Structural identification of silicene on the Ag(111) surface by atomic force microscopy

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Silicene is a two-dimensional atomic layer material with buckled honeycomb arrangements of Si atoms. The diversity of those arrangements, which expands its potential applications, makes it difficult to determine its structure in any particular case. In this paper, we show that atomic force microscopy (AFM) has the capability of structural determination of unknown phases of silicene. We carried out an AFM observation of $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ silicene of unknown structures on Ag(111). Remarkably, it was shown that all constituent Si atoms forming a honeycomb lattice can be resolved by AFM whereas scanning tunneling microscopy (STM) can image only the topmost Si atoms. High-resolution AFM imaging allowed us to identify two types of buckled structure of $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ silicene on Ag(111), which had not been previously discriminated. The structure models obtained by theoretical simulation reproduced AFM images as well as previous STM images. In addition, the mechanism of high-resolution AFM imaging was elucidated by force spectroscopy combined with first-principles calculations. Namely, attractive interaction with the tip pulls up buckled down Si atoms, causing local flips of the buckled structures.

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I. INTRODUCTION

Two-dimensional (2D) materials have been extensively studied in the past decade from the viewpoint of their technological applications as well as from a plethora of fundamental science perspectives [1-5]. Among these materials, silicene, which is an Si allotrope with a buckled honevcomb lattice, is expected to be compatible with current silicon-based electronics and hence a good candidate for numerous applications. The first proof-of-concept silicene field-effect transistor was demonstrated in 2015 [6]. However, unlike graphene, silicene lacks a layered parent material from which a monolayer silicene can be exfoliated. Hence, many experimental investigations of silicene have been focused on epitaxial growth on various substrates, e.g., Ag [7,8] and ZrB₂ [9]. The necessity of epitaxial growth on substrates and the fact that Si has a preference towards sp³ rather than sp² hybridization gives rise to the structural diversity of silicene on the surface. Single-monolayer silicene on a Ag(111) surface has been intensively investigated as a prototypical system, and a variety of superstructures has been reported, including (4×4) [7,8,10–17], $(\sqrt{13} \times$ $\sqrt{13}$ R 13.9° [8,10,12,14,15,18–24], and $(2\sqrt{3} \times 2\sqrt{3})$ R 30° [11-13,21,23,25-28] with respect to the Ag(111) unit cell. Whereas the $(2\sqrt{3} \times 2\sqrt{3})$ structure can uniformly cover the Ag(111) surface at relatively high Si coverage and high

temperatures, $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ structure tends to coexist with (4×4) , implying their comparable stability [29]. When we define α as the angle between the Si[110] and the Ag[110] directions [24,27], (4×4) and $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ structures are characterized by $\alpha = 0^{\circ}$ and $\alpha = 5.2^{\circ}$, respectively.

The structures of silicene dictate the electronic and chemical properties that may lead to potential applications. Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) have been mainly used as characterization methods for analysis of those structures. Although the structure of (4 × 4) silicene was first proposed by STM along with density functional theory (DFT) calculations [7] and then determined by tensor LEED [16], that of $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ has not been fully understood. This is because STM can image only upper-buckled Si atoms. As for LEED, it has difficulty determining surface structures which do not show uniform surface growth. Both the structural diversity of silicene and the blending of its structures create the need for a new imaging method to determine the precise structures.

In the present paper, we demonstrate structural identification of silicene $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ with $\alpha = 5.2^\circ$ by highresolution atomic force microscopy (AFM) observation and first-principles calculation. Recently, AFM was found to have the ability to resolve all constituent Si atoms of silicene in the (4×4) phase [30]. Here, we found that high-resolution AFM can distinguish all Si atoms of different heights in the $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ phase and reveal that there are two types of buckled structures. The energetic stability of the two types

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of structures is rationalized by DFT calculations. Moreover, we shed light on the origin of high-resolution AFM imaging with the aid of theoretical calculations including Si tip models.

II. EXPERIMENT AND THEORY

The experiments were carried out by using frequency modulation AFM systems in ultrahigh vacuum (UHV) at room temperature. Commercial Si cantilevers were used after Ar ion sputtering in UHV. Typical values of the resonance frequency (f_0) and the spring constant (k) of the cantilevers were 130– 160 kHz and 20-30 N/m, respectively. Optical interferometers were used to detect the deflection of the cantilevers. The oscillation amplitude (A) was set to be 10-20 nm. AFM topographic images were obtained by maintaining the frequency shift (Δf) of the oscillated cantilevers. The contact potential difference between the tip and the sample was compensated for by applying the corresponding voltage (V_s) to the sample. We cleaned Ag(111) samples by repeated cycles of Ar ion sputtering and subsequent annealing (600 °C). Then Si was deposited onto the clean Ag(111) surface by holding it at 250 °C so that silicene was obtained.

