Reaction pathway for Sb-dimer rotation in conversion of Sb_4 precursors on Si(001)

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We report first-principles total-energy calculations that provide detailed reaction pathways for Sb-dimer rotation in evolving processes of Sb_4 precursors on the Si(001) surface. We find that the total energy for the Sb dimer perpendicular to the subsurface Si dimers is lower than the parallel dimer by 0.45 eV. We also find a plausible reaction pathway for the Sb-dimer rotation during which only a single dangling bond is created. The calculated activation energy for the rotation is 1.0 eV, indicative that the dimer rotation is rate-determining in the evolving process of Sb_4 precursors.

Surfaces of covalent semiconductors are in general accompanied with relaxation of surface and occasionally subsurface atoms (reconstruction). Epitaxial growth on the semiconductor surface is thus regarded as destruction of the reconstruction and subsequent formation of new bonds with arriving foreign atoms. The arriving species, on the other hand, are usually of molecular form in epitaxial-growth techniques: In molecular-beam epitaxy, for instance, group-V atoms come in quadrimolecular or dimolecular forms and group-IV atoms in several different molecular forms.[1] In order to understand microscopic aspects of epitaxial growth, it is therefore imperative to reveal reaction pathways from the molecular or dissociative adsorption of the arriving species toward formation of epitaxial layers.

Recently, Mo[2] has obtained microscopic information for such reaction pathways in an example scientifically typical and technologically important: i.e., Sb molecules on the Si(001) surface. Based on scanning tunneling microscopy (STM) measurements on the Si(001) slightly exposed to Sb_4 flux, he found four metastable precursor states for the adsorption. Although microscopic atomic structures of the four states are not determined unequivocally, he has identified the four as follows: a ball cluster labeled A, a pair of dimers labeled B with the dimer bonds parallel to those of the substrate dimers, a dumbbell labeled C with the long axis parallel to the substrate dimer rows, and a rotated dumbbell labeled D with the long axis perpendicular to the dimer rows. Further, two different reaction pathways from A, C, or D state to B state are deduced: a reaction $A \rightarrow D \rightarrow B$ and the other, $C \rightarrow B$, with the activation energies being 0.7 eV, 0.9 eV, and 0.8 eV for $A \rightarrow D$, $D \rightarrow B$, and $C \rightarrow B$, respectively. He also found that the metastable B finally converts to the stablest state, a pair of dimers labeled E with the dimer bonds perpendicular to those of the substrate dimers. Hence the reaction pathway from B to E, for which no microscopic information is available, is crucial for the understanding of whole reactions from the molecular adsorption to the deposition of an epitaxial layer.

In this paper, we report first-principles total-energy calculations within the local-density approximation (LDA) performed to search the reaction pathway for the rotation of an Sb dimer (corresponding to the reaction $B \leftrightarrow E$) on the Si(001). We find that the total energy of the stablest state E is lower than that of the metastable B by 0.45 eV per dimer:

This relatively small value is consistent with the reversible dimer rotation as is indeed observed by STM.[3] Moreover, we first find the detailed microscopic reaction path for the Sb-dimer rotation: In the most plausible reaction path, the two Sb atoms forming the dimer move consecutively to reduce the number of dangling bonds during the reaction. The calculated energy barrier from B to E is 1.0 eV per dimer.

In the calculation the surface is simulated by a repeating slab model in which typically eight atomic layers and an 8.14 Å vacuum region are included, and the periodicity in the lateral directions is set to be 2×2. The slab has C_2 symmetry with the rotation axis in the lateral direction. We use norm-conserving pseudopotentials,[4] Ceperley-Alder[5] exchange-correlation energy in the LDA, the plane-wave basis set with the cutoff energy of typically 8 Ry, and the $4k$ points in a wedge in the surface Brillouin zone (SBZ) integration. The nonlocal part of the pseudopotential with the d pseudopotential being regarded as the local component is further treated by the Kleinman-Bylander procedure.[6] Both the electronic and the geometric degrees of freedom are optimized by the highly efficient conjugate gradient minimization technique as reported elsewhere.[7,8] The symmetry unrestricted geometry optimization has been performed for all atoms except for the ones in the innermost two atomic layers in the slab. In the optimized geometries the remaining forces acting on the atoms are less than 0.004 Ry/Å. Most calculations in this paper have been performed with the above set of calculational parameters. Yet the key results are confirmed by using a more extensive set of parameters such as the 12-atomic-layer slab, the 10 Ry cutoff energy, the 10.9 Å vacuum region, and the $9k$ points in the wedge in the SBZ. We have found that the values in the total-energy difference presented here are accurate to 0.1 eV.

