Structural stability and scanning tunneling microscopy images of strained Ge films on Si(001)

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We investigate energetics and scanning tunneling microscopy (STM) images of several Ge films on Si(001) substrates using a first-principles total-energy calculation within the density-functional theory. We calculate the film energies of various Ge films with dimer-vacancy lines (DVL) and 90° dislocation cores (DC) deposited on Si(001) substrate as a function of Ge-layer thickness. Our energetics calculation suggests that 90° DC structure becomes stable when sufficiently thick Ge overlayers are deposited on Si(001) substrate. We also calculate the STM images of $p(2 \times 2)$, 2×8 DVL, and 90° DC structures, and we find that STM images of their surface structures are distinguishable from one another.

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I. INTRODUCTION

The high-quality films of germanium and silicon-germanium alloy on silicon substrates have attracted much attention due to the compatibility with conventional Si-related technology and relevant applications in electronic and opt-electronic devices.[1–3] For example, Ge and SiGe layers are often used as transport channels in high-performance field-effect transistors, and they are also used as buffer layers to obtain tensily strained Si layers because tensily strained Si as well as Ge are known to have enhanced carrier mobility for electrons and holes, compared with unstrained Si.[4,5]

Epitaxial growth of Ge films on Si substrate is a key technology for realizing such Ge-based electron devices in the semiconductor industry[6] and provides fundamental knowledge of heteroepitaxial growth of strained films.[7] In the heteroepitaxial growth, the strain energy, which arises from a ∼4% lattice mismatch between Si and Ge, increases with increasing the Ge layers. Beyond a critical thickness of Ge films, the relaxation of the strain energy proceeds via formations of three-dimensional (3D) islands or introductions of dislocations in two-dimensional (2D) films.[6]

With the use of surfactants such as hydrogen[8,9] or under low temperatures below ∼300 °C,[10] it has been reported that 3D islanding does not take place, and the strain-relaxed 2D films are formed on Si substrates. Under these growth conditions, the misfit strains of Ge films are released by the introduction of the 90° dislocation with the Burgers vector along the ⟨110⟩ direction near the Ge/Si interface.[10,11] In order to form the high-quality Ge films on Si substrates, it is essential to bury the 90° dislocation core (DC) near the Ge/Si interface.[10,11]

Recently, we have reported on the epitaxial growth of hydrogen-covered Ge films upon Si(001) using a first-principles density-functional calculation.[12,13] In the literature, a pair of five- and seven-membered rings is proposed as the atomic core structure of the 90° dislocation, and it is revealed that the proposed 90° DC structure becomes stable when the sufficiently thick Ge layers are deposited on Si substrate.[12,13] On the other hand, there are several first-principles studies of the epitaxial growth of Ge films on Si(001) substrates without surfactant effects. However, they are devoted to only the formation of a 3D hut island.[14,15] Hence, our knowledge as to a link between the epitaxial growth of the bare Ge film without H coverages and the formation of the 90° dislocation remains unknown at present.

In this paper, we report atomic structures, energetics, and scanning tunneling microscopy (STM) images of various strained Ge films on Si(001) surfaces, based on a first-principles total-energy calculation. We calculate the film energies of $p(2 \times 2)$, 2×8 dimer-vacancy-line (DVL), and 90° dislocation core (DC) structures. From results of energetics, it is found that a 90° DC structure is favored in energy when sufficiently thick Ge overlayers are deposited on the Si(001). The critical thickness of Ge films at which 90° dislocation occurs is estimated. The STM images of $p(2 \times 2)$, 2×8 DVL, and 90° DC structures are demonstrated, and it is found that they are distinguishable from one another.

II. METHODOLOGY

First-principles total-energy calculations have been performed using the real-space finite-difference approach[16] in the framework of the density-functional theory (DFT), as implemented in the Real-Space Density-Functional Theory (RSDFT) code.[17] The interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials,[18] and exchange-correlation effects are treated using the local density approximation (LDA) parameterized by Perdew and Zunger.[19] The grid spacing in the real-space calculations is taken to be 0.32 Å corresponding to a cutoff energy of 27.5 Ry, and the sixth-order finite difference is adopted for the kinetic operator.

