Dimer-breaking-assisted exchange mechanism in surfactant-mediated epitaxial growth of Ge on Si(001): *Ab initio* total energy calculations

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We report *ab initio* identification of the exchange pathways in surfactant-mediated growth of Ge on Si(001) surface. Throughout the exchange process, a dimer-breaking-assisted exchange (DBAE) mechanism is revealed due to the lowering of energy barriers. When one Ge dimer is adsorbed on the surfactant dimer row or in the trough between surfactant dimer rows, the Ge dimer can both exchange one by one with the subsurface surfactant atoms through the DBAE process. The DBAE process together with a *rolling-over* process of the surface diffusion can lead to the nucleation of Ge under the surfactant layer, giving a fully natural explanation for the experimental observation.

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Using a surfactant to control the growth mode is a promising method to create high-quality heterostructures.[1–3] Group-V elements (e.g., As or Sb and more recently Bi) have been used as surfactants to modify the growth mode of Ge epitaxial films on Si(001) for several years.[4–8] During growth, surfactant atoms segregate from the interface to the surface, and the rapid exchange between Ge and surfactant atoms lets the growing species incorporate in a subsurface site rapidly. Experimentally, one found that the Ge incorporation on the surfactant-covered Si(001) occurs in a highly local process without significant step flow.[5] Since then, several models[5,9–11] have been proposed to understand the kinetics of the dimer exchange processes between the growing species and the surfactants. However, the details of the kinetics (e.g., diffusion and exchange processes) in those dimer exchange mechanisms are controversial and ambiguous in the previous studies, which are decisive in determining the growth mode.[12–15]

In this study, we report a detailed study of the energetics and kinetics of the processes for the surfactant (Sb and Bi) mediated growth of Ge on Si(001) surfaces using first-principles total energy calculations. A dimer-breaking-assisted exchange (DBAE) mechanism is revealed. The Ge dimer which is adsorbed on the dimer rows can exchange with the subsurface surfactant (Sb or Bi) atoms easily with the DBAE process. On the other hand, the Ge dimer being adsorbed in the trough can translate into the most stable state through the DBAE process of dimer exchange and a *rolling-over* process of surface diffusion. The DBAE process together with the rolling-over process of the surface diffusion can lead to the nucleation of Ge under the surfactant layer, which provides a natural explanation for the experimental observation.

The reported *ab initio* total energy calculations are carried out using VASP code,[16] which is based on an iterative solution of the Kohn-Sham equations of density-functional theory in a plane-wave basis set with Vanderbilt ultrasoft pseudopotentials.[17] We employ a plane-wave basis set with a cutoff energy of 220 eV and the generalized gradient approximation.[18] The Brillouin zone is sampled using the Monkhorst-Pack scheme.[19] We use a supercell with a 4×4 unit cell in the *XY* plane (16 atoms per layer) and six layers of silicon in the *Z* direction. One layer of hydrogen is set to passivate the back surface of the Si substrate with a vacuum layer of about 10 Å in the *Z* direction. Throughout the present calculations, only the bottom Si layer is fixed at the bulk structure, while the other Si atoms, surfactant atoms, and Ge atoms are fully relaxed. The energy minimization is done over the atomic and electronic degrees of freedom using the conjugate gradient iterative technique with four *k* points in the surface Brillouin zone.

We first investigate the stabilities of one Ge ad-dimer on the surfactant-covered Si(001) surfaces. Four principle binding configurations are considered.[20] There are two most stable adsorption sites: one is on the surfactant dimer rows (A) and the other one is in the trough between the dimer rows (B) as shown in Fig. 1. The binding energies per Ge ad-dimer on the surfactant-covered Si(001) surfaces are

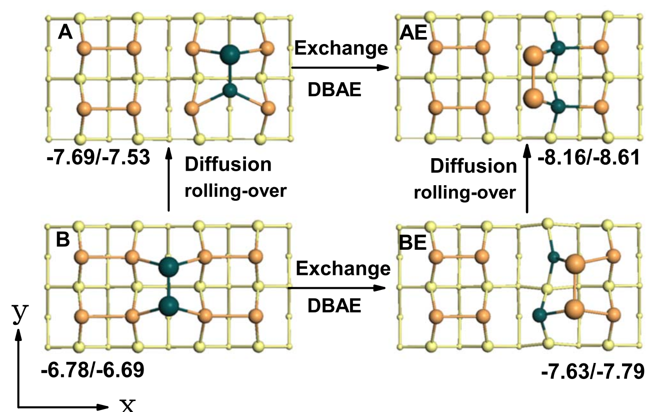

FIG. 1. (Color online) Optimized configurations and the binding energies (in eV) defined in the text for one Ge dimer on the Sb- and Bi-covered Si(001) surfaces. Green, yellow, and light yellow balls represent Ge, surfactants (Sb and Bi), and Si atoms, respectively.

