Atomic structures and energetics of 90° dislocation cores in Ge films on Si(001)

Yoshitaka Fujimoto[1,2,*] and Atsushi Oshiyama[3,2]
[1]*Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro, Tokyo 152-8551, Japan*
[2]*CREST, Japan Science and Technology Agency, Sanban-cho, Tokyo 102-0075, Japan*
[3]*Department of Applied Physics, University of Tokyo, Hongo, Tokyo 113-8656, Japan*
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We report on atomic structures and energetics of 90° dislocation cores in Ge films on Si(001) substrates on the basis of the first-principles total-energy calculations. The dislocation core structure consisting of a row of pairs of five- and seven-membered Ge rings is proposed and found to be stable with increasing Ge overlayers. The scanning tunneling microscopy images of the 90° dislocation core structure are calculated and show the possibility to observe the proposed core structure.

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I. INTRODUCTION

Epitaxial growth of thin films is an indispensable fabrication technique in semiconductor technology and at the same time offers a stage where vital scientific discussion has been raised as to missing links between atomic reactions and morphology of resultant films.[1] Growth of Ge films on Si(001) substrates is an important example: Ge on Si is a simple model system for understanding heteroepitaxial growth of strained films[2,3] and also a system which is full of potential applications such as high-mobility field-effect transistors[4] or near-infrared photodetectors.[5]

In epitaxial growth of Ge layers on Si substrate, the strain which arises from 4% lattice mismatch between Ge and Si is a key factor in determining morphology of the Ge film:[2] Growth of the Ge film on Si(001) follows Stranski-Krastanov (SK) mode in which a few Ge layers (wetting layer) grow on the Si substrate and then Ge islands are formed on the wetting layers. The islanding is usually accompanied by stress-releasing 60° dislocations which are caused by the $\langle 110\rangle/\{111\}$ slip in the diamond structure.[6] The generation of the 60° dislocation degrades the quality of the Ge film with rough surface morphology.

It has been shown that surfactants dramatically suppresses the Ge island formation and promotes layer-by-layer Ge growth:[7–9] under the hydrogen-surfactant epitaxy, Ge islanding does not occur and the strain-relaxed Ge film grows on Si substrate.[8,9] In these Ge/Si(001) heterostructures, the 90° edge dislocation with the Burgers vector along the $\langle 110\rangle$ direction is observed near the Ge/Si interface.[10,11] The generation of the 90° dislocation in the surfactant epitaxy is now a key technique to grow high-quality Ge films on Si(001). Yet knowledge as to the structure of the dislocation is totally lacking at the microscopic level. It is thus imperative to identify the atom-scale core structure and the energetics of the 90° dislocation from accurate microscopic calculations.

In this paper, we present the first-principles total-energy electronic-structure calculations that clarify atomic and electronic structures and energetics of the 90° dislocation core (DC) in Ge films on Si(001). We propose a structure consisting of five- and seven-membered Ge rings (Fig. 1) as the core of the 90° dislocation. To discuss the energetics of 90° DC structure, we define the film energy corresponding to the total energy of the system, and examine the 90° DC structure as well as other relevant Ge film structures covered by hydrogen. We also calculate the scanning tunneling microscopy (STM) image of the 90° DC structure and demonstrate that STM experiment is able to observe the DC even with the presence of Ge overlayers.