We use the $p(2 \times 2)$ and the (2×8)-dimer-vacancy-line (DVL) [see Fig. 1(a)] reconstructed surfaces for Ge layers deposited on Si(001). For the 90° dislocation core (DC) structures, a single core, which consists of a pair of five- and seven-membered rings [see Fig. 1(b)], is introduced into 24 lateral periodicity along the [110] direction. By introducing the 5–7 membered rings, number of ⟨110⟩ atomic plane in the Ge films can be reduced, and therefore the misfit strains along the [110] direction are released.[20] The top surfaces of Ge films in all calculations are composed of the buckled dimers.

The lattice parameter is fixed at our calculated Si bulk lattice constant of 5.38 Å, and thus the Ge layers on Si(001) are laterally compressed by the calculated lattice mismatch (4.3%)

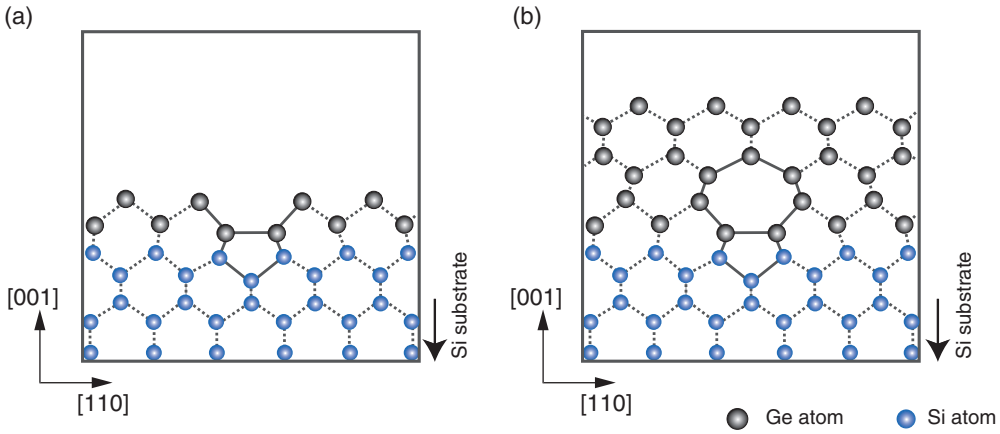

FIG. 1. (Color online) Atomic structures of several Ge films on Si(001): (a) dimer-vacancy line (DVL) structure and (b) 90° dislocation core (DC) structure. In the DVL structure, a dimer in a Ge top surface is missing. The core of 90° DC structure is composed of a pair of five- and seven-membered Ge rings (solid lines). The illustrations of the DVL and the 90° DC structures correspond to Ge films consisting of two Ge layers and six Ge layers deposited on Si substrates, respectively.

between Si and Ge. We have used repeating slab models in which the thickness of the vacuum layer is kept more than 16 Å for all cases. The atomic slab we have treated in this calculation is composed of seven Si atomic layers, and the bottom Si layer of the slab is terminated by the hydrogen atoms. Brillouin zone integration is performed with (6 × 6), (6 × 3), and (6 × 1) k-point grids for the $p(2 \times 2)$, the 2 × 8 DVL, and the 90° DC structures, respectively. The Si atoms in the bottom layer and H atoms attached to the bottom Si atoms are fixed to mimic the Si substrate. Other atoms are fully relaxed until forces acting on the atoms are smaller than 0.05 eV/Å.

To determine the structural stability of Ge layers deposited on Si substrates, we introduce the film energy γ_F defined as

$$\gamma_F = \frac{E_{\rm tot} - m_{\rm Si}\mu_{\rm Si} - m_{\rm Ge}\mu_{\rm Ge} - m_{\rm H}\mu_{\rm H}}{A} - \Gamma_b. \qquad (1)$$

Here $E_{\rm tot}$ is the total energy, and the chemical potentials $\mu_{\rm Si}$, $\mu_{\rm Ge}$, and $\mu_{\rm H}$ are the energies per atom in the equilibrium Si bulk, the biaxially compressed Ge bulk, and the hydrogen molecule, respectively, and $m_{\rm Si}$, $m_{\rm Ge}$, and $m_{\rm H}$ are the number of Si, Ge, and H atoms in the slab, respectively. Γ_b is the surface energy arising from the bottom surface of the slab and is obtained by independent LDA calculations using different slab models in which both top and bottom surfaces consist of Si atoms with H termination.

