

Diffusion and Dimer Exchange in Surfactant-Mediated Epitaxial Growth

Byung Deok Yu and Atsushi Oshiyama

Fundamental Research Laboratories, NEC Corporation, Miyukigaoka, Tsukuba 305, Japan

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We propose a new dimer-exchange mechanism for surfactant-mediated epitaxial growth of Ge on Si(001) surfaces based on first-principles total-energy calculations. We find that, on Si(001) covered by As surfactants, Ge dimers are formed *not on As dimers but between As-dimer rows*, and then substitute for the As atoms at subsurface sites. This exchange process leads to As-capped needlelike growth of Ge along $\{1\bar{1}0\}$ direction which prevents islanding at high Ge coverage.

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Heteroepitaxy of one material onto another shows characteristic growth modes depending on surface and interface free energies and lattice strain. Ge on Si, for instance, grows layer-by-layer up to critical thickness (~ 3 monolayers), followed by islanding due to lattice mismatch ($\sim 4\%$) of the two materials (Stranski-Krastanov mode). Yet it was found that the islanding can be suppressed effectively by a monolayer (ML) of surfactants such as an As or Sb layer adsorbed before Ge growth [1,2]: The layer-by-layer growth continues beyond the critical thickness and the surfactant atoms segregate from the interface to the surface. Since the surface terminated by group-V atoms is energetically favorable compared with the Ge-terminated surface, incorporation of Ge atoms into subsurface layers and appearance of As atoms at the topmost layer is thermodynamically understandable. Little is known, however, about microscopic processes, diffusion and exchange processes, which lead to the surfactant-mediated layer-by-layer growth.

Recently, Tromp and Reuter [3] proposed a two-dimer correlated exchange process for As-surfactant-mediated growth of Ge on Si(001) based on their low-energy electron microscopy measurements. In their model, two Ge dimers which are formed on As dimer rows concertedly substitute for the As atoms underneath. However, exchange between a Ge dimer and underlying As atoms is energetically unfavorable as long as the Ge dimer is formed on the As dimer row. Our total energy calculation [4] shows that this type of the exchange reaction is endothermic with the energy cost of 0.8 eV. In fact, an inverse reaction, i.e., exchange between a dimer of group V atoms and underlying group IV atoms, is energetically favorable, and leads to the substitutional As adsorption on dimerized Si surfaces commonly observed in growth of GaAs on Si [5].

In this Letter, we propose a different novel reaction pathway for the surfactant-mediated growth based on a variety of total energy calculations within the local density approximation (LDA). We find that an arriving Ge atom on the As-covered Si(001) surface is adsorbed on a site between the As dimer rows. We also find that a Ge dimer is formed *not on an As dimer row but at the site between the dimer rows* since the activation en-

ergy for Ge diffusion is small compared with the energy cost to break the existing As dimer. We then find that the exchange of this Ge dimer with the underlying As atoms is energetically favorable. The energy gained in this exchange is 1.1 eV per dimer. Successive formation of a new Ge dimer and its substitution for underlying As atoms, which we find is exothermic, lead to a needlelike growth of a Ge 1 ML island capped by As atoms in a direction perpendicular to the original As dimer rows. The exchange mechanism proposed here provides a natural explanation of the surfactant-mediated epitaxial growth and is consistent with experimental data available.

All calculations have been carried out by use of norm-conserving pseudopotentials [6] and LDA [7] combined with conjugate-gradient minimization technique as reported elsewhere [4,8]. The surface is simulated by a repeating slab model in which typically 10 atomic layers and an 8.14 Å vacuum region are included. We find that the $p(\sqrt{8} \times \sqrt{8})R45^\circ$ periodic cell in the lateral directions, the 4 \mathbf{k} points in surface Brillouin zone, and the 8-Ry cutoff energy in the plane wave basis set are necessary to obtain well converged results [9]. The symmetry-unrestricted geometry optimization has been performed for all atoms except for the ones in the innermost 2 atomic layers in the slab. In the optimized geometries the remaining forces acting on the atoms are less than 0.004 Ry/Å.

We start with adsorption and diffusion of an arriving Ge atom on the 1 ML-As-covered Si(001) surface. The As atoms form symmetric dimers and the dimer rows are aligned in the $\{110\}$ direction in the optimized geometry of the starting As-covered Si surface [4,10]. The calculated total energy surface for the Ge atom on this As-covered surface is shown in Fig. 1. In obtaining this total-energy surface, we first fix the Ge atom at a site in the lateral plane, and then relax all the surrounding atoms and also the Ge atom itself in the vertical direction. We repeat these total-energy calculations for 15 sites spaced 0.96 Å apart in an irreducible quarter of the $p(2 \times 1)$ lateral cell as shown in Fig. 1, and then interpolation with 15 irreducible plane waves are used to obtain global features of the total-energy surface.