DFT calculations within a generalized gradient approximation [31,32] were performed using the OPENMX code based on norm-conserving pseudopotentials generated with multireference energies [33] and optimized pseudoatomic basis functions [34,35]. For each Si atom, two, two, and two optimized radial functions were allocated for the s, p, and d orbitals, respectively, as denoted by s_{2p2d2} . For Ag and H atoms, s_{2p3d2} and s_{1p1} basis functions were adopted, respectively. The cutoff radius of 7 bohr was chosen for the basis functions of Si and Ag atoms, whereas 5 bohr were chosen for H atoms. The regular mesh of 220 Ry in real space was used for the numerical integrations and for the solution of the Poisson equation. A $(5 \times 5 \times 1)$ mesh of k points was adopted to study a slab consisting of one silicene layer on five Ag layers. The bottom two Ag layers, whose coordinates were obtained by geometrical optimization of the bulk calculation, were kept fixed to simulate the bulk crystal termination of the surface. The STM images were simulated by the Tersoff-Hamann scheme [36]. The force on each atom was relaxed to be less than 0.0005 hartree/bohr. The binding energy, which was defined as $E_{\text{binding}} = (E_{\text{silicene}} + E_{\text{Ag}} - E_{\text{silicene/Ag}})/N_{\text{Si}}$, was 0.657 eV/Si atom. Here, $E_{silicene}$, E_{Ag} , and $E_{silicene/Ag}$ are the energy of silicene without a substrate, a Ag substrate, and silicene supported by a Ag substrate, respectively. $N_{\rm Si}$ is the number of Si atoms. The binding energy of silicene on the Ag surface was found to be lower than that of silicene on a ZrB₂ (0001) surface, which was previously estimated to be more than 1 eV [37]. This supports the hypothesis that silicene on Ag has a larger variety of superstructures than silicene on ZrB₂. For AFM simulation, the force between the surface atoms and the Si(111) symmetric tip shown in Fig. 5(a) was calculated by the sum of the force on the fixed atoms. The six hydrogen-terminated Si atoms of the tip, which were assumed to be attached to the Si(111) surface and the bottom two Ag layers, were kept fixed during the AFM simulation. In our calculations, the eigenvector following method [38] has been used for the geometry optimizations.

For comparison, we also performed AFM simulations of a (2×2) supercell of the $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ phase on three Ag layers and Si(111)- (7×7) consisting of five layers using the previously used Si(001) dimer tip model [39]. For Ag atoms in the supercell calculation, s_{2p2d1} basis functions were adopted to reduce computational resources. The bottom single Ag layer or the bottom two Si layers were kept fixed during the calculations. The other computational details were the same as those of the primitive cell of the ($\sqrt{13}$ × $\sqrt{13}$ R13.9° silicene. In addition to the cases of the (1 × 1) model with five Ag layers and the (2×2) supercell model with three Ag layers, DFT calculations for the (2×2) model with five Ag layers were performed to confirm the cell size dependency and influence of the number of Ag layers. The results indicated that the cell size dependency is much smaller than the effect of the number of Ag layers. Although the height differences of the silicenes between the (1×1) model with five Ag layers and the (2×2) supercell model with five Ag layers were less than 0.017 Å, the height differences of the silicenes between the (2×2) model with three Ag layers and the (2×2) supercell model with five Ag layers were less than 0.15 Å. However, it can be concluded that even the effect of the number of Ag layers does not change the global shape of each silicene type.

III. STRUCTURE DETERMINATION OF THE $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ SILICENES

Figure 1 shows some typical AFM images of silicene on Ag(111) substrates. By measuring the periodic lengths and the angles relative to the Ag(111) surface, the corresponding phases could be identified. Figure 1(a) shows an AFM image with the honeycomb imaging mode by which all constituent Si atoms could be resolved [30]. The honeycomb pattern formed by Si atoms could be identified as shown by the hexagonal rings. The left and right parts in Fig. 1(a) are identified as the $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ phase with $\alpha = 5.2^{\circ}$ and a (4 × 4) phase with $\alpha = 0^{\circ}$, respectively. AFM directly substantiated the honeycomb arrangement of Si atoms in silicene's $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ phase in addition to the arrangement in the (4×4) phase [30]. We also observed the $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ phase with different values of α , which will be discussed elsewhere. Hereafter, we focus our analysis on the $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ phase with $\alpha = 5.2^{\circ}$, which we simply call the $(\sqrt{13} \times \sqrt{13})$ phase.

Figures 1(b) and 1(c) are two AFM images of the same area of silicene's ($\sqrt{13} \times \sqrt{13}$) phase on Ag(111) but with different imaging modes due to the different tip states [30]. The same unit cells are indicated by the rhombuses. Figure 1(b) is in the honeycomb imaging mode where the contrast of each atom is less distinct. After the spontaneous change in the tip in the scanning process, the image in Fig. 1(c) was obtained. In this image, honeycomb features as in Figs. 1(a) and 1(b) were not imaged, but the height differences of the atoms were more distinct. We call this the $\sqrt{13} \times \sqrt{13}$ imaging mode since it is easy to identify $\sqrt{13} \times \sqrt{13}$ unit cells by the variations in the topographic heights of the Si atoms.

