Adsorption, diffusion, and site exchange for Ge ad-dimers on Sb-covered Si(001) from first-principles total-energy calculations

En-Zuo Liu,[1] Chong-Yu Wang,[1,2] and Jian-Tao Wang[3]
[1]*Department of Physics, Tsinghua University, Beijing 100084, China*
[2]*The International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China*
[3]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*
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The adsorption and diffusion of Ge adatoms and ad-dimers on the one-monolayer Sb-covered Si(001) surface are studied using first-principles total-energy calculations. It is shown that Ge adatoms and ad-dimers can both break Sb dimers because of the weak bonding of the Sb dimers on Si(001). As a result, the most stable sites are both on the Sb dimer rows for Ge adatoms and ad-dimers, which is in significant contrast to the conventional picture that the most stable site for a Ge ad-dimer is in the trough between the group-V element dimer rows. We have also examined the energetics of the site exchange between Ge and Sb atoms for the surfactant-mediated growth and find that Ge ad-dimers tend to exchange with the subsurface Sb atoms one by one perpendicular to the surface dimer rows.

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I. INTRODUCTION

The use of surfactants to modify the growth mode of epitaxial films has been of interest for several years.[1] Surfactants can change the surface energetics and kinetics which determine the epitaxial film growth mode. So using a surfactant to control the growth mode is a promising method to create high-quality heterostructures. Group-V elements such as As, Sb, and Bi are well known to be used to create high-quality Ge/Si heterostructures.[1–5] Adding one-monolayer (1-ML) group-V element capping layer on Si substrate before the Ge deposition can improve the layer-by-layer growth mode and suppress islanding. At the same time, the Ge/Si intermixing at the interface is strongly suppressed.[2]

The analysis of the surface free energy as a function of chemical potential has given thermodynamic evidence of the surfactant-aided layer-by-layer growth.[6] On the other hand, during growth, surfactant atoms segregate from the interface to the surface, and the rapid exchange between Ge and surfactant atoms allow Ge adatoms to incorporate in the subsurface sites rapidly. Thus the diffusion of the growing species is restricted and the islanding is prevented. Since group-V element strongly reduces the surface free energy, the site exchange is energetically understandable.[1] However, the microscopic details of the site exchange between growing species and surfactants are still controversial.

Based on experimental observation, Tromp and Reuter found that the Ge incorporation on the surfactant-covered surface occurs in a highly local process without significant step flow, which indicates that the Ge incorporation is unrelated to the presence of steps, and proposed a two-dimer correlated exchange process.[7] In their model, the Ge dimers are first formed on the broken surfactant dimers. However, Yu and Oshiyama[8] performed theoretical calculations and found that Ge dimers are formed not on As dimers, but in the trough between the As dimer rows, and proposed a one-dimer exchange process. Using scattered MeV ion energy distributions, Boshart *et al.*[9] investigated the bonding geometry of Ge and Sb on Si(001). They found that the above two models do not fit the experimental data well and proposed an all-dimer model. Furthermore, the results of Boshart *et al.*[9] also indicate that there may be new initial bonding states not investigated so far.

In this study, we investigate the microscopic surfactant effects of Sb on the Ge/Si(001) heteroepitaxy growth using first-principles calculations. We find that the most stable sites for Ge adatoms and ad-dimers are both on the Sb dimer rows but not in the trough between the Sb dimer rows. We have also examined the energetics of the site exchange between Ge and Sb atoms in the surfactant-mediated growth and find that Ge ad-dimers tend to exchange with the subsurface Sb atoms one by one perpendicular to the Sb dimer rows.

II. METHOD AND MODELS

We have performed the *ab initio* total energy calculations using VASP (Vienna *ab initio* simulation package),[10] 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.[11] We employ a plane-wave basis set with a cutoff energy of 220 eV and the generalized gradient approximation (GGA).[12] The Brillouin zone is sampled using the Monkhorst-Pack scheme.[13] We use a supercell with a 8×2 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. The 1-ML Sb-covered Si(001) substrate has a simple (2×1)-Sb structure with Sb dimers having a bond length of 2.97 Å. Throughout the present calculations, only the bottom Si layer is fixed at the bulk structure, while the other Ge, Sb, and Si 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.