Figure 1 clearly shows three stable adsorption sites for

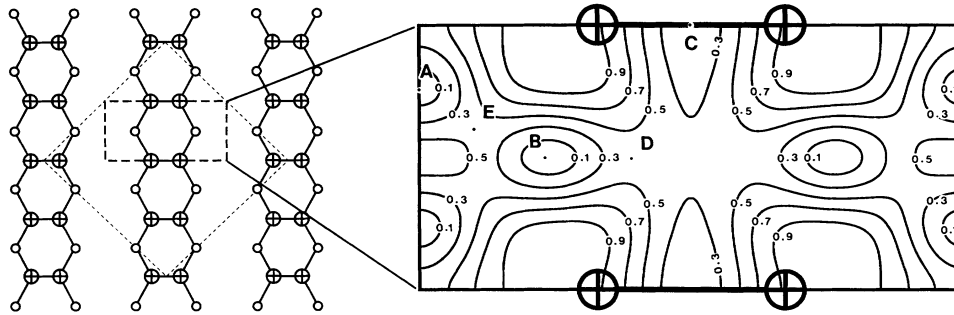


FIG. 1. Calculated total-energy surface for an additional Ge atom on the 1 ML-As-covered Si(001) surface (As: crossed circle; Si: open circle). Sites *A*, *B*, and *C* are stable adsorption sites, and *D* and *E* are saddle points for Ge diffusion. The first contour represents the energy line of 0.1 eV with respect to the most stable adsorption site (*A*) and the subsequent contour spacing is 0.2 eV. In the left part, the $p(2 \times 1)$ unit cell, in which the energy surface is shown, is indicated by the dashed line and the $p(\sqrt{8} \times \sqrt{8})R45^\circ$ unit cell, in which the calculations have been performed, by the thin dashed line.

the Ge atom (sites *A*, *B*, and *C*). An important finding is that the adsorption sites between the rows of the As dimers (sites *A* and *B* in Fig. 1) are more stable by ~ 0.15 eV than the site on the As dimers (site *C* in Fig. 1). The adsorption energies for the sites *A* and *B* are found to be both 2.8 eV. This value is much smaller than the corresponding values for Si adsorption on Si(001) (4–5 eV), and is obviously attributed to electronically inactive lone-pair orbitals on the As-covered surface. In the optimized geometry for site *A*, the Ge atom is located at the middle of a valley between the nearby As dimer rows, and is bonded to an As atom of each row. The bond of the As dimer of each row thus becomes significantly weak (weak bonds). The distance between the Ge atom and the neighboring As atom is 2.40 Å, the height of the Ge atom is 0.44 Å above the As atoms, and the bond angle is about 120° characteristic for sp^2 hybridization. On the other hand, in the optimized geometry for site *C*, the Ge atom is located about 2.10 Å above the two As atoms which still form a dimer with As-As distance of 2.41 Å. One may thus expect that the total energy of a breaking-dimer geometry in which the Ge atom intervenes between the As atoms and breaks the As dimer is lower than that of the geometry *C*. We have examined such a breaking-dimer geometry, and found that the total energy becomes lower by 0.8 eV. More importantly, however, we find that there is an energy barrier of 0.7 eV for the Ge atom to break the As dimer [11]. This energy barrier, of necessity, prevents the Ge atom from intervening between the two As atoms and reaching the stable breaking-dimer geometry.

Figure 1 also reveals the microscopic mechanism of Ge diffusion on the As-covered Si surface. The diffusion pathway parallel to the As-dimer rows is a motion along *BCBCB...* passing through a saddle point *D* in Fig. 1, and the pathway perpendicular to the rows is one along *ABCBA...* passing through a saddle point *E*. We find that the activation energies for the Ge diffusion along the directions parallel and perpendicular to the As dimer

rows (Q_{\parallel} and Q_{\perp}) are 0.4 eV and 0.5 eV, respectively. This nearly isotropic diffusion with relatively small activation energies is in contrast to the diffusion of a Si atom on the clean Si(001) surface ($Q_{\parallel}=0.6$ eV and $Q_{\perp}=1.0$ eV) [12]. This is reasonable since the clean surface covered by dangling bonds is replaced by As-capped surface with lone-pair orbitals remaining. Note that the energy barrier for a Ge atom to move from the metastable adsorption site *C* is very small: 0.25 eV for the motion from *C* to *B*, and 0.17 eV from *C* to another *C*.