The STM images of various Ge/Si(001) structures are generated based on the Tersoff-Hamann approximation.[21] Due to its simplicity, the method is widely used and is well known to be valid for many systems.[22] In this method, the tunneling current is assumed to be proportional to the local density of states (LDOS) of the surface at the tip position integrated over an energy range restricted by the applied bias voltage. Consequently, the STM images can be generated from the isosurface of the spatial distribution integrated by the LDOS $\rho(r;\epsilon)$ at spatial points r and energy ϵ by several sampling k points of the Brillouin zone over the energy range from $E_F - eV$ to E_F with applied voltage V and the Fermi energy E_F:

$$I \propto \int_{E_F - eV}^{E_F} \rho(r;\epsilon)\, d\epsilon. \qquad (2)$$

The STM images generated in this way correspond to experimental constant-current images. The isosurface of the STM images is taken at ∼3 Å from topmost atomic position of the Ge top surface.

III. RESULTS AND DISCUSSION

Figure 2 shows the calculated film energies for the $p(2 \times 2)$, the 2 × 8 DVL, and the 90° DC structures as a function of the number of the deposited Ge layers on Si(001). We also plot in Fig. 2 the film energies of Si(001)-$p(2 \times 2)$ surface without deposited Ge layers. The film energy of the Ge-covered Si(001)-$p(2 \times 2)$ structure is considerably lower than that of Si(001)-$p(2 \times 2)$ without Ge layers since the dangling-bond energy of Ge is lower compared with that of Si. The film energy of $p(2 \times 2)$ reconstructed Ge-covered Si structure decreases as the number of Ge layers increases, and it becomes close to an asymptotic value when the number of the Ge layers exceeds about 4. Thus, the film energy defined by Eq. (1) is expected to approach a sum of the top-surface energy of Ge film and Ge/Si interface energy as the number of Ge layers increase.

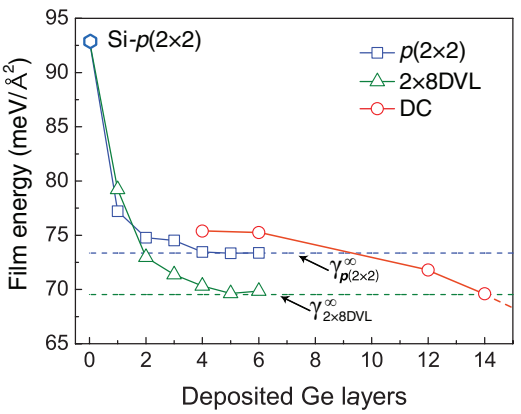

FIG. 2. (Color online) Film energies of various Ge films on Si(001) as a function of Ge layer thickness. The squares, triangles and circles denote the $p(2 \times 2)$, 2 × 8 DVL, and 90° DC structures, respectively. The hexagon denotes Si(001)-$p(2 \times 2)$ surface.

This is because any interactions between the top surface of Ge film and interface of Ge/Si are expected to diminish with increasing the number of the Ge layers. To validate this expectation, we have calculated the surface energy $\Gamma^{Ge}_{p(2\times2)}$ of the biaxially compressed Ge(001)-$p(2 \times 2)$ surface and the interface energy I_{GeSi} of the heterostructure consisting of the equilibrium Si bulk and the biaxially compressed Ge bulk. We define $\gamma^{\infty}_{p(2\times2)} \equiv \Gamma^{Ge}_{p(2\times2)} + I_{GeSi}$ and the value $\gamma^{\infty}_{p(2\times2)}$ is plotted in Fig. 2 as the horizontal dotted line. We thus confirm that the asymptotic value of the film energy $\gamma_{p(2\times2)}$ is quantitatively in good agreement with the value $\gamma^{\infty}_{p(2\times2)}$.