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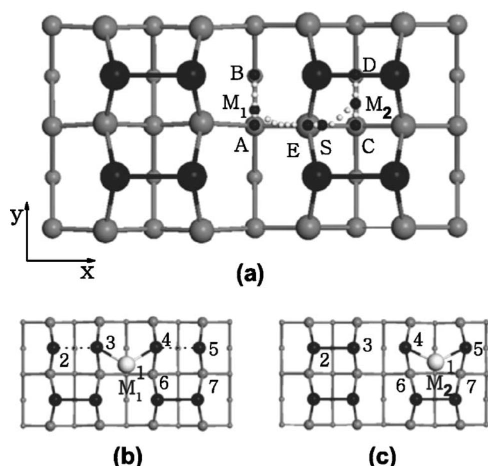

FIG. 1. (a) Atomic models for the diffusion of a Ge adatom on the 1-ML Sb-covered Si(001) surface. Black balls, gray balls, and small gray balls represent the Sb, Si, and inner-layer Si atoms, respectively. In an irreducible quarter $ABDC$, the small white balls indicate the diffusion pathways we have studied and the labeled small black balls indicate the special sites mentioned in the text; (b) and (c) are the fully relaxed geometries when one Ge atom (the white ball) is adsorbed at the (local) minimum sites M_1 and M_2, respectively. The dotted lines in (b) indicate weak bonds.

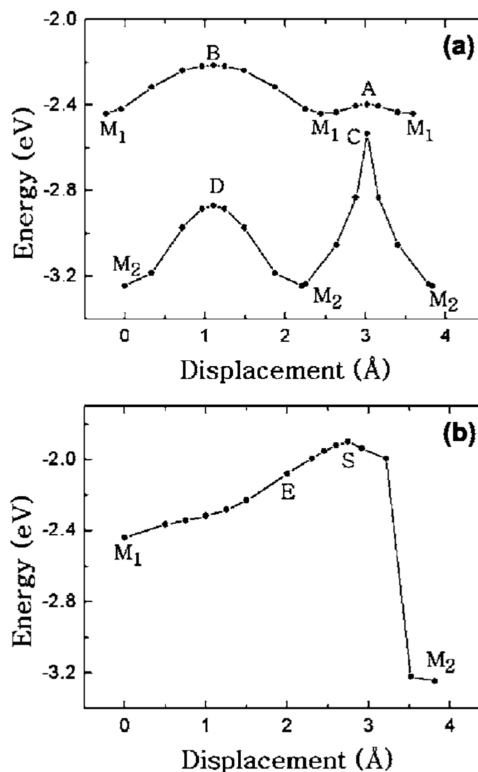

FIG. 2. The binding energies of one Ge adatom along different diffusion pathways [see Fig. 1(a)]: (a) $P1(M_2DM_2CM_2)$ and $P2(M_1AM_1BM_1)$ which are along the Sb dimer rows; (b) $P3(M_1ESM_2)$ which is across the dimer rows.

III. RESULTS AND DISCUSSION

A. Adsorption and diffusion of a single Ge adatom

In this section, we study the adsorption and diffusion of Ge atoms on the 1-ML Sb-covered Si(001) surface. In order to find the stable sites and the possible diffusion pathways of the Ge adatoms, we have calculated the binding energies of a Ge adatom along the paths AB, CD, and AC (see Fig. 1) where the stable adsorption sites for Ge adatoms are possibly located by fixing the Y or X direction (along the paths) of the Ge adatom, while relaxing all the surrounding atoms and the other two directions of the Ge adatom. The calculated geometries and binding energies are shown in Table I and Fig. 2. The binding energy per Ge atom is defined as