Figure 1(d) is another AFM image of the $(\sqrt{13} \times \sqrt{13})$ structure. The superstructures in Figs. 1(c) and 1(d) have the same periodic length and the same orientation, indicating that



FIG. 1. High-resolution AFM topographic images of the ($\sqrt{13}$ × $\sqrt{13}$ R13.9° phase of silicene on Ag(111) surface. (a) The ($\sqrt{13}$ × $\sqrt{13}$ R13.9° phase coexisting with the (4 × 4) phase. The unit cells are indicated by the rhombuses, and the honeycomb arrangements of Si atoms are shown by the hexagons. (b) The $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ phase of type A with the honeycomb imaging mode. (c) The same area as (b) but imaged by the $(\sqrt{13} \times \sqrt{13})$ imaging mode. The unit cells shown by the dashed rhombuses 180° rotated from the unit cells shown by the solid rhombuses. There is a linear defect area between the two phases with the opposite directions. (d) The $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ phase of type B with the $(\sqrt{13} \times \sqrt{13})$ imaging mode. In this image, the unit cell of type A is also found as shown by the dashed rhombuses. The Δf set points are (a) -24.9 Hz, (b) -20.8 Hz, (c) -20.4 Hz, and (d) -26.0 Hz. The values of the corresponding normalized frequency shift γ are (a) $-4.18 \, \text{fN} \sqrt{\text{m}}$, (b) $-3.22 \text{ fN}\sqrt{\text{m}}$, (c) $-3.16 \text{ fN}\sqrt{\text{m}}$, and (d) $-8.92 \text{ fN}\sqrt{\text{m}}$.

both can be ascribed to the $(\sqrt{13} \times \sqrt{13})$ structure. Although both of the superstructures in Figs. 1(c) and 1(d) are defined as the $(\sqrt{13} \times \sqrt{13})$ phase, they show different imaging patterns, implying that their buckled structures are different. Note that previous STM studies could not differentiate them [20,23,24]. We refer to the superstructure observed in Fig. 1(c) as type *A*, and the superstructure in Fig. 1(d) as type *B*.

Figure 2(a) presents a high-resolution AFM image zoomed in to a single unit cell of the $(\sqrt{13} \times \sqrt{13})$ phase of type A. From the different brightnesses of the protrusions in the AFM image, the type A buckled structure can be identified. Some of the bright protrusions are numbered as shown in Fig. 2(b). Si-1 to Si-14 in the unit cell are defined as shown in the inset of Fig. 3. The bright protrusions at the corners of the unit cell (black rhombuses) are set to be Si-1. Besides Si-1, there are three other bright protrusions (Si-6, Si-8, and Si-12) with almost the same brightness forming a triangle in the half unit cell. In the other half of the unit cell, there is another relatively bright protrusion (Si-4) that can be distinguished as well. The other Si atoms are shown at low brightness or are unable to be resolved in this AFM image. Type A has threefold symmetry around the center of the triangle constituted by three Si atoms (Si-6, Si-8, and Si-12).

Figure 2(f) shows a high-resolution AFM topographic image of the $(\sqrt{13} \times \sqrt{13})$ phase of type *B*. We could identify the buckled structure of type B according to the different brightnesses of the protrusions in the AFM image. As shown in Fig. 2(g), we set the brightest protrusions to be the corners of the unit cell (black rhombuses) to Si-1. Inside the half unit cell, there are two bright protrusions (Si-6 and Si-8), which are also bright in type A. Type B breaks the threefold symmetry that type A has; this is the most distinct difference between type A and type B. In another half part of the unit cell, there is another relatively bright protrusion (Si-3), which is dimmer than the above-mentioned bright two. Besides these bright protrusions, other Si atoms of lower brightness can be visualized as well. For instance, Si-12 and Si-4 can be resolved but with lower brightnesses than those in type A, which is also a distinction between type A and type B.