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shown in Fig. 1, which are defined as $E_b=(E_T-E_0)/n$, where E_T is the cohesive energy of the surfactant-covered Si(001) with n Ge ad-dimers, which is the energy difference between the Ge/Sb/Si(001) system and its isolated atoms, E_0 is the cohesive energy of the corresponding surfactant-covered Si(001), and n is the number of Ge ad-dimers. Configuration A is more stable by 0.90 and 0.84 eV than configuration B on the Sb- and Bi-covered Si(001) surfaces, respectively. When one Ge ad-dimer is on the surfactant dimer row (A), it is largely buckled and the height differences are 0.95 and 0.96 Å for the surfactants Sb and Bi, respectively. The buckled Ge ad-dimer bond lengths are 2.50 Å for Sb system and 2.47 Å for Bi system. The buckled state is thought to be stabilized by a rehybridization of the dangling orbitals, accompanied by charge transfer.[20,21]

After the Ge dimer is exchanged with the subsurface surfactant atoms, there are two possible structures AE and BE, as shown in Fig. 1. Configuration AE is more stable by 0.54 eV (or 0.82 eV) than configuration BE when surfactant Sb (or Bi) is used. The energy gains due to the exchange processes are 0.47 eV (A→AE) and 0.85 eV (B→BE) for the surfactant Sb and 1.08 eV (A→AE) and 1.10 eV (B→BE) for the surfactant Bi, respectively. The driving force of the site exchange is the reducing of the dangling bonds on the Ge atoms which are replaced by long pairs on the replaced surfactant atoms in configuration A for A→AE, or the reducing of the weak bonds between surfactant atoms in configuration B for A→BE.

We now study the dynamic behavior of Ge ad-dimers on the Sb- and Bi-covered Si(001) surfaces. To get a systemic understanding, two possible dimer exchange processes, A→AE and B→BE, are both considered. As to the exchange process A→AE, since the Ge ad-dimer in structure A is highly buckled and the two Ge atoms are nonequivalent, we here propose a DBAE pathway that the lower Ge atom, which is much closer to the subsurface Si atoms, is exchanged with the surfactant atom first, and then the other Ge atom incorporates under the surfactant layer in succession. To search for a reaction path, we get the energies of the system by fixing only the X direction of the Ge atom being exchanged while relaxing all other atoms, with starting configurations along the straight exchange path. The configurations near the saddle points have been carefully examined. Near the saddle points, the intervals of the X coordinates of the Ge atom being exchanged are less than 0.06 Å, and the energy differences between the neighboring points are less than 0.10 eV. Because there are constraints in our calculation, the exchange barriers we got are the upper limits to the true barriers.

The pathway and the relative energy changes of the DBAE process A→AE between Ge and Sb atoms are shown in Fig. 2. We first move the lower Ge atom toward the nearby Sb atom (A→A1→A2). When the Ge atom starts to interact with a second layer Si atom, the bonding between the repelled Sb atom and the second layer Si atoms is weakened, as well as the bonding between the two Ge atoms (A1). While the lower Ge atom further moves toward the nearby Sb atom, the bonding between the two Ge atoms is broken, as well as the bonding between the being substituted

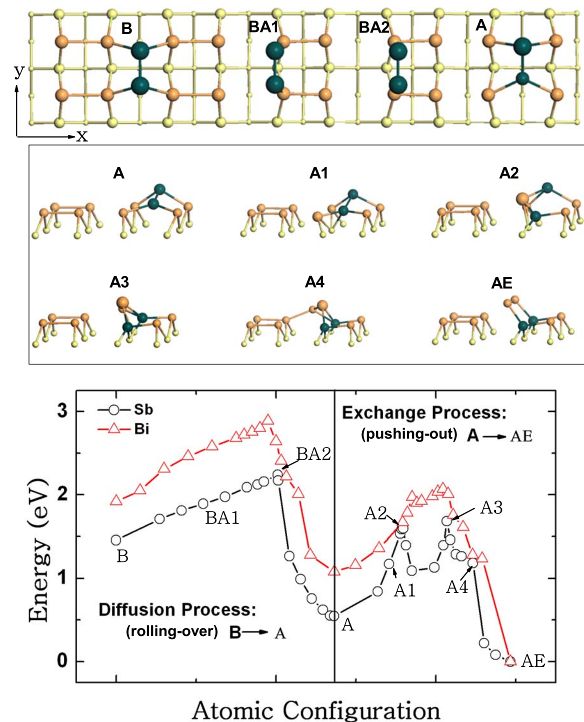

FIG. 2. (Color online) (a) The diffusion pathway B→A under rolling-over process and the dimer exchange pathway A→AE under DBAE mechanism. Green, yellow, and light yellow balls represent Ge, Sb, and Si atoms, respectively. (b) The relative energy changes along the pathways.