$$E_b = (E_T - E_0)/n, \tag{1}$$

where E_T is the total binding energy with n Ge atoms on the 1-ML Sb-covered Si(001) surface, E_0 is the total binding energy of the 1-ML Sb-covered Si(001), and n is the number of Ge adatoms. We find that there exist two types of symmetric minimum sites: M_1 in the trough between the Sb dimer rows and M_2 on the Sb dimer row as shown in Figs. 1(b) and 1(c). Site M_2 is more stable than site M_1 by 0.81 eV due to the weakened Sb-Sb bonds [Sb2-Sb3 and Sb4-Sb5 in Fig. 1(b)]. Interestingly, we note that when one Ge atom is adsorbed on the Sb dimer row, the Ge atom can break the Sb dimers without a barrier, whereas for the adsorption on the As-covered Si(001), a barrier of 0.7 eV has to overcome for breaking the As dimers.[8] Such different behaviors in the systems Ge/Sb/Si(001) and Ge/As/Si(001) can be understood from the different bonding behaviors of group-V element

TABLE I. The binding energies E_b (eV) of a single Ge adatom and the vertical heights H (Å) of the adatom from the Sb layer, when the Ge atom is adsorbed at the special sites on the 1-ML Sb-covered Si(001) surface, as shown in Fig. 1. Also the calculated structural parameters (Å) when one Ge adatom is at the minimum sites M_1 and M_2. The atom numbers refer to Fig. 1(b) and 1(c). "Sub" corresponds to the clean 1-ML Sb-covered Si(001) surface.

Site	A	B	C	D	E	S	M_1	M_2
E_b (eV)	−2.40	−2.22	−2.53	−2.87	−2.08	−1.90	−2.44	−3.25
H (Å)	1.04	1.57	1.19	1.49	1.91	2.03	1.01	0.94

	Ge1-Sb4	Sb2-Sb3	Sb4-Si6	Sb5-Si7
M_1	2.80	3.26	2.56	2.59
M_2	2.71	3.00	2.61	2.61
Sub		2.97	2.60	2.60

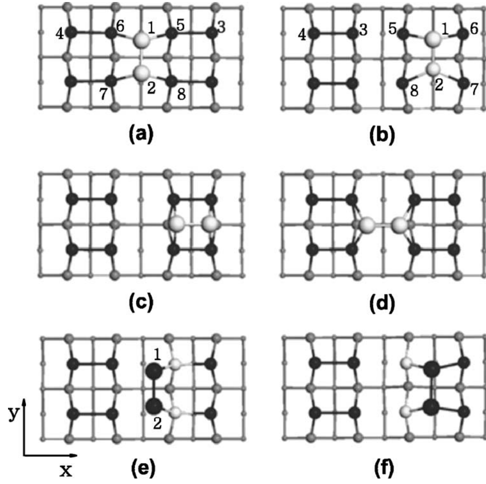

FIG. 3. The relaxed geometries for one Ge ad-dimer on the 1-ML Sb-covered Si(001) surface. (a), (b), (c), and (d) are the four principal initial binding configurations for one Ge ad-dimer on the 1-ML Sb-covered Si(001); (e) and (f) are the seed geometry and the geometry with the exchanged Sb dimer on the Sb dimer row, respectively, after the Ge ad-dimer in structure (b) is exchanged with the subsurface Sb atoms. White balls, black balls, and gray balls represent Ge, Sb, and Si atoms, respectively.

dimers. In fact, the dimerization of the Sb atoms to form the 2×1 reconstructed Si(001) surface leads to an energy gain of 0.41 eV per dimer, relative to the 1×1 surface, while for As dimers the energy gain is 0.84 eV.

In Fig. 2, the calculated binding energies of one Ge adatom along three diffusion pathways are shown. $P1(M_2DM_2CM_2)$ and $P2(M_1AM_1BM_1)$ are along the Sb dimer rows, and $P3(M_1ESM_2)$ is across the dimer rows. In the calculation for finding the energy barriers of one Ge adatom along the three diffusion paths, we calculate the binding energies of the Ge adatom along the paths by fixing only one direction of the Ge adatom (the Y direction for $P1$ and $P2$ and the X direction for $P3$) while relaxing all the degrees of freedom of the other atoms and the other two directions of the Ge adatom. We find five saddle points (A,B,C,D,S) as listed in Table I. For the path $P1$ on the Sb dimer rows, the energy barrier is 0.71 eV. For the path $P2$ in the trough, the energy barrier is only 0.22 eV, as shown in Fig. 2(a). On the other hand, the energy barrier for a Ge atom to move from M_1 to M_2 across the Sb dimer rows is 0.54 eV, while the counterreaction barrier from M_2 to M_1 is 1.35 eV, as shown in Fig. 2(b). So when a Ge adatom is adsorbed in the trough, it can easily move up onto the Sb dimer row, whereas when a Ge adatom is adsorbed on a dimer row, it can move along the dimer row, but hardly move across the dimer row.