To find the stable structures of the $(\sqrt{13} \times \sqrt{13})$ phase, we carried out DFT calculations. We found two buckled structures that reproduced type A and type B obtained from the AFM observation by using initial guess structures inspired by the AFM images. Although we performed geometry optimizations by using other several kinds of initial structures to confirm the possibility of the existence of several competing silicene structures, all the structures were relaxed to the structure type A or type B. Figure 2(d) shows the top view of the calculated structure model of the $(\sqrt{13} \times \sqrt{13})$ phase of type A. Figure 3 presents the calculated heights of constituent Si atoms inside the unit cell of silicene (see the plots of solid circles). In the calculations, we set the origin of the atomic heights as the height of the first layer of Ag atoms before relaxation caused by the growth of the silicene layer. According to the calculation result, the highest Si atoms in the buckled structure are Si-1, Si-6, Si-8, and Si-12, whose heights are about 3.0 Å. Note that the topmost Si atoms are located on the positions near the top sites of the first Ag layer. The calculated height of another relatively high Si atom (Si-4)



FIG. 2. (a)–(e) Type A and (f)–(j) type B of the $(\sqrt{13} \times \sqrt{13})R13.9^{\circ}$ phase of silicene on the Ag(111) surface. (a) and (f) High-resolution AFM images of the unit cells. (b) and (g) The same unit cells as (a) and (f), but some Si atoms are numbered. (c) and (h) Simulated STM images of type A and type B at $V_s = -1.0$ V. (d) and (i) The structure models of type A and type B obtained by DFT calculations. (e) and (j) The calculated structure models of 180° rotated type A and type B. The color code in the structure models is as follows: blue corresponds to Si, gray corresponds to first layer Ag, and yellow corresponds to second layer Ag.



FIG. 3. Calculated atomic heights of each Si atom of silicene with type A and type B and their 180° rotated ones. The horizontal axis presents the number of each Si atoms defined as the inset. The vertical axis presents the atomic heights. The origin is set to be the height of Ag atoms at the first layer before relaxation caused by the growth of silicene.

is 2.7 Å. The calculated heights of the lower Si atoms are 2.2– 2.3 Å. Type A has threefold symmetry around the center of a triangle constituted by three Si atoms (Si-6, Si-8, and Si-12) in good agreement with the corresponding AFM images.

Figure 2(i) shows the top view of the calculated structure model of the $(\sqrt{13} \times \sqrt{13})$ phase of type *B* on Ag(111). Figure 3 presents the calculated height of each Si atom inside the unit cell (see the plots of solid triangles). The result of the calculations indicated that Si-1, Si-6, and Si-8 are the highest Si atoms in the buckled structure with heights of about 3.1 Å. Beside these highest atoms, there is also one Si atom (Si-3) at an intermediate height, whose calculated height is 2.8 Å. The other Si atoms are at lower positions in the buckled structure with heights of 2.2–2.5 Å. Type *B* breaks the threefold symmetry of type *A*, in good agreement with the corresponding AFM images.

Here, we compare our structure models with the models proposed previously. The buckled structure of type *A* is similar to the structure models proposed previously [13,20,40] because all of these models show the same threefold symmetry feature with our model. In addition, it was predicted theoretically that the $(\sqrt{13} \times \sqrt{13})$ phase has two buckled structures [41]. One of the structure models is similar to our type *A* model but slightly breaks the threefold symmetry. The other buckled structure may correspond to our type *B* model. This model shares a feature with our type *B* model; that is, the atomic heights of Si-1, Si-3, Si-6, and Si-8 are higher than those of the other Si atoms. However, the previous model has twofold symmetry around the midpoints of Si-1 and Si-8 (and the midpoints of Si-3 and Si-6), which is broken in our type *B* model. Our AFM images of type *B* show different topographic heights of Si-3 and Si-6, so the twofold symmetry is broken.

The height order of the Si atoms obtained by the DFT calculations is in good agreement with AFM observations for both type A and type B. That is, the Si atoms at higher positions are imaged with more brightness in AFM images. However, the height differences among Si atoms in AFM topography are quantitatively different from those of the calculations. The height differences by AFM are less than the height differences obtained by the calculations. For example, from the measurement in the AFM image of Fig. 2(b), the height difference between Si-1 and Si-3 is about 0.13 Å. But according to the calculations, the corresponding height difference is 0.77 Å. The discrepancy was also obtained in a previous study on the (4×4) phase [30]. This will be further discussed in the next section.

To compare our results with previous STM studies, we simulated STM images based on the structural models obtained by DFT calculations. Simulations of STM images for type A and type B are shown in Figs. 2(c) and 2(h), respectively. The pattern of the STM simulated images was not affected by the bias polarity or the energy window. Similar to the AFM images, the simulated STM images reflected the atomic heights; thus, they originated from geometric effects rather than electronic effects. In both type A and type B, higher Si atoms appear brighter in the STM images.

Previously, it has been difficult for STM to discriminate type A and type B since only the topmost Si atoms could be visualized and the height information of the other Si atoms was inaccessible. However, using the present information obtained by AFM observation and simulated STM images, we could differentiate the two types of $(\sqrt{13} \times \sqrt{13})$ observed in some previous STM studies. Some $(\sqrt{13} \times \sqrt{13})$ phases in previous studies are supposed to be type A because three atoms with almost the same brightness forming a triangle inside each unit cell can be distinguished [11,15,20,24]. We also found that the STM image of the silicene $(\sqrt{13} \times \sqrt{13})$ phase, which was proposed to have an atomic structure similar to that of type A, should be classified into type B because the threefold symmetry is broken [20].