Sb atom and the Si atoms (A2). This requires an energy cost of 1.05 eV. In the process A1→A2, while the Ge atom moves toward the nearby Sb atoms, we move the Sb atom being exchanged up toward the site in the seed geometry simultaneously. Next, the other Ge atom exchanges with the Sb atom through a similar exchange process (A2→A3→A4→AE) as described above, and a barrier of only 0.32 eV has to be overcome. Similar behavior is also found for the Bi system, and the energy barrier is estimated to be 0.99 eV, as shown in Fig. 2.

In order to prove the necessity of the DBAE mechanism in the dimer exchange process, we have examined that the two atoms of the Ge dimer on the dimer row are simultaneously exchanged with the subsurface Sb atoms. We find that the energy barrier is higher than 1.2 eV, which is indeed larger than the DBAE process. The lower energy barrier of the DBAE process results from the less bonds being broken in the process. In the DBAE process, there are only two bonds (one Sb-Si bond and one Ge-Ge bond) needed to be broken simultaneously, while there are three bonds being broken when the two atoms of the Ge dimer on the dimer row are simultaneously exchanged. Furthermore, we have also examined the diffusion B→A with a rolling-over process as shown in Fig. 2. The energy barriers are 0.78 and 0.97 eV for surfactants Sb and Bi, respectively. Considering the energy difference between configurations A and B (see Fig. 1), we can also estimate the counterreaction barriers from A to B to be 1.68 and 1.81 eV per Ge ad-dimer for Sb and Bi, respectively. So, it is an easy pathway for a Ge ad-

TABLE I. The exchange and diffusion energy barriers (in eV) during the dimer exchange processes for Ge ad-dimers on the surfactant (Sb,Bi)-covered Si(001) surface.

	Sb	Bi
	Exchange barrier	
A → AE	1.05	0.99
B → BE	0.87	0.63
T1 → TE1	0.95	0.92
T2 → TE2	0.93	0.42
T3 → TE3	0.99	0.86
	Diffusion barrier	
B → A	0.78	0.97
T2 → T3	0.37	0.60
BE → AE	0.93	0.55

dimer to diffuse from the site in the trough to the most stable site on the dimer row, while it is very difficult for Ge dimers to diffuse along the opposite direction. The relaxation and dimer breaking of Sb dimers because of Ge ad-dimers' adsorption may slow down the diffusion of Ge dimers perpendicular to the dimer rows and lead to the DBAE mechanism. Thus, a dimer exchange path B → A → AE is determined in the Ge growth on the Sb- or Bi-covered Si(001) surface.

We next examine the other exchange path B → BE. The exchange path under the DBAE mechanism is similar to the exchange path A → AE. We find that the exchange barrier is 0.87 eV for the Sb system. On the other hand, if the two atoms of the Ge ad-dimer are simultaneously exchanged with the subsurface Sb atoms, the exchange barrier from B to BE is 1.07 eV, which is much larger than the exchange barrier (0.87 eV) under the DBAE mechanism. So, in the study about the energy barrier of the dimer exchange process, the DBAE mechanism is preferred. We have also calculated the exchange barrier on the Bi-covered Si(001) with DBAE mechanism, which is only 0.63 eV. So, the site exchange process B → BE is another possible pathway. Moreover, the exchanged surfactant dimer in configuration BE will diffuse into the more stable configuration AE through a rolling-over process with the energy barriers of 0.93 and 0.55 eV for the surfactants Sb and Bi, respectively, and the stable configuration AE is reached as shown in Fig. 1.

Based on the above results, the DBAE mechanism is revealed. Two possible pathways, B → A → AE and B → BE → AE, are found in our calculations. Because of the difference of the atomic sizes of Sb and Bi,[22,23] the exchange barrier for a Ge ad-dimer on the Sb-covered Si(001) is larger than on the Bi-covered Si(001), while the diffusion barrier for a Ge ad-dimer on the Sb-covered Si(001) is smaller, as shown in Table I. This results in the different preference of the two pathways when Sb and Bi are used as surfactants. On the Sb-covered Si(001), B → A → AE is preferred, while on the Bi-covered Si(001), B → BE → AE is preferred. These two exchange paths can initiate the site exchange process and eventually lead to the nucleation of Ge under the surfactant layer.

