Initial stages of the adsorption of Ge atoms on the Si(111)-(7×7) surface

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Using scanning tunneling microscopy and first-principles density functional calculations, we have investigated systematically the initial stages of single Ge atoms adsorbed on a Si(111)-(7×7) surface. When the deposition is at an elevated temperature of 420 K, single Ge atoms are found to substitute for the Si adatoms randomly. When the deposition is at room temperature, single Ge atoms do not replace the Si adatoms but move frequently within half unit cells. When the room temperature prepared sample is imaged at 78 K, the Ge atoms are observed to either adsorb at the stable high coordination sites near the corner Si adatoms or hop among the high coordination sites near the center Si adatoms. The adsorption sites of Ge atoms at high coordination positions have been determined by first-principles calculations and comparisons with measured scanning tunneling microscopic images.

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I. INTRODUCTION

The growth of germanium on silicon surfaces has received much attention in recent years due to its important potential applications in hetero-semiconductor micro/nanoelectronic and photonic devices. Because of its complex periodic structure and diverse bonding configurations, a Si(111)-(7×7) surface serves as a good substrate for growing various Ge nanostructures such as nanoislands[1–5] and reconstructed Si(111)-(7×7)-Ge and Si(111)-(5×5)-Ge surfaces.[6–10] The exact nature of the bonding between Ge atoms and Si(111)-(7×7) surface at the initial stage of adsorption is particularly important for understanding the interactions between Ge and Si, but it is still under dispute both experimentally and theoretically.

Early experimental and theoretical works suggested that Ge atoms prefer to occupy the on-top sites of Si adatoms and rest atoms,[11–15] but these results were not confirmed by later experimental observations. Comprehensive transmission electron diffraction investigations by Kajiyama *et al.*,[7] however, suggested that Ge atoms randomly substitute for Si atoms in the Si(111)-(7×7)-Ge interface at elevated temperature. Carlisle *et al.*[16] also found evidence in their core-level photoemission spectroscopy measurements that there is some preference for Ge atoms to substitute for Si adatoms in annealed samples of Ge deposited on a Si(111)-(7×7) surface. Using scanning tunneling microscopy (STM) and first principles calculations, Wang *et al.*[17] recently investigated the adsorption of Ge on Si(111)-(7×7) at low coverages by depositing Ge onto the substrate at an elevated temperature (420 K). By comparing topographic STM images and results from calculations on four configurations, they concluded that Ge atoms must substitute for Si adatoms during the initial stage of adsorption. All the above results seem to consistently support the conclusion that Ge atoms substitute for Si adatoms on Si(111)-7×7 surfaces. This conclusion is in strong contrast with the calculation results obtained by Cho and Kaxiras,[18,19] who, in an earlier theoretical study of the adsorption of Ge atoms on Si(111)-(7×7), using a 4×4 unit cell with density functional-total-energy calculations, found that high-coordination bridge (B_2) sites are the most stable adsorption sites for Ge. The difference between the two calculations by Wang *et al.*[17] and Cho and Kaxiras[18,19] is in the initial configurations. The former assumed that a single Si adatom diffused away from the unit cell while the latter retained all Si adatoms in position. Thus, one might ask whether the configuration used by Cho and Kaxiras can be experimentally achieved?

In the present work, we employed scanning tunneling microscopy combined with full Si(111)-(7×7) unit cell first-principles calculations to examine the initial stages of single Ge adsorption on a Si(111)-(7×7) surface. We deposited Ge atoms onto the Si surface at different substrate temperatures, namely, at room temperature (RT) and an elevated temperature, to investigate whether metastable states of adsorption exist. While our experimental results on the sample prepared at elevated temperature are consistent with the abovementioned studies, we found that, for RT deposited sample, single Ge atoms indeed adsorb at positions near the B_2 sites, but rapidly diffuse in the half-unit cell of the 7×7 reconstructed surface at room temperature. When imaged at a low temperature (78 K), the Ge atom can either stably reside at the position near the B_2 site if it is close to the corner Si adatoms or it can hop among the different adsorption sites if it is close to the center Si adatoms in the half-unit cells. Our work clearly clarifies the controversial issue on the adsorption and diffusion of Ge on Si(111)-(7×7) and provides further understanding of the interactions of Ge with silicon surfaces.