B. Adsorption and diffusion of one Ge ad-dimer

Next we study the adsorption of one Ge ad-dimer on the 1-ML Sb-covered Si(001) surface. In our calculations, four principal binding configurations are considered, as shown in Figs. 3(a)–3(d). The calculated binding energies are shown in Table II. The most stable adsorption site for one Ge ad-dimer is on the Sb dimer rows with the Sb dimers broken [Fig. 3(b)], which is more stable by 0.91 eV per dimer than the site in the trough between the Sb dimer rows [Fig. 3(a)], similar to the single-Ge-adatom behavior as stated above. This is in agreement with Tromp and Reuter's suggestion.[7] On the other hand, for comparison, we have also studied the adsorption of one Ge ad-dimer on the 1-ML As-covered Si(001) and find that the Ge ad-dimer is more favorable in the trough between the As dimer rows than on the As dimer rows by 0.88 eV, in agreement with Yu and Oshiyama's results.[8] The different behavior of one Ge dimer on the As/Si(001) surface and on the Sb/Si(001) surface can be related to the difference in atomic size mismatch and the reactions between As-Si and Sb-Si. Two compounds AsSi and As_2Si exist in the equilibrium phase diagram,[14,15] while no counterpart exists in the Sb-Sicase.

TABLE II. The binding energies E_b (eV) per Ge atom when one Ge dimer is adsorbed on the different sites of the 1-ML Sb-covered Si(001), as shown in Fig. 3. Also the structure parameters of the two most stable initial configurations Figs. 3(a) and 3(b). The atom numbering refers to Fig. 3.

	One Ge dimer				Site exchanged	
	(a)	(b)	(c)	(d)	(e)	(f)
E_b (eV)	−3.36	−3.81	−2.97	−3.11	−4.05	−3.78

Bond Length (Å)			Angle (deg)		
Bond	(a)	(b)	Angle	(a)	(b)
Ge1-Ge2	2.54	2.50	5-1-6	108.9	111.8
Ge1-Sb5	2.87	2.79	5-1-2	101.8	86.5
Ge2-Sb8	2.87	2.67	8-2-1	101.8	117.2
Sb4-Sb6	3.10		8-2-7	108.9	125.0
Sb3-Sb4		3.00			

In Table II, some local structure parameters of Figs. 3(a) and 3(b) are listed. In the structure in Fig. 3(b), the Sb-Sb bond length is 3.00 Å, which is only a little larger than the Sb-Sb bond length of the 1-ML Sb-covered Si(001) surface (2.97 Å). The average Sb-Ge bond length is about 2.73 Å, which is almost equal to the sum of the covalent radii of Ge and Sb atoms. However, the Sb-Sb and Sb-Ge bond lengths are 3.10 Å and 2.87 Å, respectively, when one Ge dimer is adsorbed in the trough between the Sb dimer rows [the structure in Fig. 3(a)]. So when one Ge dimer is adsorbed in the trough, there is a larger distortion in the structure, which makes the configuration less stable. A comparison of the band structures between the configurations in Figs. 3(a) and 3(b) shows that the two highest occupied states of the configuration (b) are pushed to lower energies. This determines the higher stability of Fig. 3(b). Furthermore, the Ge dimer on the Sb dimer rows is largely buckled with one Ge atom tending to form at the M_2 site, and the height difference is 0.95 Å. From Table II, comparing the geometry angles in Figs. 3(a) and 3(b), we can see that the Ge adatoms in Fig. 3(a) appear as sp^3-like hybridization while in Fig. 3(b) the lower Ge atom approaches planar sp^2-like hybridization. Due to the dimer buckling, the lower Ge atom obtains an occupied planar sp^2 configuration and an empty p_z dangling bond,