In order to gain an insight into the nucleation of Ge layer under the surfactant layer, we have studied the exchange processes for a second Ge ad-dimer on structure AE as shown in Fig. 3. There are three adsorption sites (T1, T2, and T3) for the second Ge ad-dimer near the exchanged surfactant dimer, and the corresponding exchanged configurations are TE1, TE2, and TE3. In fact, configurations T1 and TE1 have been mentioned in the study of Yu and Oshiyama.[9] In configuration T2, the behavior of the additional Ge ad-dimer being

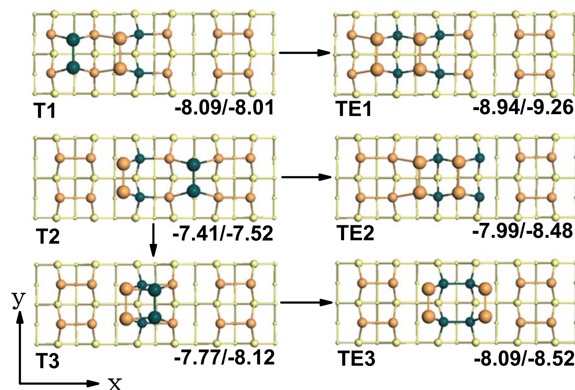

FIG. 3. (Color online) Optimized configurations and the binding energies (in eV) defined in the text for two Ge dimers on the Sb- and Bi-covered Si(001) surfaces. T1, T2, and T3 show the second Ge ad-dimer position on structure AE after the first Ge ad-dimer exchanged; TE1, TE2, and TE3 are the exchanged configurations of T1, T2, and T3, respectively. Green, yellow, and light yellow balls represent Ge, surfactants (Sb and Bi), and Si atoms, respectively.

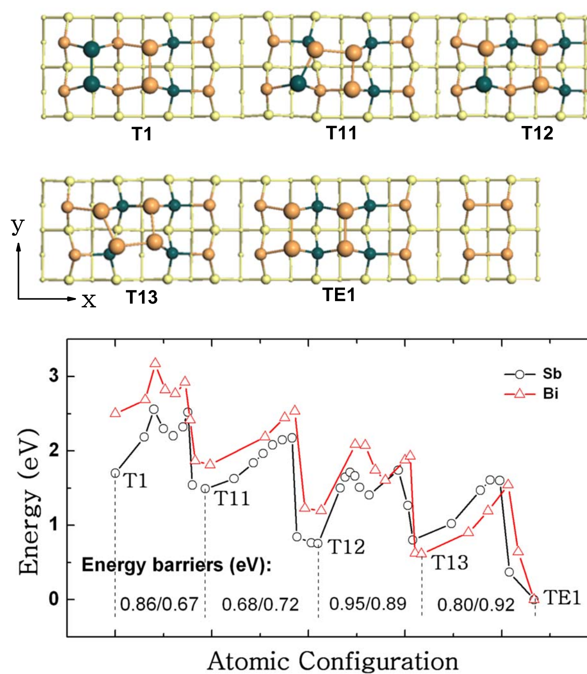

FIG. 4. (Color online) (a) The dimer exchange pathway T1 → TE1 under the DBAE mechanism. (b) The relative energy changes along the pathway. The energy barriers during the dimer exchange process on the Sb- and Bi-covered Si(001) surfaces are also listed.

adsorbed in the trough is similar to the Ge dimer in configuration B, and there are two possible pathways: T2→TE2 and T2→T3→TE3. The energy barriers of the diffusion and the dimer exchange processes are shown in Table I. For T1→TE1, the exchange process is studied by Lee *et al.*,[11] with the two Ge atoms exchanged simultaneously and the energy barrier is estimated more than 2 eV, which is almost dynamically prohibited. However, we propose here another exchange process for T1→TE1 under the DBAE mechanism together with rolling-over process as shown in Fig. 4. We find that the exchange process T1→TE1 also happens, and the energy barriers are 0.95 and 0.92 eV for the surfactants Sb and Bi, respectively. Moreover, based on the exchange mechanism for one or two Ge ad-dimers mentioned above, we can deduce the exchange process for three or more Ge ad-dimers through the *multiple DBAE+rolling-over* process, which eventually leads to the nucleation of Ge under the surfactant layer.

In summary, we have studied the kinetic processes in surfactants (Sb and Bi) mediated epitaxial growth of Ge on Si(001). Throughout this study, one basic dimer-breaking-assisted exchange (DBAE) mechanism is revealed due to the lowering of energy barriers.[24,25] Considering both the DBAE process and the rolling-over processes of the surface diffusion, two possible pathways are found in our calculations. One pathway, B→A→AE, is preferred on the Sb-covered Si(001), while the other one, B→BE→AE, is preferred on the Bi-covered Si(001) due to the difference of atom sizes between Sb and Bi. The DBAE process together with the rolling-over process of the surface diffusion can lead to the nucleation of Ge under the surfactant layer. These results provide an excellent account for experimental observations and elucidate their underlying atomistic origin that may offer useful insights for other surface reaction processes.

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