Unique Dynamic Appearance of a Ge-Si Ad-dimer on Si(001)

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We carry out a comparative study of the energetics and dynamics of Si-Si, Ge-Ge, and Ge-Si ad-dimers on top of a dimer row in the Si(001) surface, using first-principles calculations. The dynamic appearance of a Ge-Si dimer is distinctively different from that of a Si-Si or Ge-Ge dimer, providing a unique way for its identification by scanning tunneling microscopy (STM). Its "rocking" motion, observed in STM, actually reflects a 180° rotation of the dimer, involving a piecewise-rotation mechanism. The calculated energy barrier of 0.74 eV is in good agreement with the experimental value of 0.82 eV.

The epitaxial growth of Si and Ge on Si(001) has been intensively investigated because of its technological importance in the microelectronic industry and because it serves as an ideal model system for fundamental study. Much attention has recently been focused on the very early stage of the growth, in which small, generally metastable structures are formed [1–17]. Their configuration, stability, and dynamic behavior not only contain information about adatom adsorption and diffusion [5] but also provide the missing link from nucleation to growth as these metastable nonepitaxial structures transform into epitaxial islands [15].

The combination of scanning tunneling microscopy (STM) and first-principles calculation (FPC) has greatly advanced our research capability in surface science and thin-film growth. STM allows us to observe not only static surfaces but also dynamic processes of growth at the atomic level. FPC is capable of resolving the detailed atomic structure and kinetic pathways for dynamic processes. Both techniques have been extensively applied to the investigation of the growth of Si and Ge on Si(001), such as the adsorption and diffusion of Si and Ge adatoms [1–4], the stability and diffusion of Si and Ge ad-dimers [5–13], and the rotation dynamics of a Si-Si ad-dimer [5–8] on top of a Si(001) dimer row. Despite these many successes, it has been a challenge to differentiate a Ge atom from a Si atom by STM during deposition of Ge on Si(001) because of the very similar chemical and electronic properties of Si and Ge. Recent progress has been made to identify Ge atoms in the Si(001) surface by using high-resolution low-bias STM [16]. Here, we combine STM and FPC to study the rocking and rotation dynamics of an ad-dimer on top of a Si(001) dimer row. We demonstrate that the dynamic appearance of an ad-dimer can be used as a signature to differentiate a hetero-ad-dimer (mixed Ge-Si dimer) from a homo-ad-dimer (Si-Si or Ge-Ge dimer) by conventional STM imaging.

When a fraction of a monolayer (ML) of Ge atoms is deposited on a Si(001) surface at room temperature, adsorbed dimers, clusters, and small islands form on the surface. Among those adsorbed dimers residing on the top of

the substrate dimer rows, we observe many in which one of the atoms of the dimer is much higher than the other, with their dimer bond parallel to the substrate dimer row direction (Fig. 1). At room temperature, they appear to "rock" between the two tilted configurational states that are mirror symmetric with each other [17]. The transitions between the two states occur randomly, on an average time scale of 3 sec at room temperature, which allows conventional STM imaging to resolve the two tilted states (Figs. 1a and 1b). Detailed atom-tracking STM (AT-STM) measurements of the "rocking" rate as a function of temperature yield a rocking energy barrier of 0.82 eV [17].

The observed rocking behavior at room temperature is clearly distinct from the behavior of pure Si-Si dimers, which rotate between two orthogonal orientations each having complete mirror symmetry [5–7]. Therefore, we conclude that the rocking dimers must contain Ge. However, just from the STM images, we cannot tell whether the dimer contains one Ge (a mixed Ge-Si dimer) or two Ge atoms (a pure Ge-Ge dimer). Furthermore, because the time scale of the rocking transition is many orders of magnitude faster than the time resolution of AT-STM, the details of the dynamic process are unresolved. The rocking appearance could reflect a true rocking motion of the dimer along the main axis connecting the two atoms, or it could result from a 180° rotating motion of the dimer.