Due to the accumulation of the strain energy of Ge films, $2 \times N$ DVL reconstructed structures have been often observed at the early stage of the epitaxial growth of Ge/Si(001).[23] To determine the optimal N value, we have calculated the asymptotic values $\gamma^{\infty}_{2\times N\mathrm{DVL}}$ of the $2 \times N$ DVL structures for $N = 6$, 8, and 10. It is found that the value $\gamma^{\infty}_{2\times N\mathrm{DVL}}$ for $N = 8$ is the lowest, and this value is in agreement with the experimental result.[23] Note that the surface energies of Ge/Si(001)-$(2 \times N)$ DVL structures with $N = 4$, 6, 8 and 10 are usually lower than those with $N = 5$, 7, 9 and 11.[14] We thus choose the 2×8 DVL structure as a representative of $2 \times N$ DVL structures and plot in Fig. 2 the film energies of the 2×8 DVL structure as a function of the number of Ge overlayers. The film energy of the 2×8 DVL structure also decreases with increasing the number of Ge layers as in the case of $p(2 \times 2)$ structure, and asymptotically approaches the value $\gamma^{\infty}_{2\times8\mathrm{DVL}}$ $(=\Gamma^{Ge}_{2\times8\mathrm{DVL}} + I_{GeSi})$. Here $\Gamma^{Ge}_{2\times8\mathrm{DVL}}$ denotes the surface energy of the biaxially compressed Ge(001)-(2×8) DVL surface. $\gamma^{\infty}_{2\times8\mathrm{DVL}}$ is lower than $\gamma^{\infty}_{p(2\times2)}$ by $\sim$10 meV/Å^2. The film energy of the 2×8 DVL structure is lower than that of $p(2 \times 2)$ structure for more than $\sim$2 Ge overlayers.

We here discuss the film energy of the 90° dislocation core (DC) structure. The film energy of the 90° DC structure decreases when the Ge layer increases from 4 to 14 Ge layers. Because the Ge layers deposited above the DC are free from the lateral compression caused by the lattice mismatch of Si and Ge,[20] the film energy of the 90° DC structure would decrease, and the structure of the Ge overlayers becomes close to that of the strain-relaxed Ge film as the number of the deposited Ge layers increases. Therefore, the film energy of the 90° DC structure is expected to decrease as in $n_l \Delta\gamma$, where n_l is number of Ge overlayers and $\Delta\gamma$ is the energy difference per layer between the compressed and the strain-relaxed Ge bulks. The energy difference $\Delta\gamma$ is calculated to be –1.18 meV/Å^2.[24] We plot $n_l \Delta\gamma$ in Fig. 2 as an oblique dashed line for more than 14 Ge layers.

We now consider the critical thickness of Ge layers where 90° dislocation occurs. The film energy of 2×8 DVL structure decreases with increasing the number of Ge layers, and it becomes almost unchanged to be $\gamma^{\infty}_{2\times8\mathrm{DVL}}$ beyond five Ge layers, whereas the film energy of the 90° DC structure decreases continuously. Therefore, the film energy of 90° DC structure is lower than that of 2×8 DVL structure when Ge layers are more than 14 layers. We thus conclude that the critical thickness is 14 Ge layers at which 90° dislocation occurs.

Figure 3 shows the simulated STM images of the $p(2 \times 2)$ reconstructed Ge/Si(001) structure at applied bias voltages of (a) $V = -0.5$ eV (filled state) and (b) $V = +0.5$ eV (empty state). In the filled-state image, the dimer row makes a zigzag pattern along the [110] direction: one atom in a buckled dimer looks bright, and the other is absent due to the existence of dangling bonds[25–27] [see Fig. 3(a)]. On the other hand, the zigzag corrugation in the empty-state image is considerably different from that in the filled-state image, as shown in Fig. 3(b). The two bright protrusions run along the [110] direction. Similar features in the STM images are also observed in the cases of Si(001)-$p(2 \times 2)$ as well as unstrained Ge(001)-$p(2 \times 2)$ surfaces.[25,27]

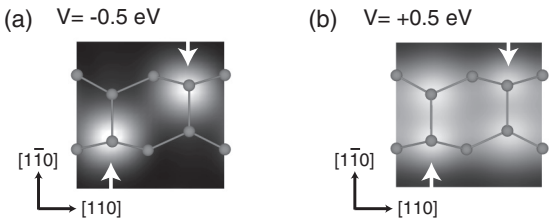

FIG. 3. Simulated STM images of the Ge/Si(001)-$p(2 \times 2)$ structure, in which Ge film on Si(001) is composed of six Ge layers. The STM images are generated at bias voltages of (a) –0.5 eV (filled state) and (b) +0.5 eV (empty state), respectively. The white arrow represents the position of an upper atom of a buckled Ge dimer. Gray ball denotes a Ge atom.