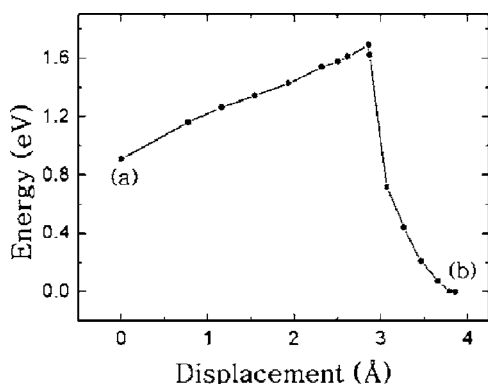

FIG. 4. The variation of the relative total energy when one Ge ad-dimer diffuses from the site in the trough between the Sb dimer rows [the site in structure Fig. 3(a)] to the site on the Sb dimer row [the site in structure Fig. 3(b)] along the X direction.

while the upper Ge atom retains its sp^3 configuration, and all orbitals are doubly occupied. The shift of one electron into the "long pair configuration" on the upper Ge atom reduces the energy, and this is the driving force for the buckling.[16] Moreover, because of the reduction of dangling bonds when two Ge adatoms form one Ge ad-dimer on the surfactant-covered Si(001) surface, the energy gain per Ge dimer (7.62 eV—i.e., 3.81 eV per Ge atom) due to adsorption is significantly larger than the gain for a single Ge adatom (3.25 eV for the M_2 site). This result indicates that Ge atoms being adsorbed on the 1-ML Sb-covered Si(001) surface will preferably form dimers on the Sb dimer rows.

We have also examined the diffusion barrier of one Ge ad-dimer from the structure in Fig. 3(a) to the structure in Fig. 3(b) and find that the energy barrier is only 0.78 eV (Ref. 17) per Ge ad-dimer (see Fig. 4). In the diffusion process of the Ge ad-dimer, we suppose that the two Ge atoms move simultaneously along the X direction and calculate the binding energies of the Ge ad-dimer along the diffusion path by fixing only one direction of the two Ge adatoms (the X direction) while relaxing all the degrees of freedom of the other atoms and the other two directions of the Ge adatoms. Considering the energy difference between the structures Figs. 3(a) and 3(b) (see Table II), we can also estimate the counterreaction barrier from state (b) to (a) to be 1.69 eV per dimer. So it is very difficult for one Ge dimer to diffuse from the most stable site on the dimer rows to the site in the trough, while the opposite diffusion is an easy process.

By now we have determined the stabilities of the initial bonding states of one Ge adatom and one Ge ad-dimer on the 1-ML Sb-covered Si(001) surface, respectively. We have also tested and checked our calculations with different supercells[18] and find the changes of the energy differences between the adsorption configurations are about 0.05 eV. Since the energy differences between sites M_1 and M_2 in Fig. 1 and between structures (a) and (b) in Fig. 3 are much larger, ~0.8 eV, all the present results are reliable. However, in the calculation of Jiang *et al.*[19] by using the discrete variational X_α (DV-X_α) method, they reported that the most stable adsorption site is in the trough between the Sb dimer rows for both one Ge adatom and ad-dimer. This is contrary to our