To answer these questions, we carry out a comparative study of the energetics and dynamics of Si-Si, Ge-Ge, and
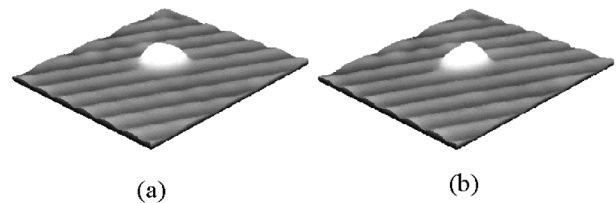

FIG. 1. Empty-state STM images of an adsorbed ad-dimer sitting on top of a substrate Si dimer row rocking between two tilted configurations [(a) and (b)] at room temperature. The substrate dimer rows appear as dark lines in the image.

Ge-Si ad-dimers on top of a Si(001) dimer row, using a series of comprehensive first-principles calculations. We find that the observed dynamic rocking appearance is a unique signature of a mixed Ge-Si ad-dimer that actually results from a 180° rotation of the dimer with the Ge atom always staying in the up-position. The calculations also reveal the lowest-energy-barrier pathway for the dimer rotation. The dimer rotates by a piecewise mechanism, with the two atoms moving in sequence one at a time, rather than in the concerted motion of a rigid rotation. The calculated rotational energy barrier agrees well with the experimental value derived from the rocking ad-dimer motion.

The calculations are performed using the first-principles pseudopotential plane-wave total-energy method in the framework of density functional theory within the local density approximation. The Kohn-Sham orbitals were expanded in plane waves with an energy cutoff of 12 Ryd. The surface is modeled by a periodically repeated slab, which contains 8 Si layers with 16 Si atoms per layer and a vacuum region of at least 12.5 Å thickness in the direction normal to the surface. The top surface layer is arranged in a $p(4 \times 4)$ unit cell with $c(4 \times 2)$ reconstruction, while the bottom surface layer is passivated by H atoms. A set of four special k points is chosen to sample the surface Brillouin zone [18]. Both the Ceperley-Alder functional with parametrization of Perdew and Zunger [19] and the Wigner interpolation formula [20] are used and compared for the exchange-correlation functional [21].

We first examine the stability of a mixed Ge-Si ad-dimer on Si(001). We find that a mixed Ge-Si ad-dimer, similar to a pure Si-Si or Ge-Ge ad-dimer, has four principal binding configurations on Si(001) [21]. The lowest-energy configuration for all three ad-dimers is the one in which the ad-dimer is sitting on top of the substrate dimer row with the ad-dimer bond lying along the dimer row direction, called dimer A (see Fig. 4A below). For this configuration, all of the ad-dimers are buckled (tilted). A pure Si-Si or Ge-Ge ad-dimer has two degenerate energy states with either the left or right atom at the up-position (looking in the direction perpendicular to the substrate dimer rows). A mixed Ge-Si ad-dimer, however, has four energy states: two degenerate with Ge at the up-position (left or right) and two degenerate with Si at the up-position. The states with Ge at the up-position are 0.16 eV lower in energy than those with the Si atom at the up-position. In the buckled ad-dimer, there is a certain amount of charge (electron) transfer from the down-atom to the up-atom in the surface states. It is energetically favorable for electrons to be transferred from Si at the down-position to Ge at the up-position because the electron affinity of Ge is larger than that of Si. Also, Ge may prefer to sit at the up-position to relax strain more effectively.