The calculated results described above lead to a new picture about adsorption and diffusion of Ge atoms as follows. The most stable adsorption site for a Ge atom is located between rows of As dimers (site *A*). The site *C* on the As dimer is metastable, but the activation energy for diffusion from the site is very small (~ 0.2 eV). Further the breaking-dimer geometry which has lower total energy is difficult to reach because of relatively large energy barrier for breaking the As dimer (0.7 eV). We thus expect that the sites between the As-dimer rows are energetically favorable for Ge atoms to form dimers [Fig. 2(b)]. We have indeed performed the total-energy optimization for a Ge dimer between the As-dimer rows, and find that the geometry shown in Fig. 3 is stable. This geometry we have found is in sharp contrast to a prevailing assumption about the location of Ge dimers: Ge atoms were postulated to break the existing As dimers and form Ge dimers 90° rotated. We presented here theoretical evidence that a reaction pathway of the Ge diffusion to the site between the As-dimer rows and of the successive Ge-dimer formation at the site is energetically favorable, although the breaking of the As dimer is also a possible but much less frequent reaction.

Once a Ge dimer is formed between As-dimer rows [Figs. 2(b) or 3], exchange between the Ge dimer and As atoms at subsurface sites [Fig. 2(c)] is energetically favorable. Figure 4 is the obtained total-energy minimized geometry, and the calculated energy gained from this exchange (from Fig. 3 to Fig. 4) is 1.1 eV [13]. The

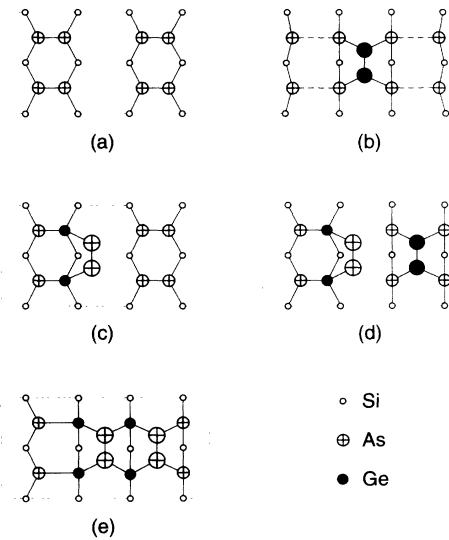


FIG. 2. Schematic top views of several geometries in the exchange mechanism for the surfactant-mediated epitaxial growth. Black, crossed, and open circles denote Ge, As, and Si atoms, respectively. Thin dashed lines represent the 4×2 lateral cell. (a) 1 ML-As-covered Si surface, (b) Ge dimer between As dimer rows (dashed lines depict weak bonds), (c) As dimer between the original As dimer rows after exchange, (d) additional Ge dimer on the As dimer rows, and (e) As dimers with Ge atoms at subsurface sites after exchange.

obtained adsorption energy for Fig. 4 is 4.2 eV per Ge atom significantly larger than that for the adsorption of a single Ge atom. In Fig. 4 [or Fig. 2(c) schematically], the top-layer As atoms are bonded only to the subsurface Ge atoms which are further rebonded to another neighboring As atom. The As atoms on the adjacent dimer row which formerly show the weak bonds in the geometry [Fig. 2(b) or Fig. 3] before the exchange are also rebonded to each other. Through such a complicated reconstruction, there remain a lone-pair and a dangling bond at each of the two top-layer As atoms [Fig. 2(c)], whereas, before the exchange, there are two dangling bonds of the Ge atoms and four weak bonds of As atoms [Fig. 2(b)]. The driving force for the present exchange reaction is thus reducing the number of dangling and weak bonds. Further reconstruction for the total-energy reduction is accomplished

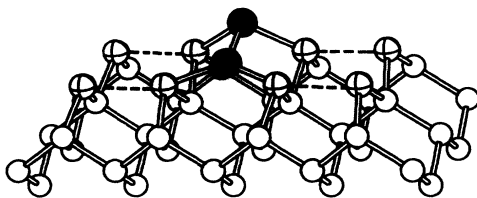


FIG. 3. Metastable Ge dimer between the As-dimer rows, corresponding to the schematic illustration of Fig. 2(b). Black, crossed, and open spheres denote Ge, As, and Si atoms, respectively, and dashed lines denote the weak bonds.

by a formation of a π -bonded structure between the top-layer As atoms: The distance between the top-layer As atoms is found to be 2.23 Å which is fairly shorter than the bond length (2.55 Å) of the symmetric As dimer.