We start with the calculated atomic structure of an Sb overlayer on the Si(001). The Sb overlayer shows the 1×2 reconstruction in which the Sb dimers are perpendicular to the substrate Si dimers. We find that the Sb dimer is symmetric in accord with experiment[9] and the DMOL calculation.[10] Each Sb atom is bonded to two Si atoms at subsurface sites and to the partner Sb atom in the dimer. This leaves the two Sb atoms threefold coordinated with a doubly occupied lone-pair state for each. The Sb dimer-bond length, the Sb-Si backbond length, and the vertical distance between Sb and the Si surface are 2.96 Å, 2.58 Å, and 1.70 Å, re-

TABLE I. Calculated values of the Sb-dimer bond length $l_{Sb\text{-}Sb}$, the Sb-Si backbond length $l_{Sb\text{-}Si}$, and the vertical distance h between Sb and the Si surface of the 1×2 reconstructed Sb/Si(001) surface. These values are compared with experiment and the DMOL calculation.

	Present cal.	DMOL (Ref. 10)	Expt. (Ref. 9)
$l_{Sb\text{-}Sb}$ (Å)	2.96	2.93	2.88
$l_{Sb\text{-}Si}$ (Å)	2.58	2.61	2.63
h (Å)	1.70	1.73	1.74

spectively. These values are in good agreement with the experiment[9] and with the DMOL calculation[10] (Table I for comparison).

Using the same calculational parameters, we perform total-energy calculations for the B state and the E state which appear during dissociative adsorption of Sb_4 molecules on the Si(001). Figure 1(a) is the atomic structure of the precursor B with the Sb-dimer bond parallel to the substrate Si dimers.[11] The optimized atomic geometry is shown in Fig. 2(a). In the structure, each Sb atom is bonded to dangling bonds of two Si atoms at subsurface sites and to the partner Sb atom in the dimer without destroying the Si dimer at the subsurface. The reduction of the number of the dangling bonds makes the geometry of state B energetically stable. The Sb dimer-bond length and the Sb-Si backbond length are 2.90 Å and 2.74 Å, respectively. The bond length of the Si dimer at the subsurface is slightly stretched from 2.31 Å to 2.42 Å since the dangling bonds of the Si dimers having formed the π bonded structure without Sb are now
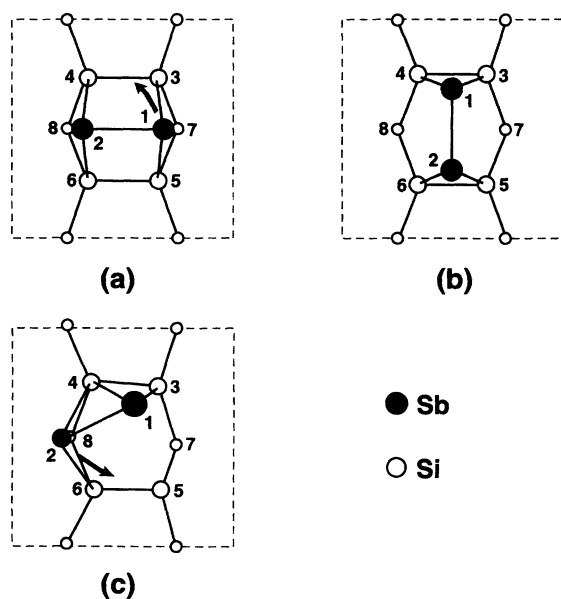

FIG. 2. Geometry-optimized atomic structures of (a) the precursor state B, (b) the final state E, and (c) the transition state in the Sb-dimer rotation on Si(001). The open and solid spheres denote the Si and Sb atoms, respectively.