II. METHOD

We have performed the first-principles total-energy calculations using the real-space finite-difference approach in the framework of the density-functional theory.[13,14] The interactions between the ions and the valence electrons are described by the norm-conserving Troullier-Martins pseudopotentials,[15] and exchange-correlation effects are treated using the local density approximation (LDA) parameterized by Perdew and Zunger.[16]

We consider the film energy γ_F to discuss the energetics of Ge overlayers on Si substrates. The film energy per area A of the lateral cell is defined using the total energy of the slab system E_t as

$$\gamma_F = \frac{E_t - m_{Si}\mu_{Si} - m_{Ge}\mu_{Ge} - m_H\mu_H}{A} - \Gamma_b. \quad (1)$$

Here the chemical potentials μ_{Si}, μ_{Ge}, and μ_H are the energies per atom in the equilibrium Si crystal, the biaxially compressed Ge crystal, and the hydrogen molecule, respectively, and m_{Si}, m_{Ge}, and m_H are the number of Si, Ge and H atoms

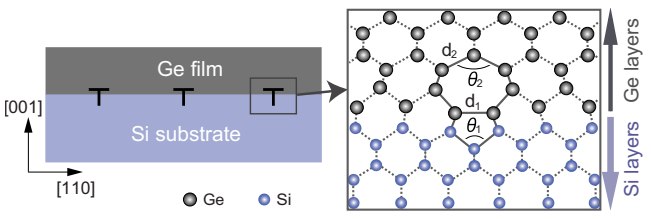

FIG. 1. (Color online) Schematic view (the left panel) of the 90° dislocation of Ge films on Si(001) and atomic structure (the right panel) of the dislocation core. The core structure is composed of a pair of five- and seven-membered Ge rings (solid lines). θ_i ($i=1$ and 2) and d_j ($j=1$ and 2) denote the characteristic bond angles and bond lengths, respectively.

in the slab, respectively. The surface energy Γ_b is the energy cost to generate 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.

For the calculation of the STM images, the Tersoff-Hamann approximation is used. In this scheme, the tunneling current is proportional to the surface local density of states (LDOS) at the tip position integrated over an energy range restricted by the applied bias voltage. Hence the STM images are generated from the isosurface of the spatial distribution formed by integration of the LDOS over the energy range from the Fermi energy E_F to $E_F - eV$ with applied voltage V.[24] The isosurface of the STM images is taken at ~4 Å from topmost atomic position of the Ge top-surface.

Figure 1 shows the schematic view of the 90° dislocation in the Ge film on the Si substrate and the atomic structure of the DC that we propose. The pairs of five- and seven-membered rings form a row at the interface along $[1\bar{1}0]$ direction.[12] Owing to the pair of five and seven rings, number of ⟨110⟩ atomic planes in Ge overlayers is reduced, hereby releasing the misfit strain along [110] direction. Corresponding to the 4.3% lattice mismatch, we introduce the single core in the 2×24 lateral periodicity. To investigate the energetics of the DC, we have examined three distinctive structures for Ge overlayers: the 2×1 structure in which no DC is introduced and surface Ge atoms are dimerized with hydrogen termination, the 2×24 DVL (dimer vacancy line) structure in which an H-terminated surface dimer is missing in every 24 dimers forming DVL along $[1\bar{1}0]$ direction again without the DC, and finally the DC structure in which the DC exists near the Ge/Si interface. For the DC structure, there are several variants as shown in Fig. 2(a) (see below).

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%) 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 are composed of seven Si atomic layers, and the bottom Si layer of the slab is terminated by the hydrogen atoms. In the real-space calculations, the grid spacing is taken to be 0.60 a.u. corresponding to a cutoff energy of 27.5 Ry, and the sixth-order finite difference is adopted for the kinetic energy operator. Brillouin zone integration is performed with (6×12), (6×1), and (6×1) k-point grids for the 2×1, the 2×24 DVL and the 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.

III. RESULTS AND DISCUSSION

We have calculated the film energy defined in Eq. (1) to discuss the stability of the Ge films on Si(001) substrate. Figure 2(b) shows the calculated film energies for the 2×1, the 2×24 DVL, and the DC structures as a function of the number of the deposited Ge layers on Si(001).

