of the Sb dimer at the step edge is 2.21 eV, similar to that on top of a dimer. This trend is similar to Si diffusion on pure single [14] and double [7] layer steps without Sb. However, the local minimum energy between two dimer rows is higher by 1.09 eV than that on top of a dimer. With a reasonable thermal diffusion energy such that adatoms reside in the lowest energy configuration, Si adatoms would favor diffusion on top of a dimer row.

We consider now diffusion of an Si dimer in the presence of an Sb dimer at the step edge. This seems to be reasonable because an Si dimer can easily be formed on the surface or the Si adatoms can easily be accumulated near the step edge of an upper terrace due to the higher diffusion barrier in the presence of an Sb dimer at the step edge. We first test various stable sites of an Si dimer in the presence of an Sb dimer at the step edge. The Si dimer on top of a dimer row parallel to the two adjacent dimers is taken as a reference [Fig. 3(a)]. The Si dimer on top of a dimer row perpendicular to the two adjacent dimers gives a higher total energy by 0.6 eV. One may also consider an Si dimer which is similar to Fig. 3(a) but the dimer is pushed to the trough between the dimer rows. The total energy in this case is higher by 0.84 eV. This is in contrast with the stable position of adatoms on the $D_B$ step without an Sb dimer at the step edge where all three positions are energetically favorable [8]. We therefore consider the dimer position of step (i) of Fig. 3(a) only.

Two pathways may be considered, as shown in Fig. 3. Various pathways on a pure Si $D_B$ step have been tried elsewhere [8]. We first consider the rolling-over mechanism where an Si dimer rolls over the Sb dimer at the step edge. Step (i) illustrates the stable site of an Si dimer on the dimer row, similar to an $H$ site for single adatomic diffusion [8,11]. The Si dimer rolls over the Sb dimer, as shown from step (ii) to step (vi), finally generating one step further than the step edge to the left. The barrier exists in step (ii) with a barrier height of 1.55 eV, which is lower than the value of 2.72 eV for an Si dimer to roll over the step edge without the presence of an Sb dimer as shown in Fig. 4. This energy difference again results from the surface free energy difference between Si and Sb. A local minimum exists in step (iii) where the energy is lowered by less bond angle distortion between the top Si dimer and the Sb dimer.

We next consider the pushing-out mechanism, as shown in Fig. 3(b). Unlike the rolling-over mechanism, the Sb dimer is replaced by Si as shown in Fig. 3(b). The Sb and Si dimers keep the bondings with their adjacent atoms while moving, which is a significant difference from path I. Surprisingly, these pathways require an additional Schwoebel barrier of 0.71 eV only, which is significantly lower than the barrier without an Sb surfactant at the step edge, as shown in Fig. 4. The Sb dimer is pushed out to the step edge by generating one step further from the left and finally a nonrebonded step edge is formed. We emphasize here that in order to reach step (i) of Fig. 3(b) over the top of a dimer from the right direction the Si adatom should have enough thermal energy to overcome the surface activation barrier of 0.35 eV [8]. (This is not shown in Figs. 3 and 4.) Once they reach the step edge, the additional Schwoebel barrier is significantly reduced to 0.71 from 1.55 eV in the presence of an Sb surfactant. We have also tested the relative stability of Sb dimers at the nonrebonded $D_B$ step. We find that the Sb dimer favors the step edge over the inner Sb dimer on the surface by 0.41 eV, similar to the general trend of the rebonded $D_B$ step where the energy difference is 0.06 eV.