We found two structures for the $(\sqrt{13} \times \sqrt{13})$ phase in both experiment and simulations. The atomic structures of type *A* and type *B* have a similar honeycomb lattice; that is, the in-plane coordinates of each Si atom in type *A* and type *B* are almost the same, but their buckling patterns are different. Note that Si-3 binds to both Si-4 and Si-12, indicating that the buckling of Si-4, Si-3, and Si-12 is the main difference between type *A* and type *B* (see Fig. 3). Type *A* can be converted into type *B* by flipping these three Si atoms. Namely, in type *A*, Si-3 buckles downward, whereas Si-4 and Si-12 buckle upward. After flipping, Si-3 buckles upward, and Si-4 and Si-12 buckle downward, corresponding to the structure of type *B*.

The calculation results show that type A is more stable than type B. But, the energy difference per a unit cell of $\sqrt{13} \times \sqrt{13}$ including 14 Si atoms is only 0.05 eV so that both of them can coexist on the Ag(111) surface. Indeed, the AFM observation proves the coexistence of type A and type B. In Fig. 1(d), most of the unit cells in this area are identified as type B (see the solid rhombuses). However, there is a unit cell characterized as type A, which has the three protrusions forming a triangle as shown by the dashed rhombuses. This result also indicates that the two different patterns of AFM images do not originate from tip effects but reflect intrinsic structure differences.

The Ag(111) surface has threefold symmetry about the [111] axis and the mirror planes perpendicular to the $[0\overline{1}1]$ axis. Thus, two types of the $(\sqrt{13} \times \sqrt{13})$ phase can grow along six equivalent directions with respect to the Ag(111)substrate. However, from the AFM measurement, we found that the $(\sqrt{13} \times \sqrt{13})$ phases coexist with their 180° opposite ones on the same surface. As shown in Fig. 1(c), the unit cells in solid rhombuses and dashed rhombuses are both ($\sqrt{13}$ × $\sqrt{13}$) phases of type A but in opposite directions. The half unit cell including a triangle constituted by three Si atoms (Si-6, Si-8, and Si-12) is downward in solid-line rhombuses whereas the half unit cell is upward in the dashed-line rhombuses. This result suggests that the $(\sqrt{13} \times \sqrt{13})$ phase of type A can grow in 12 orientations with respect to the Ag(111) surface. We found that the transition area in the AFM observation with the honeycomb imaging mode [Fig. 1(b)] agrees well with the model of linear defect formation presented for the $(\sqrt{13} \times \sqrt{13})$ phase [24]. This identification of the structure of the domain boundary is important because it affects the carrier mobility of silicene [42].

We also performed DFT calculations of 180° rotated silicene for both type A and type B. For these calculations, we have switched the second layer and the third layer of Ag substrates to prepare initial structure models of 180° rotated type A and type B. The structures determined by these calculations are shown in Figs. 2(e) and 2(j), respectively. The calculated heights of Si atoms in these respective structures are presented in Fig. 3 (see the open symbols). We found that the atomic heights in one direction are almost the same as those in the opposite direction. We show that for both type A and type B, the 180° rotated types have about 0.01-eV difference per a unit cell of $\sqrt{13} \times \sqrt{13}$ from those before rotation, indicating that both exist stably on the Ag(111) surface. This agrees with the experimental results. That is, the buckled structure of the $(\sqrt{13} \times \sqrt{13})$ silicene phase is influenced mainly by the Ag atoms on the first layer. Note that a 180° rotation operation of a silicene sheet is equivalent to the lateral shift of the sheet with respect to the Ag substrate as shown in Figs. 2(d), 2(e) 2(i), and 2(j). This has been mentioned in previous studies [20,24].

IV. MECHANISM FOR HIGH-RESOLUTION AFM IMAGING OF SILICENE

In order to clarify the imaging mechanism of high-resolution AFM on silicene, we conducted site-specific force spectroscopy on a type *B* surface. Figure 4(a) shows $\Delta f(z)$ curves acquired on Si atoms with higher (Si-1), intermediate (Si-3), and lower (Si-12) height positions. The origin of *z* is defined as the tip-surface distance where the tip is located above Si-1 under the feedback regulation with $\Delta f = -26.0$ Hz. We used the same tip as that used for Fig. 1(d). Since these curves contain a long-range force contribution, which does not produce an atomic-scale contrast, we evaluated the background forces by measuring $\Delta f(z)$ curves at the center of the silicene honeycomb. A van





FIG. 4. (a) $\Delta f(z)$ curves measured on Si atoms of type *B* silicene. The tip state is the same as that used in Fig. 1(d). The acquisition parameters are $f_0 = 158345$ Hz, A = 145 Å, and k = 31.1 N/m. The origin (z = 0) corresponds to the topographic height when the tip is located above Si-1 at $\Delta f = -26.0$ Hz. The van der Waals fitting curve of a sphere over a plane is shown, the distance dependence of which is $z^{-1.5}$. The radius of the sphere is estimated to be 9.1 nm. (b) The short-range force curves derived from (a).

der Waals model of a sphere over a plane was fitted onto the obtained curve [see Fig. 4(a)] and then was extracted from the $\Delta f(z)$ curves of the Si atoms. By applying a standard force conversion method to these data [43], we finally obtained short-range force curves as shown in Fig. 4(b).