Next, we calculate the energy barrier for the rocking motion of a Si-Si, Ge-Ge, or Ge-Si ad-dimer on top of the substrate dimer row, as it seemed to appear in the STM im-

ages of Fig. 1. We gradually move the geometrical center of the ad-dimer from one energy state to the other along the substrate dimer row. At each position, the coordinate of the geometrical center of the ad-dimer parallel to the substrate dimer row is fixed while all other coordinates are fully relaxed. The results are plotted in Fig. 2. The Si-Si and Ge-Ge ad-dimers rock between two degenerate energy states with a barrier of 0.14 and 0.043 eV, respectively. The Ge-Si ad-dimer rocks nonsymmetrically between a lower-energy state with Ge at the up-position and a higher-energy state with Ge at the down-position. The energy barrier for the rocking from the lower-energy position to the higher-energy position is 0.25 and 0.09 eV in the reverse course. The saddle points for all three types of ad-dimers are located at the positions where ad-dimers have the unbuckled configuration.

The calculated energy barrier for rocking is rather small (less than 0.25 eV) for all three ad-dimers. A Si-Si or Ge-Ge ad-dimer rocks between two degenerate states with equal residence time. Using the Arrhenius relation and an attempt frequency of 10^{13}, we estimate that a Si-Si or Ge-Ge ad-dimer will rock at a frequency of at least 6×10^8 per second at room temperature, which is much too fast to be resolved by STM. Consequently, the rocking motion smears out the buckling of the ad-dimer; the Si-Si and Ge-Ge ad-dimers should appear as a symmetric bean shape in a STM image (i.e., the average image over the two degenerate states), as has been seen for a Si-Si ad-dimer [5]. (It is well known that, for the same reason, the Si(001) substrate surface dimers appear as a bean shape in STM at room temperature.) A mixed Ge-Si ad-dimer, however, has to rock between two states differing in energy by 0.16 eV. Detailed balance requires that the ad-dimer stays in the low-energy state with Ge at the up-position; the
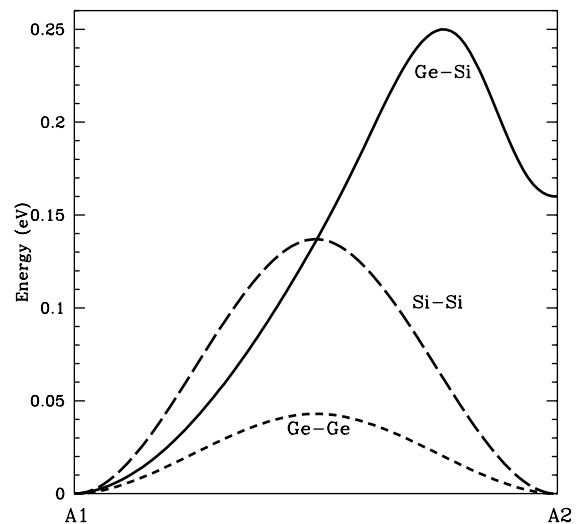

FIG. 2. Energy variations along the rocking pathways. The solid line corresponds to the mixed Ge-Si ad-dimer. The long-dashed line corresponds to the Si-Si ad-dimer. The short-dashed line corresponds to the Ge-Ge ad-dimer.

probability of appearing in the low-energy state is about 500 times higher than in the high-energy state, according to the Boltzmann distribution.

We can therefore conclude from the calculations that the tilted ad-dimer observed by STM in Fig. 1 must be a mixed Ge-Si ad-dimer. The tilted appearance provides us with a simple and unique method for its identification. The formation of a large amount of mixed Ge-Si ad-dimers during the deposition of Ge on Si(001) indicates the ease with which a deposited Ge atom can exchange with substrate Si atoms [17]. Energy calculations also show that the formation energy of a mixed Ge-Si ad-dimer is lower than the average formation energy of a Si-Si and a Ge-Ge ad-dimer [21]. Furthermore, the calculation implies that the observed rocking behavior of such a mixed Ge-Si ad-dimer in Fig. 1 cannot be a true rocking motion but is, instead, more likely due to a 180° rotation of the ad-dimer.