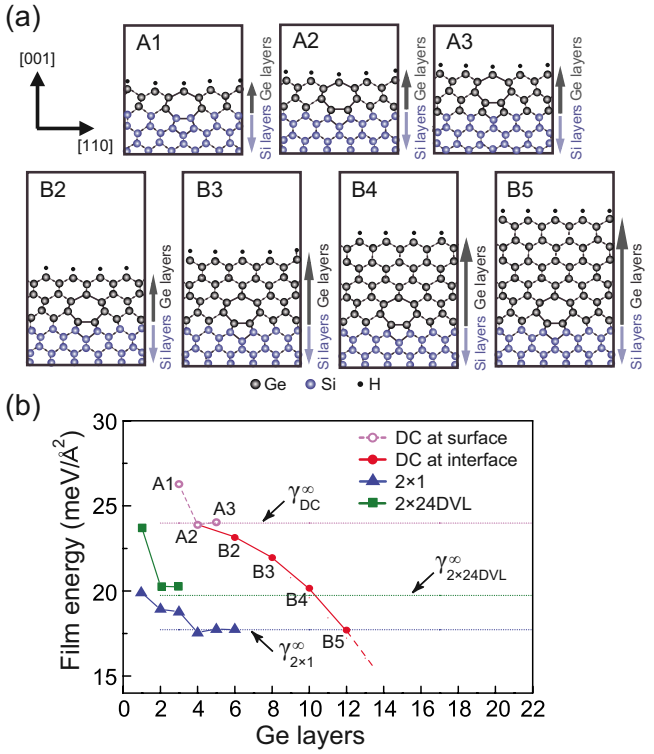

FIG. 2. (Color online) (a) Side views of various 90° dislocation core (DC) structures with pairs of five- and seven-membered rings. In A1, A2, and A3, the 90° DC is located at the top-surface of the Ge film, whereas it is at the interface in B2–B5, hereby forming the strain-relaxed Ge overlayers above the 90° DC. (b) Film energies for various Ge/Si(001) structures as a function of the number of Ge layers.

We begin with the 2×1 structure. The film energy of the 2×1 structure $\gamma_{2\times1}$ decreases with increasing Ge layers and approaches an asymptotic value. The film energy defined as (1) is expected to approach a sum of the top-surface energy and the interface energy when the number of Ge overlayers increases and hereby the coupling between the top-surface and the interface diminishes. To validate this expectation, we have calculated the surface energy $\Gamma^{Ge}_{2\times1}$ of the biaxially compressed hydrogenated Ge(001)-(2×1) surface and the interface energy I_{GeSi} of the heterostructure consisting of the equilibrium Si bulk and the biaxially compressed Ge bulk. Calculations have been performed using suitable slab models. We define $\gamma^{\infty}_{2\times1} \equiv \Gamma^{Ge}_{2\times1} + I_{GeSi}$ and plot this value by the horizontal dotted line in Fig. 2(b), which shows that the asymptotic value of $\gamma_{2\times1}$ quantitatively agree with the top-surface energy plus the interface energy.

At the early stage of the epitaxial growth of Ge/Si(001) without surfactants, $(2\times N)$ DVL structures are commonly observed,[17] and it is known that the reconstruction of Ge surface varies depending on Ge layer thickness, implying the competition of several interaction energies.[2,17] In the hydrogen-surfactant epitaxial growth, accordingly, the H-terminated Ge/Si(001)-$(2\times N)$ DVL reconstructed surface is also expected to be one of the possible surface structures. We here have examined $(2\times N)$ DVL structures with H surfactants for $N=16$, 20, 24, 26, and 28, and found that

$N=24$ is the lowest in energy for biaxially compressed Ge(001) surface. We thus consider the (2×24)-DVL structure as a representative of the $(2\times N)$ DVL structures. To clarify stability of the DVL structures with H surfactants, we have calculated the film energy $\gamma_{2\times24\ \mathrm{DVL}}$ as a function of the number of Ge layers [Fig. 2(b)]. $\gamma_{2\times24\ \mathrm{DVL}}$ is larger than $\gamma_{2\times1}$ by about 5–10 meV/Å^2. Again the film energy approaches an asymptotic value $\gamma^{\infty}_{2\times24\ \mathrm{DVL}}$ in this case, which is a calculated sum of the corresponding surface energy and the interface energy.