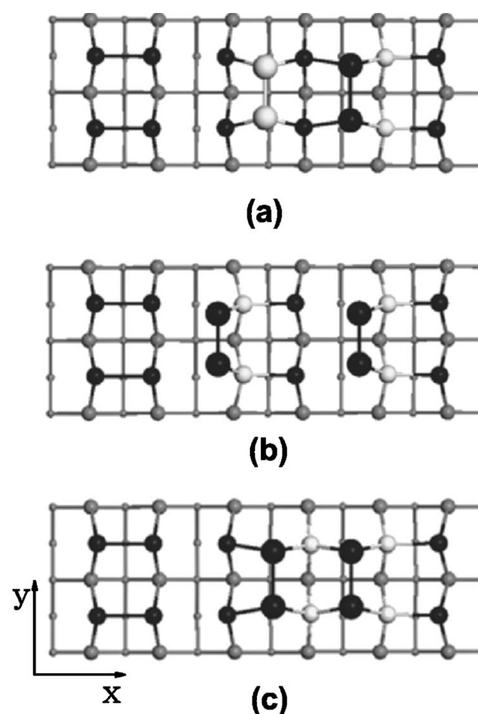

FIG. 5. The relaxed geometries for two Ge ad-dimers on the 1-ML Sb-covered Si(001) surface. (a) The geometry when one additional Ge dimer is adsorbed near the top-layer Sb dimer; (b) the geometry when the subsurface Sb atoms have been pushed up by the additional Ge ad-dimer of (a); (c) the final bonding geometry after two Ge dimers have exchanged with subsurface Sb atoms and the two Sb dimers are formed on the surface in a row along the X direction.

present results and previous studies,[8,20] that for a broken-dimer geometry, the most stable adsorption site is on the surfactant dimer rows.

C. Energetic analysis of the Ge/Sb site exchange

Finally, we discuss the possible Ge/Sb site exchange on the Sb-covered Si(001) surface. When the Ge dimer has exchanged with the subsurface Sb atoms in the structure in Fig. 3(b), there are two possible stable structures as shown in Figs. 3(e) and 3(f). According to the binding energies listed in Table II, the structure (e), the so-called seed geometry,[8] is more stable by 0.47 eV than the structure in Fig. 3(b), whereas the structure (f) whose Sb dimer is formed on the dimer row is less stable than the structure in Fig. 3(b). So the configuration (e) is the final state when one Ge ad-dimer is exchanged with the subsurface Sb atoms.

According to the above results, a new site exchange process may exist: when one Ge dimer is formed on the Sb dimer row [structure Fig. 3(b)], the Ge atoms will move towards the sites of the sublayer Sb atoms and repel the Sb atoms into the trough between the Sb dimer rows, and finally the seed geometry is formed in the trough [structure (e)]. In structure in Fig. 3(b), all Sb and Ge atoms are threefold coordinated, leaving a lone-pair orbital on each Sb atom and a dangling bond on each Ge atom. Whereas in structure (e)

after the site exchange, Ge atoms are fourfold coordinated. The top-layer Sb atoms 1 and 2 are bonded only to the subsurface Ge atoms and another neighboring Sb atom. But the distance between the two Sb atoms is only 2.70 Å, which is much shorter than the bond length of the Sb dimers (2.97 Å) in 1-ML Sb-covered Si(001) surface, and between the two Sb atoms, a π-bonded structure is formed, which reduces the total energy. So the driving force for the site exchange is reducing the number of dangling bonds.

To get a fully understanding of the Ge/Sb site exchange, we have also studied possible configurations with two Ge dimers on the 1-ML Sb-covered Si(001) surface (see Fig. 5). The calculated binding energies are −4.03, −4.05, and −4.45 eV per Ge atom for Figs. 5(a)–5(c), respectively. When we add a new Ge dimer on the adjacent Sb dimer row of the structure (e) in Fig. 3, we can obtain a new configuration [Fig. 5(a)]. The energy gain due to the new Ge addimer in the configuration Fig. 5(a) is 8.02 eV, which is much larger than the energy gain due to the adsorption of the Ge dimer in structure Fig. 3(b) (7.62 eV) where the Ge dimer adsorbs on the bare 1-ML Sb-covered Si(001) surface. After the site exchange of the additional Ge ad-dimer with the subsurface Sb atoms in Fig. 5(a), there may exist two possible configurations [Figs. 5(b) and 5(c)]. Here, Fig. 5(b) is indeed similar to the structure (e) in Fig. 3 with the same binding energy, −4.05 eV per Ge atom. We find that Fig. 5(c) is energetically more favorable by 1.60 eV than Fig. 5(b). So after two Ge ad-dimers have exchanged with the subsurface Sb atoms, the final bonding configuration is Fig. 5(c), which is the same as the experimental result for Ge/Sb/Sicase.[9] This also indicates that the Ge/Sb site exchange tends one by one along the X direction. After the site exchange from Fig. 5(a) to Fig. 5(c), the dangling bonds on the additional Ge dimer are replaced by long pairs on Sb atoms and the energy gain of this site exchange is 1.68 eV. So the site exchanges of Ge/Sb are exothermic.