II. EXPERIMENT

The experiments were conducted with a low temperature scanning tunneling microscope (Omicron GmbH, Germany)

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in an ultrahigh vacuum with a base pressure below 7×10^{-11} torr. Chemically etched tungsten STM tips were cleaned by cycles of Ar^{+} sputtering in advance to guarantee the quality of both the STM images and tunneling current recorded as a function of time. The Si(111) wafer was *n*-type phosphorus doped with a resistivity of 7–10 Ω cm, and was first degassed for 24 h at ~930 K by direct current heating. A clean and well-reconstructed Si(111)-(7×7) surface can be routinely obtained by repeated cycles of flashing the sample to ~1500 K for 30 s and rapid cooling to 1180 K, followed by a slow cooling down to RT at a rate of about 1 K/s. All substrates were checked by STM to ensure that they had a well-ordered and low-defect (7×7) reconstruction before any deposition.

Ge was deposited onto the Si(111)-(7×7) surface from a molybdenum crucible in an *e*-beam evaporator with a deposition rate of ~0.01 monolayer (ML) per minute (1 ML $=7.84 \times 10^{14}$ atoms/cm^2). During evaporation, the pressure in the chamber was lower than 2×10^{-10} torr. Unlike the thermal evaporation method employed by Wang *et al.*,[17] in *e*-beam evaporation the substrate was positioned as far as ~15 cm away from the Ge source and the irradiative heating effect on the substrate could be avoided. In this way, we could control the substrate temperature accurately.

III. RESULTS AND DISCUSSION

A. High temperature deposition

We first examined Ge deposition onto a clean Si (7×7) surface at an elevated temperature (420 K), the same condition used in Wang *et al.*'s experiment.[17] Presumably, at this temperature the thermal energy is sufficient (i) to activate the Ge-Si exchange reaction and (ii) to diffuse away the replaced Si atom from the unit cell to the step edges.[20] Figure 1 shows the filled state STM images at low Ge coverage (~0.05 ML). In these topographic images, we can see that the surface lattice retains the original Si(111)-(7×7) reconstruction upon Ge deposition, and the faulted half-unit cell (FHUC) and the unfaulted half-unit cell (UHUC) can be distinguished as triangles due to the different electronic states [black triangles in Fig. 1(a)]. All deposited Ge atoms appear as bright protrusions at the bias of −1.5 V as compared to the Si adatoms in the 7×7 structure. Most of the deposited Ge atoms are resolved as single atoms, and a few others form small bright clusters. Single Ge atoms seem to reside on the Si adatom sites of the reconstructed Si(111)-(7×7) surface, and up to eight different structures ($F1, F2, F3, F4, U1, U2, U3, U4$) were observed in UHUC and FHUC [representatives labeled by white triangles in Figs. 1(a) and 1(b)]. The $F3$ and $U3$ structures are consistent with the type-*A* and type-*C* structures reported by Wang *et al.*[17] We also noticed that the deposited Ge atoms prefer to reside on the corner Si adatom site in the FHUC ($F1$). We did not observe any Ge atoms residing on the rest Si atom site or other high-coordination sites, including the B_2 site.

To identify the exact positions where the single Ge atoms reside, we superimposed the (7×7) lattice grid on the image as shown in Fig. 1(c). The two thick white triangles show the FHUC and UHUC with one Ge atom located in each, while the two thick black triangles are FHUC and UHUC without Ge atoms for comparison. The thin black lines indicate the Si adatom triangles. It is clear that the centers of the Ge protrusions in both FHUC and UHUC are located at the vertexes of the thin black triangles, i.e., the corner Si adatom sites. At other sample biases, the position of the Ge protrusion was all found to be the same. Our results are consistent with Wang *et al.*'s[17] work except we did not observe their type-*B* structure. They observed type-*B* structure at the coverage of 0.08 ML and 0.1 ML but not at 0.02 ML. More than 0.05 ML may be required to form type-*B*. By comparing our observations with their results, we support the conclusion that Ge atoms substitute for Si adatoms when the deposition is done at elevated temperatures.