We are now in a position to discuss the 90° DC structure which contains the five- and seven-membered rings. The Ge layers in the 90° DC structure are classified into two categories: i.e., the compressed and the strain-relaxed Ge layers. The former is the biaxially compressed Ge layer which is located between the DC and the Ge/Si interface and the latter is the strain-relaxed Ge layer which is deposited above the DC.[18] Therefore, it is of importance to know where the DC in the Ge film is located.

In order to determine the position of the DC, we first calculate the film energy γ_{DC} of the 90° DC structure in which the DC is located at the Ge top surface as shown in A1, A2, and A3 in Fig. 2(a). The film energy decreases with increasing Ge layers between the DC and the interface. It is found that the film energy becomes an asymptotic value already in the structure depicted by A2. The asymptotic value $\gamma^{\infty}_{\mathrm{DC}}$ shown by the horizontal dotted line in Fig. 2(b) is defined as a sum of the interface energy $\mathrm{I}_{\mathrm{GeSi}}$ and the surface energy $\Gamma^{\mathrm{Ge}}_{\mathrm{DC}}(\gamma^{\infty}_{\mathrm{DC}}=\Gamma^{\mathrm{Ge}}_{\mathrm{DC}}+\mathrm{I}_{\mathrm{GeSi}})$. The latter is calculated for the DC structure consisting of only Ge elements with the DC being located at the top surface. For further discussion, we therefore place the DC at the position as in the structure A2 in which three Si atoms participate in forming a five-membered ring. It is noteworthy that the structure A2 is slightly lower in energy than the structure A3 where the five-membered ring lies in the Ge layers. This is presumably because existence of the five-memebered ring causes additional strains in compressed Ge overlayers.[19]

We next study how the film energy γ_{DC} varies with increasing strain-relaxed Ge layers above the DC. We consider four structures shown in B2, B3, B4, and B5 in Fig. 2(b) where the number n_{l} of the strain-relaxed Ge layers is 2, 4, 6, and 8. We have found that the film energies for the DC structures, B2–B5, decreases with increasing number of the deposited Ge layers [Fig. 2(b)]. The structure of the Ge layers deposited above the DC is close to that of the strain-relaxed Ge film, as the number of the Ge layers increases. Hence the film energy of the 90° DC structure is expected to decrease as in $n_{\mathrm{l}}\Delta\gamma$ where $\Delta\gamma$ is the energy difference per layer between the compressed and the strain-relaxed Ge bulks. We have calculated $\Delta\gamma$ to be -1.18 meV/Å^2.[20] The calculated film energies for B2–B5 structures unequivocally exhibit this decrease with the increasing deposited layers. In Fig. 2(b), we plot $n_{\mathrm{l}}\Delta\gamma$ as an oblique dashed line for more than 12 Ge layers.

Based on the calculated film energies for Ge overlayers on Si(001) shown in Fig. 2(b), we now discuss the critical thickness of Ge overlayers at which the DC structure with the relaxed Ge overlayers appears. The present calculations have clearly revealed that the 2×1 structure is energetically favorable compared with 2×24 DVL structure during the early stage of Ge layer growth. The film energy of the 2×1 structure is unchanged to be $\gamma^{\infty}_{2\times1}$ when the number of the Ge layers are more than ~4. On the other hand, the film energy of the 90° DC decreases with increasing the deposited Ge layers. From Fig. 2(b), the 90° DC structure indeed becomes energetically favorable with respect to the 2×1 structure when Ge layers are more than 12 layers. We thus conclude that the critical thickness is 12 Ge layers. It is of interest to compare the value from the present LDA calculations with the values obtained from classical elastic theory which diverge in a range from 8 to 71 Ge layers.[21]

TABLE I. Structural parameters of dislocation structures. The bond lengths d_1 and d_2, and bond angles θ_1 and θ_2 are depicted in Fig. 1. See text for height D.