Figure 4 shows the simulated STM images of the 2×8 DVL structure at applied bias voltages of (a) $V = -0.5$ eV and (b) $V = +0.5$ eV. In the filled-state image, zigzag patterns are also seen along the [110] direction [Fig. 4(a)]. Being different from the $p(2 \times 2)$ structure, the dark line appears along the [1$\bar{1}$0] direction due to the lack of the dimer, and the width of the dark line is about 2.6 Å. The dark line in STM images is also observed in the experiments of the epitaxial growth of Ge/Si(001).[23] In the empty-state image, two bright spots, but the area on the lower atom in the buckled dimer looks brighter, stand along the [110] direction. The dark line also runs along the [1$\bar{1}$0] direction as in the filled-state image.

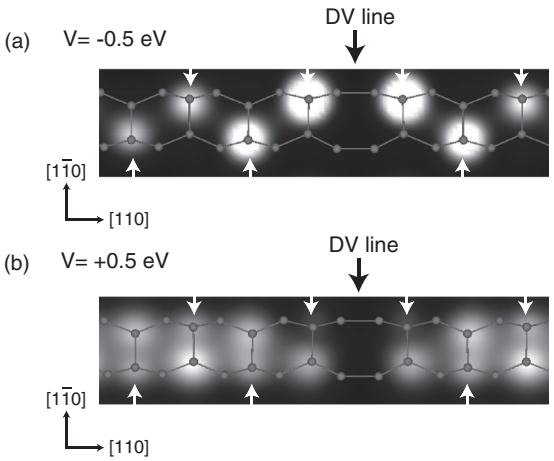

FIG. 4. Simulated STM images of the 2×8 DVL structure, in which Ge film on Si(001) is composed of six Ge layers. The STM images are generated at bias voltages of (a) –0.5 eV (filled state) and (b) +0.5 eV (empty state). The black arrows denote the position of dimer vacancy. The white arrow represents the position of an upper atom of a buckled Ge dimer. Gray ball represents a Ge atom.

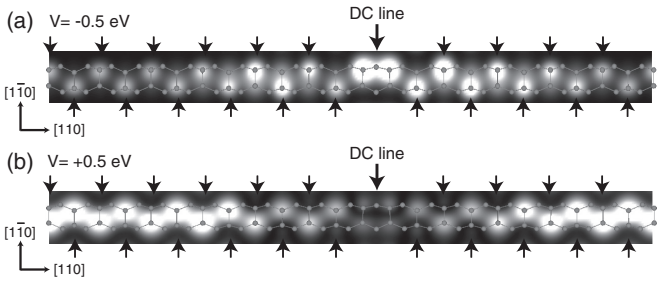

FIG. 5. Simulated STM images of the 90° DC structure, in which Ge film on Si(001) is composed of 14 Ge layers. The STM images are generated at bias voltages of (a) –0.5 eV (filled state) and (b) +0.5 eV (empty state). The black arrows denote the position of the dislocation core. The small black arrow represents the position of an upper atom of a buckled Ge dimer, and the gray ball represents a Ge atom.

In Figs. 5(a) and 5(b), the STM images of the 90° DC structure are shown at the bias voltages of $V = -0.5$ eV (filled state) and +0.5 eV (empty state), respectively. In the filled-state image, the zigzag pattern along the [110] direction is seen as in the case of the $p(2 \times 2)$ structure. The two bright oval shapes above the DC appear along the DC line, and the width of the two oval shapes is about 9.2 Å. The zigzag pattern in the empty-state STM image exhibits sharp contrast to the filled-state STM image: the bright spot is located above the lower atom in the buckled dimer. Being different from the filled-state STM image, the dark line above the DC line appears, and the width of the DC line is almost the same as that of the two bright oval shapes in the filled-state image. Accordingly, DVL and DC structures can be distinguished by looking into the bright oval shape in the filled-state STM image and the dark line in the empty-state STM image, because the appearance of the bright oval shape and the width of the dark line in STM images of both structures are different from each other.

IV. SUMMARY

In summary, we have studied the structural stability and STM images of several Ge films with the dimer-vacancy line and with the 90° dislocation core deposited on a Si(001) substrate. The 2 × 8 DVL structure is energetically favorable for more than two Ge overlayers compared with the $p(2 \times 2)$ structures. The film energy of a 90° DC structure consisting of the 5–7 membered rings diminishes with increasing number of relaxed Ge overlayers. The STM images of 2 × 8 DVL and 90° DC structures are demonstrated and can be distinguished from each other.

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