We found that the force curves have maximum attractive forces near z = 0. In Fig. 4, the origin of distance is chosen as the tip-surface distance where the tip is above Si-1 at $\Delta f =$ -26.0 Hz. Since the same Δf was used for the set point of imaging in Fig. 1(d), an AFM image of Fig. 1(d) was obtained at near maximum attractive force. This is the key to obtaining high-resolution AFM imaging. This imaging distance is the same as that found for imaging of the (4 × 4) phase although no theoretical explanation was given [30]. Tip scanning at such close distances makes it difficult to obtain atomic resolution for silicene compared with Si(111)-(7 × 7) where atomic resolution can be obtained at the onset of the short-range force [44]. The difficulty of observation on silicene was also mentioned in a previous report using AFM [18].

FIG. 5. (a) The short-range force curves on Si atoms of type B silicene obtained by DFT calculations. The tip model is shown in the inset. (b) Atomic heights of Si-1, Si-3, and Si-12 vs the tip-surface distance when the tip approaches the corresponding sites. The electron-density difference map is shown in the inset. The red color denotes electron-density enhancement, and blue denotes electron-density depletion.

Interestingly, the maximum attractive forces on the different sites show almost the same magnitude (about 1 nN). This magnitude is in the range of the chemical bonding force between two Si atoms, which has been intensively studied on Si(111)-(7 × 7) surfaces [39,45–48]. The results imply that a Si atom of the tip apex forms chemical bonds with the Si atoms of silicene.

In order to reveal the origin of the attractive forces on silicene, we performed theoretical calculations of force curves systematically on the relevant Si atoms of the $(\sqrt{13} \times \sqrt{13})$ phase of type *B*. We used a tip cluster model composed of Si atoms as shown in the inset of Fig. 5(a). The results are presented in Fig. 5(a) where the origin of the distance corresponds to the position of the Ag first layer before relaxation caused by silicene growth. Around z = 7.0 Å, the maximum attractive forces are roughly -2.5 nN, larger than the experimental values. It is well known that the maximum attractive forces on Si(111)-(7 × 7) surfaces can vary within the range of 0.5–2.5 nN depending on the tip states [46,48]. The symmetric tip shown in Fig. 5(a) is known to be the most reactive tip. Here, we also obtained smaller theoretical values for the maximum attractive force (-1.4 nN) using the

dimer tip model, which was used previously [39]. Hereafter, we discuss theoretical results using the symmetric tip model shown in Fig. 5(a).

To investigate the redistribution of electron density at the distance where the maximum attractive force is exerted, we constructed an electron-density difference map as shown in the inset of Fig. 5(b). The map clearly represents electron accommodation at the junction between the tip and the surface atoms, proving the presence of a chemical bond between them. The result is consistent with the chemical bonds observed on the Si(111)-(7 \times 7) surfaces [39].

Figure 5(a) also points out the same trend as we see in experiments in which the maximum attractive forces become almost identical in magnitude regardless of the site. This is counterintuitive since the three Si atoms originally have different heights as shown in Fig. 3 and have different backbond angles. The apparent contradiction can be explained by tip-induced atom relaxation. By plotting the vertical positions of the Si atoms as a function of the tip-sample distance at the corresponding sites, we can find how heights of Si-1, Si-3, and Si-12 evolve when the tip approaches the sites [Fig. 5(b)]. Note that the distance z is defined as the separation distance between the tip and the surface before relaxation; thus, the height changes correspond to the relaxation of surface atoms from their original positions [49]. Atomic heights at greater tip-sample distances coincide with the intrinsic heights shown in Fig. 3 where the tip was absent.

In the case of the highest Si atom (Si-1), the height position remained intact at greater tip-sample distances. It is pulled up by 0.8 Å at close to the maximum attractive force (z = 7.0 Å). This is interpreted as atom relaxation induced by the chemical interaction with the tip. Remarkably, the atom relaxation of Si atoms of silicene is larger than that of Si adatoms on Si(111)-(7 × 7). Our simulation shows that the Si adatom on Si(111)-(7 × 7) is pulled up as much as 0.3 Å at close to the maximum attractive force. In previous studies based on a different DFT code, a similar value was obtained for Si(111)-(7 × 7) [44]. This suggests that Si atoms of silicene are flexible in the out-of-plane direction.