In order to search for the optimal pathway, we have performed extensive calculations to map out a potential-energy surface (PES) for a Ge-Si ad-dimer rotation, as shown in Fig. 3. Because of the mirror symmetry, the PES is constructed only over a 90° region rotating from the initial position A (the ad-dimer parallel to the substrate dimer row, see Fig. 4A) to position B (the ad-dimer perpendicular to the substrate dimer row, see Fig. 4B). U and D denote the up- and down-atoms of the dimer at the initial position, respectively. We take the intersection of the ad-dimers at the positions A and B projected into the substrate surface as the coordinate origin O (see the upper inset of Fig. 3). α and β denote the rotation angles of the U and the D atoms, respectively, about the origin in a plane parallel to the substrate surface. The PES is generated by a 7×7 grid mesh, amounting to about fifty independent configurations to be computed. For each configuration, all atoms are fully relaxed with the U and D atoms constrained along the lines with rotating angles of α and β.

The most favorable rotation pathway for a Ge-Si ad-dimer on Si(001) is along path 1, which starts from point A, goes through point $M1$, point $M2$, saddle point S, point $M3$, and ends at point B, as depicted in Fig. 3. The saddle point is further confirmed by calculations starting from the configurations slightly away from the saddle point, which relax the ad-dimer to stable configurations at either position A or position B. The rotational energy barrier along path 1 is 0.74 eV, which is in very good agreement with the experimental value of 0.82 eV, derived from the temperature dependent rate of the changing appearance (from tilting left to right) measured by AT-STM. Therefore, the rocking appearance of a mixed Ge-Si ad-dimer, tilting left to right observed in STM, actually reflects a 180° rotational motion of the ad-dimer rather than a true rocking motion. For a 180° rotation, the ad-dimer will need to pass through the intermediate state of point B, which is found to be 0.112 eV higher in energy than the starting and the ending positions A. Thus, the residence time at point B is about 80 times shorter
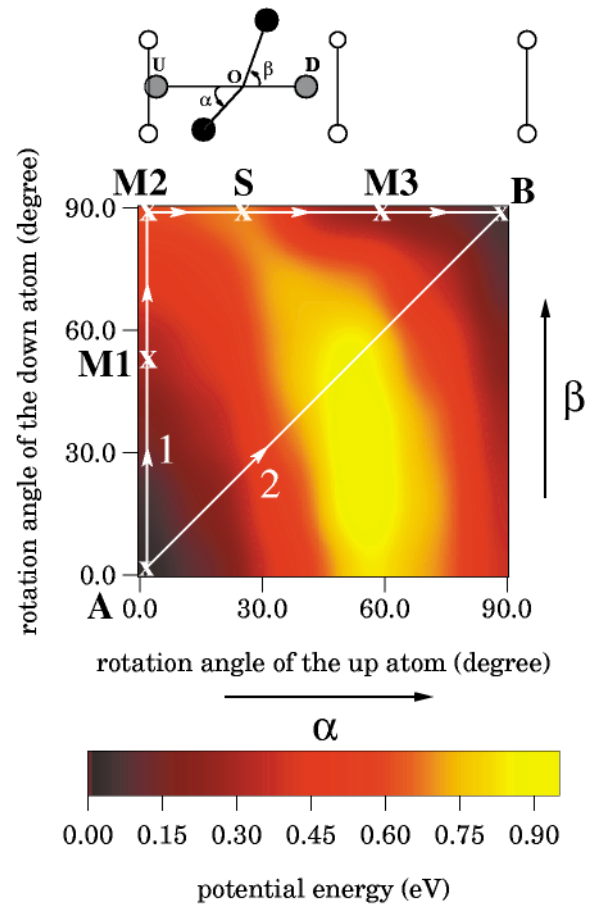

FIG. 3 (color). Potential-energy surface for the rotation of a mixed Ge-Si ad-dimer on top of a dimer row on Si(001). Path 1 represents the lowest-energy-barrier rotational pathway. Path 2 represents the "rigid" rotation. The upper inset shows schematically the notations used for the ad-dimer rotation. The open circles represent the atoms of the Si(001) substrate dimer row. The gray filled circles represent the ad-dimer at its initial position A and the black filled circles represent the ad-dimer at an intermediate rotating state. U and D indicate the up- and down-atoms, respectively. α and β denote the rotation angle of the U and D atoms, respectively, from their initial positions.

than at point A at room temperature, consistent with the experimental observation that very few ad-dimers are observed in configurations B.