Ge layers	θ_1 (deg)	θ_2 (deg)	d_1 (Å)	d_2 (Å)	height D (Å)
4	141.3	99.3	2.47	2.63	0.88
6	138.5	99.8	2.47	2.62	0.65
8	134.6	99.7	2.46	2.64	0.52
10	133.0	99.4	2.47	2.63	0.45
12	132.3	98.9	2.45	2.63	0.42

In Table I, we show the optimized structural parameters of the 90° DC structure at several numbers of the deposited relaxed Ge layers. The characteristic bond lengths d_1, d_2 and the bond angles θ_1, θ_2 around the DC are depicted in Fig. 1. The height D represents the difference between the highest and the lowest atomic positions of the hydrogen on the Ge top-surface layer. It is therefore clear that the top-surface atomic layer shows indentation even after the Ge layers are deposited. The bond angles θ_1 and θ_2 are quite different from the ideal tetrahedral bond angle 109.5°. In particular, θ_1 is larger than the ideal angle by 30%. The bond length d_1 is slightly larger than that of Ge bulk, 2.43 Å, and the bond length d_2 is larger by 8%. The large bond-angle and small bond-length variations are characteristics of structural relaxation in covalent materials.[22] These values change hardly even though the number of the Ge layers increases. Such peculiar geometrical features make the electronic structure modified as shown below. On the other hand, it is found that the height D decreases as the number of the Ge layers increases. It is reasonable that the surface comes to be flat when the sufficient Ge layers are deposited because the Ge film should relieve the strain energy.

Figure 3 shows the optimized structure and the isosurface of the total electron density of 90° DC structure which corresponds to 12 Ge overlayers deposited on Si(001) as in B5 of Fig. 2(a). From the spatial distribution of electron density, the electron densities mainly distribute between neighboring two atoms as seen in the typical sp^3 hybridized materials. However, the electron densities around two bonds above the seven-membered ring are considerably lower compared to other bonds. This is because the bond length d_2 in Table I is much larger than other bond lengths. It is interesting that the bond-length distortion in the dislocation core affects the spatial distribution of the electron density.

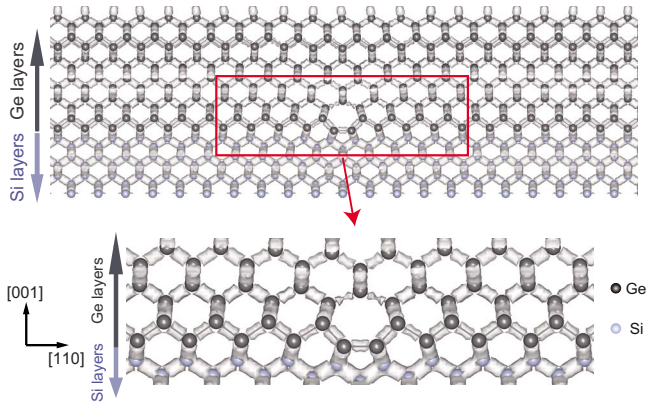

FIG. 3. (Color online) Optimized structure and isosurface of total electron density of the 90° DC in Ge films consisting of 12 Ge layers deposited on Si(001) (upper panel) and isosurface of total electron density near the 90° DC (lower panel).

Figure 4(a) shows the energy bands of the 90° DC structure. The center of the valence-band maximum (VBM) and the conduction-band minimum (CBM) is set to be 0 eV. The energy band of the DC structure exhibits the direct band gap at Γ point[23] with a value of 0.09 eV. The VBM and CBM are located in the calculated band gap of Si bulk, 0.61 eV. In Figs. 4(b) and 4(c), we show the electron density plots of VBM and CBM. The electron density of VBM is found to be localized along the DC, whereas that of CBM is highly localized at the upper position of the DC. This remarkable feature such as the localization of the electron density near the DC and the direct-gap nature might provide possible optoelectronic-device applications.