In the other two cases with intermediate Si atom (Si-3) and lower Si atom (Si-12), their positions steeply increased at some critical distance and reached a value equal to that of Si-1. Below the critical distances, one can find that a lower atom becomes relaxed toward the tip and turns into an upper-buckled atom. This can explain the similarity of maximum attractive forces obtained above different Si atoms. Tipinduced atom relaxation is the key to high-resolution AFM imaging and can explain the discrepancy in height differences between upper-buckled and other lower Si atoms (about 0.1 Å in experiments vs 0.8 Å in calculations). Individual atoms of the vertically flexible sample are imaged as they are pulled up by the attractive interaction with the tip. This imaging method is complementary to the repulsive force imaging that is used for chemical structure imaging of molecules using inert tips [50]. Attractive force imaging with tip-induced relaxation can produce high resolution even for an intrinsically corrugated surface, whereas the repulsive force imaging of nonplanar samples is challenging [51].

Regarding the tip-induced displacements of the lowerbuckled atoms, it has been unclear whether flipping or



FIG. 6. (a) Atomic heights of all constituent Si atoms of type *B* silicene when the tip approaches Si-12. (b) and (c) The side view of the structure of the tip and silicene on Ag(111) at (b) z = 9.0 Å and (c) z = 8.0 Å.

popping occurs, namely, whether or not tip-induced lift-up of the atom is accompanied by depression of neighboring atoms. Since this cannot be investigated by experiment [30], we must rely on theoretical calculations. We verified this by getting a tip to approach the Si-12 of type B silicene and then plotting heights of all constituent Si atoms as shown in Fig. 6(a). The result shows that Si-3 dramatically flops down at the moment Si-12 is pulled up by the tip at z = 8.0 Å near the onset of the chemical bond, whereas Si-11 and Si-13 are slightly depressed and lifted, respectively. This strongly indicates that the tip induces a flip-flop motion between lower- and upper-buckled atoms on silicene, similar to the previously reported action on buckled Si dimers on Si(100) [52,53] and buckled Si tetramers on Si(111) [54]. After the swapping of the height positions, the heights of Si-3, Si-11, and Si-13 start to increase with the relaxation of Si-12 toward the tip. Heights of other lowerbuckled Si atoms (Si-2, Si-5, Si-7, Si-9, Si-10, and Si-14) also start to increase slightly. These are because the approaching tip lifts not only the atom underneath it, but also the surrounding neighbor atoms as well. After the distance passes the point for the maximum attractive force (z = 7.0 Å), the repulsive force starts to increase, letting the heights of those atoms return to the equilibrium positions realized after the flipflop motion. These results show that silicene responds like a membrane, thus the 2D character of the silicene sheet appears in the mechanical properties as seen in graphene [55]. In the AFM simulations for the (2×2) supercell model with three Ag layers, the height changes in Si atoms outside of a radius of about 8 Å from the atom below the tip apex are less than 0.05 Å. Therefore, it revealed that the approaching tip makes local deformation inside the unit cell of the (1×1) model.

Interestingly, we find that Si-4, which is a second-nearestneighbor atom from Si-12, is flipped up at a critical distance (z = 8.0 Å) simultaneously with the flopping down of Si-3. Afterwards, the height of Si-4 is maintained in the flippedup position over the course of the subsequent tip approach. The result indicates that the tip can induce a local structural transition from type *B* to type *A*. Pulling up Si-12 causes a downward movement of Si-3 and upward movement of Si-4. This is likely to happen since type *A* and type *B* have almost the same energy and are thus easily converted by the flip-flopping of Si-3, Si-4, and Si-12 as discussed in the former section. This situation can be understood more by visualizing tip and surface models at z = 9.0 Å [Fig. 6(b)] and z = 8.0 Å[Fig. 6(c)].

High-resolution AFM imaging on silicene has been considered to be achieved by the pulling up of lower-buckled Si atoms, implying that other local structural transitions can also be induced by the tip on other lower-buckled atoms than Si-12. Such flip-flopped states by tip-induced structural transitions are basically not permanent but temporary at room temperature, namely, induced structures are immediately restored to their original configurations with greater tip distance in one cantilever oscillation cycle. This consideration, however, evokes the possibility of making flip-flopped states permanent at low temperatures as has been reported for dimers on Si(100) [53] and thus the manipulation of the buckling configuration (phase manipulation) of silicene in the future.