FIG. 1. Schematic top view of geometries of (a) the precursor state B, (b) the final state E, and (c) the transition state in the Sb-dimer rotation on Si(001) surface. The open and solid circles represent the Si and Sb atoms, respectively. The calculation is done for the 2×2 lateral unit cell shown by dashed lines. The thick arrows denote subsequent atomic motion for the rotation at the geometry.
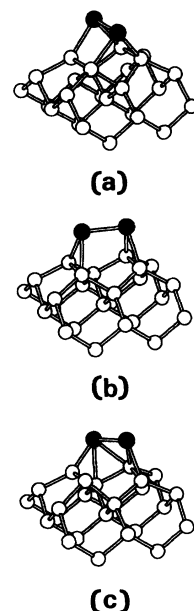
bonded to the Sb atoms at the top layer.

The atomic structure of the final state E in which the Sb dimer is perpendicular to the Si dimers in the substrate is shown in Fig. 1(b). Figure 2(b) shows the total-energy optimized structure obtained in the present calculation. A remarkable feature in Fig. 2(b) is the existence of the Si dimer at the subsurface layer, which is in contrast to the Si-dimer broken model suggested by Mo.[2] We have indeed found that the total energy of the geometry shown in Fig. 2(b) is lower than that of the Si-dimer broken geometry by 1.0 eV. The destruction of the subsurface Si dimer takes place only after an additional Sb arrives at the site between the Si dimer rows at higher coverage. The present calculation clearly shows that the Si dimer at the subsurface layer is preserved in the geometry of state E observed in the STM image. The dangling bonds of the Si dimers having formed the π bonded structure before Sb adsorption interact with the top-layer Sb dimer to reduce the number of the dangling bonds. Such a reconstruction makes the geometry of state E energetically stable. The Sb-dimer bond length and the Sb-Si backbond length are 2.90 Å and 2.64 Å, respectively. The Si-dimer bond length at the subsurface layer is slightly stretched from 2.31 Å to 2.38 Å because the π bonding of the Si dimer is diminished in state E.

The Sb-Si backbond length in state E is 2.64 Å, which is shorter than the corresponding value 2.74 Å in state B, and is closer to the favorable Sb-Si backbond length of 2.58 Å in the 1×2 Sb-dimerized geometry. The Si-Si bond length and the angle at subsurface layers are in average 2.35 Å and 108.0°, respectively, in state E, whereas they are 2.39 Å and 106.5°, respectively, in state B. The values in state E are closer to the corresponding values in bulk Si, indicating that strains in state B are larger than that in state E. We indeed

find that the total energy of the E state is lower than that of the B state by 0.45 eV per dimer. This finding is in accord with the experimental observation that the E state is the final stable state, and also indicates that the rotation of the Sb dimer from the direction parallel to the Si dimer to the perpendicular is an exothermic reaction.

We next study the reaction pathway in which the top-layer Sb dimer parallel to the Si dimers (state B) rotates on the Si(001) by 90° and leads to the Sb dimer perpendicular to the Si dimers (state E). Complete information on the adiabatic surface for the rotation is obtained by the total-energy calculations at a large number of mesh points for the four degrees of freedom corresponding to lateral coordinates of the two Sb atoms. It is not a feasible task, however. We instead adopt a more practical strategy of limiting Sb atomic motion in the whole four-dimensional configuration space: We assume that the Sb-dimer bond is not broken during the rotation from B to E. We thus obtain the total energy as a function of the angle θ of the Sb-dimer bond with respect to the Si-dimer row by optimizing all atomic positions under the constraint of the fixed bond angle.

We start from the geometry ($\theta_B = 90°$) of the metastable B [Fig. 1(a) or Fig. 2(a)]. We then rotate atom 1 (Fig. 1 for labeling) around atom 2 by a small amount $\theta_B - \theta_1$ and increase the height of atom 1 enough to avoid being trapped in a local minimum. For the geometry of this fixed bond angle θ_1, we fully relax the remaining $(3N-1)$ coordinates, where N is the number of relaxed atoms within the unit cell, and then obtain the total energy corresponding to θ_1. Using the resulting atomic geometry, we repeat this procedure until reaching the transition state ($\theta \sim 64°$) shown in Fig. 1(c) and Fig. 2(c).