The corresponding principal atomic configurations along path 1 are displayed in Fig. 4. The ad-dimer rotates via a piecewise mechanism with one atom rotating at a time. From A to $M2$, the D atom rotates while the U atom remains unrotating about the origin. At point $M2$, the D atom has rotated 90°. Beyond point $M2$, the D atom remains at the 90° position, i.e., on the line perpendicular to the substrate dimer row, while the U atom starts rotating. The system passes through saddle point S, point $M3$, and reaches point B. By rotating one atom at a time, the ad-dimer has at least one atom retaining its optimal bonding with the substrate atoms to lower the rotational energy barrier. In contrast, if the ad-dimer were rotated
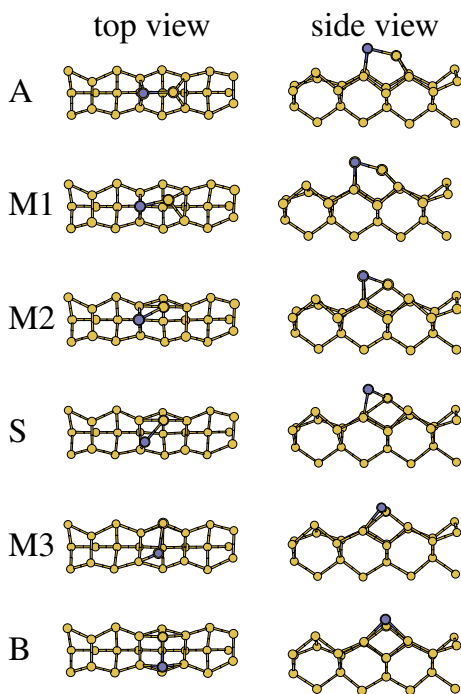
top view   side view

A

M1

M2

S

M3

B

FIG. 4 (color). Principal atomic geometries on the piecewise rotation pathway shown by line 1 in Fig. 3. The blue filled circles represent Ge, the yellow filled circles represent Si.

rigidly with the U and D atoms moving in a concerted motion (path 2 shown in Fig. 3), the energy barrier would be much higher, 0.92 eV. Similar calculations show that the piecewise rotational mechanism discussed here is also the lowest-energy-barrier pathway for the rotation of pure Si-Si and Ge-Ge ad-dimers [21].

In conclusion, we have carried out extensive first-principles calculations of the energetics and dynamics of Si-Si, Ge-Ge, and Ge-Si ad-dimers on top of a Si(001) dimer row, in reference to STM observations. The broken symmetry in a hetero-ad-dimer (Ge-Si) makes its dynamic appearance at room temperature distinctively different from that of a homo-ad-dimer (Si-Si or Ge-Ge). This dynamic appearance provides us with a unique and simple method for recognizing mixed Ge-Si ad-dimers during the deposition of Ge on Si(001). The abundance of mixed Ge-Si ad-dimers indicates a rather low-energy barrier for deposited Ge atoms exchanging with substrate Si atoms. We demonstrate that the rocking of a mixed Ge-Si ad-dimer observed in STM actually results from a 180° rotational motion of the ad-dimer rather than from a true rocking motion. The lowest-energy-barrier pathway for rotation proceeds via a piecewise mechanism, with one atom rotating at a time instead of a concerted rigid rotation of both atoms. Such a piecewise mechanism might be a general feature of dynamic processes of metastable clusters on surfaces [13,22].

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