The localization of the electron density also makes peculiar spatial distributions of the local density of states (LDOS), leading to distinctive STM images. Figure 5 shows the simulated STM images of the 90° DC structure. The STM images in Figs. 5(a) and 5(b) are shown at the bias voltage of −0.5 eV (filled state) and +0.5 eV (empty state), respectively. In the filled-state image, the dark line on the DC

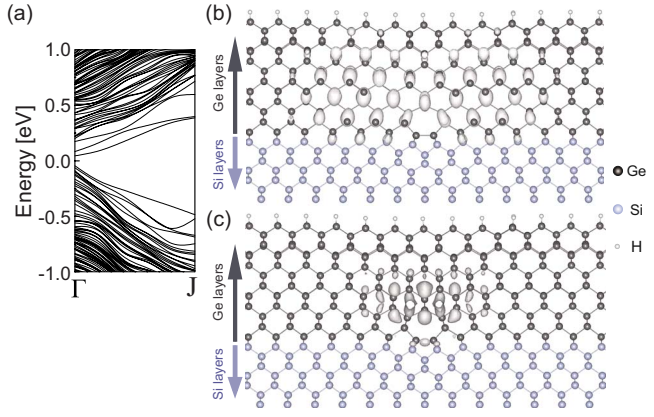

FIG. 4. (Color online) (a) Energy bands of the 90° dislocation core structure shown in B5 in Fig. 2(a). The electron densities of (b) the VBM and (c) the CBM states are shown. The Fermi energy being located at the middle between VBM and CBM are set to be zero.

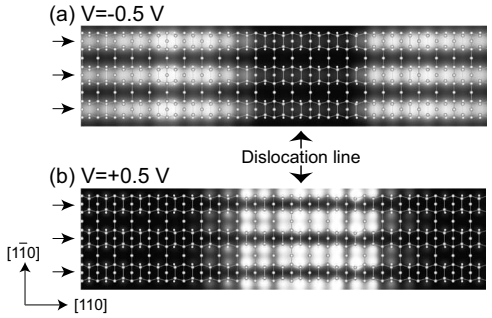

FIG. 5. Simulated STM images of the 90° dislocation in Ge film on Si(001) shown in B5 in Fig. 2(a): (a) filled-state image and (b) empty-state image. The arrows on the left hand represent the dimer row positions. Gray and small white balls represent Ge and H atoms, respectively.

runs along the dislocation line. The width of the dark line is about 24.7 Å. The bright oval shape forming on the dimer stands along [110] direction. The empty-state STM image exhibits sharp contrast to the filled-state STM image. A bright line is seen along the dislocation line and the bright oval shape appears between the dimer rows. The width of the bright line along the DC is ~28.5 Å. The difference between the filled and the empty-state STM images is attributed to the electronic states induced by the DC: In the filled-state STM image, the electronic density is mainly localized at both sides of the DC as shown in Fig. 4(b). Consequently, the filled-state STM image has two bright protrusions not on but along the DC. In the empty-state image, there is an electronic state localized largely at the upper position of the DC as shown in Fig. 4(c). This makes a bright protrusion above the DC. It is thus expected that the 90° dislocation line is able to be found in atomic scale by STM experiments.

IV. SUMMARY

We have revealed the atomic structure and the energetics of the 90° dislocation core in Ge films on Si(001) substrate. The core structure of the 90° dislocation has been proposed and found to be stable with increasing the number of relaxed Ge overlayers. We have also found that the 90° dislocation lines are clearly observable in the simulated STM images, with being a dark line in the filled-state image and a bright line in the empty-state image.

ACKNOWLEDGMENTS

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*fujimoto@stat.phys.titech.ac.jp

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