As the top-layer Sb dimer rotates from the metastable B toward the transition state, the Si atoms [3–6 in Fig. 1(a)] bonded to the Sb dimer distort from their metastable positions and follow the rotation motion by stretching the bond length between atoms 1 and 5. At the transition state, the bond between atoms 1 and 5 is broken,[12] and a new bond between atoms 1 and 4 is formed: The energy gain due to the bond formation between atoms 1 and 4 compensates for the energy loss caused by the breaking of the 1-5 bond. Sb atom 2 is bonded to Si atom 8 at the subsurface layer without breaking other bonds. The position of atom 2 is located near the stable binding site for an additional group-V atom on the Si(001) surface.[13] As a result, there remains only one dangling bond at the atom 5 site since the dangling bond of atom 1 is bonded to atom 4 [Fig. 1(c) and Fig. 2(c)]. The bond lengths around atom 5 range from 2.36 Å to 2.42 Å close to the bond length of the bulk Si 2.35 Å. The bond angles around atom 5 range from 98° to 99° much smaller than the tetrahedral angle 109.5°. This implies that the dangling bond at the atom 5 site has more s component to lower the nonbonding orbital energy.[14] The 2-4 and 2-8 Sb-Si bond lengths are 2.84 Å and 2.90 Å, respectively. These values are slightly longer than the Sb-Si backbond length (2.58 Å) in the Sb 1 monolayer covered Si(001). The bond length between atoms 2 and 6 is 2.62 Å close to the Sb-Si backbond length of 2.58 Å.

After the transition state, we then rotate atom 2 around atom 1 by a small amount since atom 1 already sits on top of the Si dimer. We also increase the height of atom 2 enough to
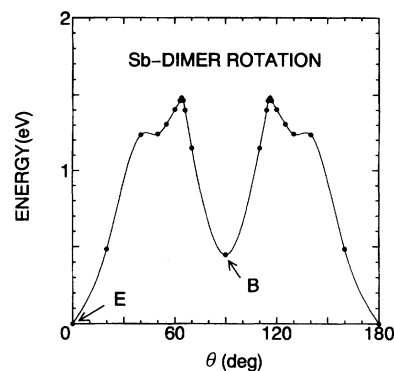

FIG. 3. Calculated total energy of the Sb dimer on Si(001) along the reaction path shown in Fig. 1. The total energy of the final state E ($\theta = 0°$) is 0.45 eV lower than that of the precursor B ($\theta = 90°$). The filled circles are the calculated values and the solid line is a spline to guide the eye.

avoid being trapped in a local minimum. This procedure is repeated until reaching the geometry ($\theta = 0°$) corresponding to the stable state E [Fig. 1(b) or Fig. 2(b)]. Finally we obtain the total-energy curve as a function of the Sb-dimer bond angle θ (Fig. 3) along the reaction path. We find that the activation energy for the rotation of the Sb dimer, i.e., the conversion from B to E, is 1.0 eV. This value is significantly lower than the energy required to break the dimer bond,[15] and thus justifies the present assumption that the Sb dimer is preserved during the reaction. The present activation energy 1.0 eV should be regarded as an upper bound since we relax only a part of the whole atomic coordinates. We have actually examined several different reaction pathways, however, and obtained larger activation energies. An important feature in the present reaction pathway is that only one dangling bond is created during the reaction. This renders the total energy at the transition state significantly. The calculated energy barrier 1.0 eV is larger than the barriers estimated for different reaction processes,[2] $A \rightarrow D \rightarrow B$ and $C \rightarrow B$, indicating that the process $B \rightarrow E$ is rate-determining in the whole reaction pathways from the molecular adsorption to the deposition of an epitaxial layer. According to the present results, the reverse reaction from $E \rightarrow B$ requires additional energy 0.45 eV, which could be supplied from the STM tip as is observed by experiment.[3]

In summary, we have presented the first-principles total-energy calculations for the Sb-dimer rotation on Si(001). The conversion of the precursor B to the stable E is found to be energetically favorable with the energy gain of 0.45 eV per dimer. In contrast to the previously suggested model, the Si-dimer bond in the substrate is preserved. We have also shown that the rotation of the Sb dimer on the Si surface occurs via the concerted motion of the top-layer Sb atoms and the Si atoms at subsurface sites. Only one dangling bond is created during the reaction pathway we have found here. The calculated activation energy for the conversion from B to E is 1.0 eV significantly lower than the energy needed to break a dimer bond.

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[12] In general, the bond charge is diminished when the distance of the two atoms becomes larger than 3 Å.

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