We now discuss how the island can be flattened by the Sb surfactant based on our calculations. In island formation the {311} facets always appear because the island reduces the surface free energy by minimizing the surface area [6] and the {311} facets composed of repeating rebonded $D_B$ steps are known to be stable [7]. With the in-

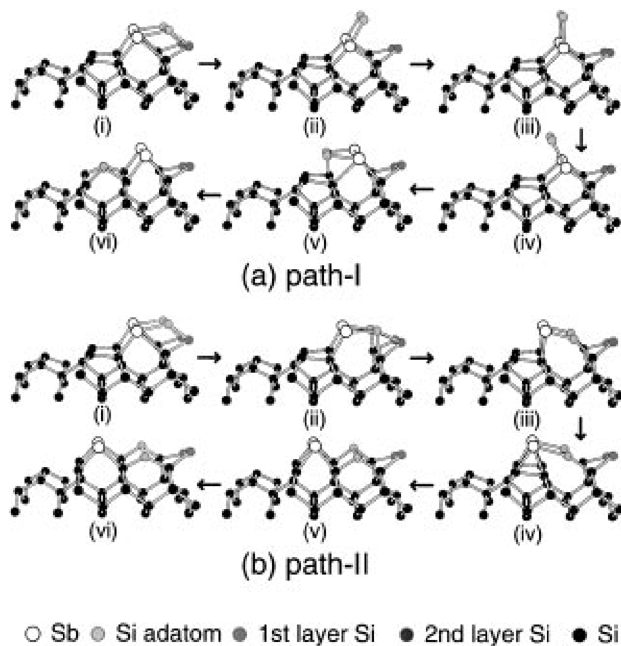


FIG. 3. Two pathways for the migration of the Si dimer along the [110] direction. Path I is the rolling-over mechanism and path II is the pushing-out mechanism.

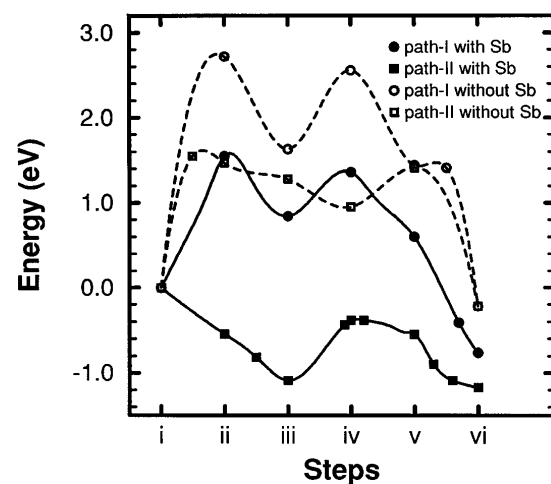


FIG. 4. The total energy variations for path I and path II in terms of the steps taken along the [110] direction indicated in Fig. 3. The open (filled) circles and squares with dotted (solid) lines indicate the energy variations of the corresponding pathways without (with) Sb surfactant at the step edge.

troduction of Sb on an island with {311} facets, Sb prefers the site at the step edge. Sb creates an additional diffusion barrier near the step edge for a single adatom. Hence Si adatoms can be accumulated near the step edge of an upper terrace and easily form a dimer. This Si dimer pushes out the Sb dimer to form the nonrebonded $D_B$ step using the pushing-out mechanism. The additional Schwoebel barrier for this process is not appreciable compared to the thermal energy of a conventional growth process. The {311} facets are reduced by this repeating process and finally the islands are flattened. Therefore, unlike type-I diffusion where diffusion of adatoms is suppressed by the site-exchange mechanism on a flat surface, type-II diffusion plays an important role for the island, i.e., diffusion is enhanced on the island and this eventually flattens the islands.

In summary, we find a kinetic role of a surfactant for suppression of island formation on a Si(001) surface by using an *ab initio* MD calculation. Sb favors the site at the step edge. The additional Schwoebel barrier of 2.1 eV for the diffusion of a single Si adatom appears near the step edge of an upper terrace in the rebonded $D_B$ step in the presence of an Sb dimer. Therefore Si adatoms can be accumulated near the step edge of an upper terrace at the initial growth stage. When an Si dimer is formed on the upper terrace, the Si dimer replaces the Sb dimer using a pushing-out mechanism. The pushing-out mechanism requires an additional Schwoebel barrier of 0.71 eV only at the step edge, whereas the rolling-over mechanism requires a barrier of 1.55 eV. The {311} facets are reduced by the pushing-out mechanism and ultimately islands are flattened.

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