An interesting feature of the geometry shown in Fig. 4 is the displacement of the top-layer As atoms towards Ge atoms from the middle of a valley between the As dimer rows by 1.19 Å in the lateral plane. This displacement leads to an asymmetric profile of scanning tunneling microscopy (STM) images along the direction perpendicular to the top-layer As-As bond. It can be discernible from STM images of the geometry with the top-layer Ge dimer before the dimer exchange [14]. The single-dimer exchange process demonstrated here has an electronic origin, and is in sharp contrast to the two-dimer correlated exchange process proposed by Tromp and Reuter [3]. The key finding which causes this difference is the formation site of the Ge dimer: The dimer was assumed to be formed on the As dimer rows in the past, whereas it is found to be formed between the As dimer rows from the present calculation.

The As dimer between original As dimer rows [Figs. 2(c) or 4] is a seed of the surfactant-mediated epitaxial growth. Other Ge atoms approach this seed and form a dimer on its neighboring site [Fig. 2(d)]. In this geometry, contrary to the case that Ge dimers are first formed on the As dimer rows, subsequent exchange between the Ge dimer and the subsurface As atoms [Fig. 2(e)] is energetically favorable: Dangling bonds of the additional Ge atoms and of the adjacent top-layer As atoms are replaced by lone pairs through this exchange process. We have indeed optimized the total energy of the exchanged geometry corresponding to Fig. 2(e), and obtained the stable geometry shown in Fig. 5. The adsorption energy of this geometry is 4.9 eV per Ge atom which is larger than that of the seed geometry [Fig. 2(c) or 4] by 0.7 eV. The exchange process shown in Fig. 2 is thus exothermic. Repeating this exchange process leads to needlelike growth of Ge steps capped by As dimers along the $\{1\bar{1}0\}$ direction. Advantage of the needlelike shape over a number of isolated seeds is strain release. In the seed geometry, bond lengths and angles around the Ge and the neighboring As atoms are distorted from sp^3 configuration. In the needlelike shape, although the distortion

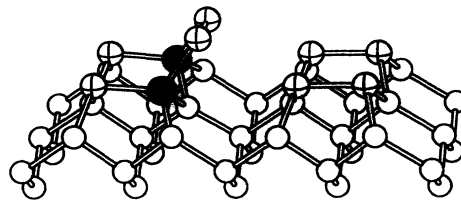


FIG. 4. Total-energy minimized geometry after exchange between a Ge dimer and subsurface As atoms, corresponding to the schematic illustration of Fig. 2(c). Black, crossed, and open spheres denote Ge, As, and Si atoms, respectively.

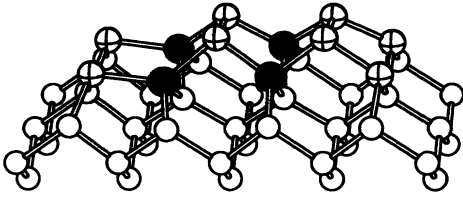


FIG. 5. Total-energy minimized geometry of two As dimers formed along the $\{1\bar{1}0\}$ direction with Ge atoms at subsurface sites after the exchange process, corresponding to the schematic illustration of Fig. 2(e). Black, crossed, and open spheres denote Ge, As, and Si atoms, respectively.

also exists at both ends of the needle, strain within the needle is small. Hence, strain accompanied with isolated seeds is significantly reduced by forming the needlelike shape. This needlelike shape also hinders the islanding since further exchange between arriving Ge atoms and the As dimers upon the needlelike step is geometrically hindered. There is no energetically favorable pathway for such an exchange reaction: i.e., the formation of the Ge dimer between the As dimer rows is impossible. The needlelike growth naturally deduced from the exchange process proposed here is thus important to prevent islanding of Ge atoms.

In summary, we have performed a variety of LDA calculations and proposed a new dimer exchange mechanism for the surfactant-mediated epitaxial growth: Ge dimers are formed between the dimer rows of the As-covered Si(001) surface; subsequent exchange of the Ge dimers with As atoms at subsurface sites is exothermic due mainly to the reduction of the number of dangling and weak bonds; additional Ge dimers is then formed at adjacent sites and again substitute for subsurface As atoms; these exchange processes lead to needlelike growth of Ge along the $\{1\bar{1}0\}$ direction covered by single-height As steps which prevents islanding of Ge atoms and achieves layer-by-layer growth of Ge films.

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