IV. SUMMARY

In summary, we have studied the initial Sb-mediated epitaxial growth of Ge on the Si(001) surface. Based on first-principles total-energy calculations, we find that both single Ge adatoms and Ge ad-dimers can break the Sb dimers on the surface, and the most stable sites for one Ge adatom and ad-dimer are both on the Sb dimer rows, contrary to the conventional picture that Ge dimers are first formed in the trough between the group-V surfactant dimer rows. We have also examined the energetics of the site exchange between Ge and Sb atoms for the surfactant-mediated growth and find that Ge ad-dimers tend to exchange with the subsurface Sb atoms one by one perpendicular to the surface dimer rows, consistent with the experimental results for Ge/Sb/Si system.

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[1] M. Copel, M. C. Reuter, Efthimios Kaxiras, and R. M. Tromp, Phys. Rev. Lett. **63**, 632 (1989).
[2] S. Kanakaraju, A. K. Sood, and S. Mohan, Phys. Rev. B **61**, 8334 (2000).
[3] A. Portavoce, I. Berbezier, and A. Ronda, Phys. Rev. B **69**, 155416 (2004).
[4] H. P. Zeindl, S. Nilsson, J. Klatt, D. Krüger, and R. Kurps, J. Cryst. Growth **157**, 31 (1995).
[5] N. Paul, H. Asaoka, J. Myslivеček, and B. Voigtländer, Phys. Rev. B **69**, 193402 (2004).
[6] S. J. Jenkins and G. P. Srivastava, Surf. Sci. **398**, L308 (1998).
[7] R. M. Tromp and M. C. Reuter, Phys. Rev. Lett. **68**, 954 (1992).
[8] Byung Deok Yu and Atsushi Oshiyama, Phys. Rev. Lett. **72**, 3190 (1994).
[9] M. A. Boshart, A. A. Bailes III, and L. E. Seiberling, Phys. Rev. Lett. **77**, 1087 (1996).
[10] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); G. Kresse and J. Hafner, *ibid.* **47**, RC558 (1993).
[11] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[12] J. P. Perdew and Yue Wang, Phys. Rev. B **45**, 13244 (1992).
[13] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[14] T. B. Massalski, J. L. Murray, L. H. Bennet, and H. Baker, *Binary Alloy Diagrams* (American Society for Metals, Metals Park, OH, 1986).
[15] J. T. Wang, H. Mizuseki, Y. Kawazoe, T. Hashizume, M. Naitoh, D. S. Wang, and E. G. Wang, Phys. Rev. B **67**, 193307 (2003); J. T. Wang, E. G. Wang, D. S. Wang, H. Mizuseki, Y. Kawazoe, M. Naitoh, and S. Nishigaki, Phys. Rev. Lett. **94**, 226103 (2005).
[16] Sorcha B. Healy, Claudia Filippi, P. Kratzer, E. Penev, and M. Scheffler, Phys. Rev. Lett. **87**, 016105 (2001).
[17] Since we did not allow for a rotation of the Ge dimer on the diffusion path, our result for the barrier is an upper limit to the true barrier.
[18] We have calculated the case when one Ge ad-dimer is adsorbed at the four different sites using the 4×2, 4×4, and 8×2 supercells, respectively, and find that the change of the energy difference between the four adsorption sites is less than 0.05 eV.
[19] Ming Jiang, Xu-yan Zhou, Bao-xing Li, and Pei-lin Cao, Phys. Rev. B **60**, 8171 (1999).
[20] Young-Jo Ko, Jae-Yei Yi, Seong-Ju Park, El-Hang Lee, and K. J. Chang, Phys. Rev. Lett. **76**, 3160 (1996).