So far, we have discussed the origin of the attractive forces on silicene and the tip-induced relaxation of Si atoms. Such strong chemical interactions allow lower Si atoms to be lifted up and thus should make high-resolution AFM observation possible. However, we still do not understand why the contrasts in high-resolution AFM images reproduce well the order of the original heights of the individual Si atoms in the unit cells (Fig. 3). This could be explained by a conventional adhesion mechanism at the atomic junction between the tip and the sample atoms [56]. Cantilever oscillation should be taken into account. Δf used for AFM topography is determined by the values of force at each position in one cantilever oscillation cycle. We should consider that the height of the Si atom below the tip is changed at each tip height during the cantilever oscillation. Although our calculation considers only the ground state at each tip-sample distance in the tipapproach path, we can also search for a metastable state at each of the distances. Here, the height of the relevant Si atom below the tip can be one of the parameters of the reaction coordinates [57].

For example, well above the critical tip-sample distance (z_1) where the lower Si atoms get flipped, the nonflipped state is regarded as the most stable state, whereas the flipped state is seen as a metastable state. On the other hand, well below the critical distance $z < z_1$, the flipped state becomes most stable, whereas the nonflipped state is metastable. Thus, we can assume that the potential-energy surface for each tip-sample distance is characterized by two minima (flipped and nonflipped states) and a transition barrier state. In this manner,

 z_1 is regarded as the distance where the transition barrier collapses in the tip-approach path of one oscillation cycle. We can also consider the same scenario in the tip-retraction path of one oscillation cycle as well where we should start the calculation from the flipped state and gradually retract the tip from the surface. In the tip-retraction path, the system has another critical distance of z_2 ($z_1 < z_2$). As a result, the theoretical force curve in one oscillation cycle should show hysteresis. Experimentally, it was shown that the dissipation signal increases at lower Si atoms in the (4×4) phase [30] thus substantiating the existence of hysteresis in the lower Si atoms. Since Δf is determined by the forces over one oscillation cycle, AFM topography should include information on the states before and after the flipping. Here, it is reasonable to assume that the shape of theoretical force curves with hysteresis is subject to the original heights of the lower Si atoms since the potential-energy surface is affected by them. This should bring about the result that hysteresis in the theoretical force curve and the resultant Δf curves for lower Si atoms tend to be shifted toward a lower tip-sample distance; in other words, the lower the position of the Si atoms, the dimmer they can be imaged at a specific Δf set point. Note that since we found that silicene reacts like a membrane, for more precise calculation of potential-energy surfaces, we may also have to consider the effect of global deformations of silicene by modeling a large silicene area and a macroscopic tip body [55].

In more detail, although we assume the situation at 0 K in the above discussion, we have to consider the effects of finite temperatures for quantitative estimation of AFM topographic heights under the existence of hysteresis. At finite temperatures, we need to take the transition state theory into account [58], which generally formulates the probability function for the system to be in either of two states (here, the flipped or nonflipped state) at a specific temperature. In this case, theoretical force curves for tip-approach and retraction paths are strongly influenced by the probability functions. For instance, although the system initially rests in the nonflipped state at greater tip-sample distances in the tip-approach path of one oscillation cycle, it can jump to the flipped state and return to the original one even before the tip-sample distance reaches z_1 . This could happen because the transition barrier becomes small enough that the system can overcome it with thermal energy. The same situation can occur in the tip-retraction path of one oscillation cycle as well. By taking all the effects of temperature and original heights of surface atoms into consideration, the AFM topographic height can be simulated as a buckled dimer on a Si(100) surface [59]. Compared to the intrinsic dimer height (about 0.7 Å [60]), the simulated AFM topographic height becomes about 0.1 Å, which is comparable to those estimated in our study of silicene. We expect that application of transition theory to all the lower Si atoms in the unit cell of the $(\sqrt{13} \times \sqrt{13})$ phase will quantitatively reproduce the experimental AFM topographic heights. To confirm these hypotheses, further experiments are needed, including dissipation spectroscopy [57] with different temperatures and theoretical calculations taking into account potential-energy surfaces at different tip-sample distances with fine steps. Such undertakings are beyond the scope of the present paper.

V. SUMMARY

Based on high-resolution AFM observations, we demonstrated that there are two types of buckled structures of $(\sqrt{13} \times \sqrt{13})$ silicene on an Ag(111) surface. They have the same honeycomb pattern on the Ag substrate, but the heights of the atoms inside the unit cell are different. The DFT calculations identified these two types of structures, and the results were in good agreement with the AFM observation as well as the previous STM images. It was demonstrated that AFM is a powerful tool to identify buckling structures that govern physics and chemistry in silicene [61]. The mechanism of high-resolution AFM imaging was also elucidated by force spectroscopy and DFT calculations. High-resolution AFM imaging based on attractive chemical interaction force accompanied by atom relaxation is a complementary method to high-resolution imaging based on Pauli repulsive force. This result remarkably indicates that high-resolution AFM can be applied not only to other phases of silicene on Ag(111),

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but also to silicene grown on other substrates [9,62,63], minor structures (defects [64] or locally formed silicon allotropes, such as pentagonal Si chains [65,66]), and other single-atomic-layer materials, such as germanene [67–70], stanene [71], and borophene [72].

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