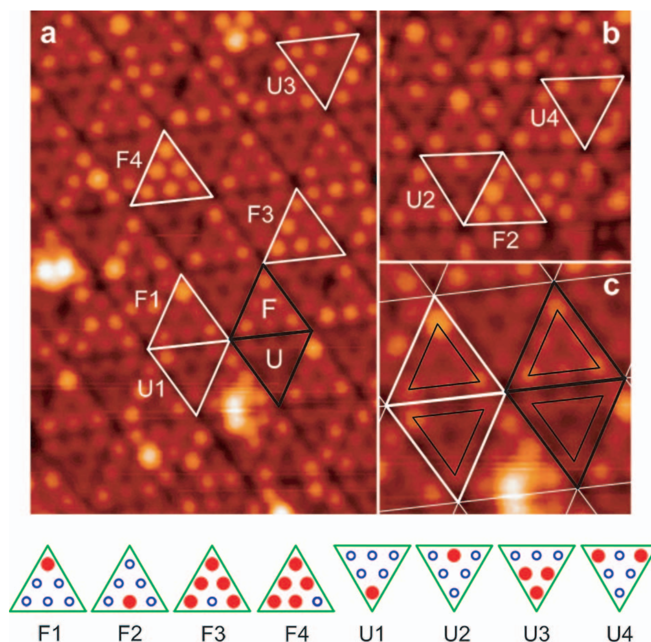

FIG. 1. (Color online) (a) and (b) RT filled state STM images (at a bias of −1.5 V) of the Si(111)-(7×7) surface with a Ge coverage of ~0.05 ML deposited at 420 K. The white triangles highlight the eight basic structures we frequently observed with their respective models shown at the bottom of the figure. (c) A zoom-in area in (a) with a superimposed lattice grid labeling the 7×7 periodicity. The thin black lines indicate the Si adatom triangles and the thick white and black triangles denote, respectively, the unit cells with/without Ge atoms.

B. Room-temperature deposition

Room-temperature deposition of Ge onto Si(111)-(7×7) has been studied before.[2,3] However, due to heating of the sample from thermal evaporation, these early experiments were not able to deposit Ge atoms to substrates truly at RT, and no information on the Ge adsorption sites nor the adsorption behavior of single Ge atoms was reported. To investigate the adsorption behaviors and to identify the corresponding adsorption sites, we prepared the sample by holding the substrate at RT during (*e*-beam) Ge deposition, followed by STM imaging at both RT and 78 K. We chose a

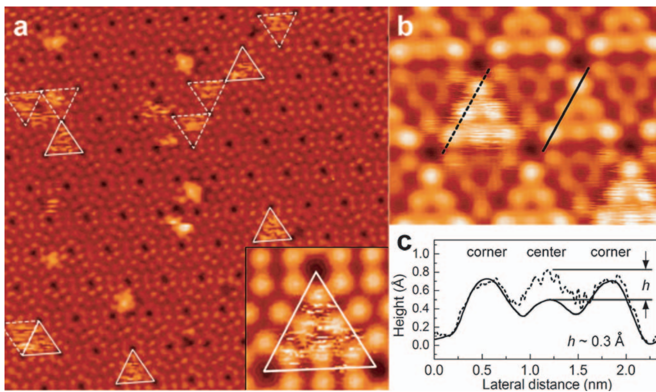

FIG. 2. (Color online) (a) RT empty state STM image (bias +1.5 V) of a 28×28 nm^2 area showing single Ge atoms (fuzzy image) and small Ge clusters adsorbed on the Si(111)-(7×7) surface. The inset is a zoom-in empty state STM image of a single Ge atom adsorbed in a FHUC. The fuzzy noise indicates the frequent hopping of a single Ge atom within the FHUC. The scanning speed was 75 nm/s. (b) A filled state image (bias −1.5 V) of single hopping Ge atoms adsorbed in FHUCs at a scanning speed of 25 nm/s. (c) Line profiles along the solid and the dashed lines in (b).

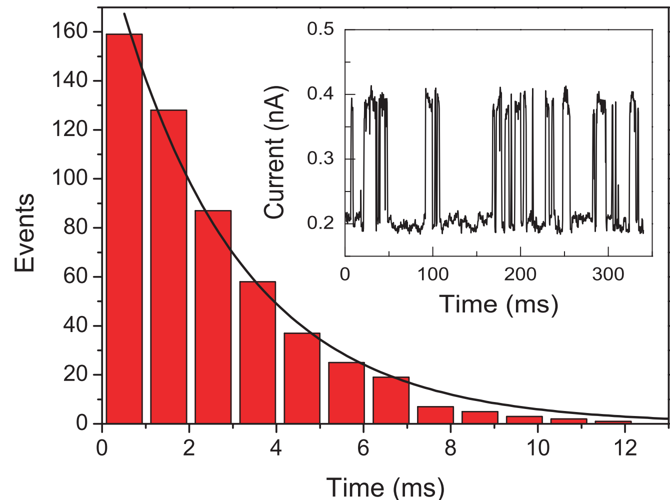

FIG. 3. (Color online) (a) The bar distribution of the events with their residence time longer than the given time on the horizontal axis. The solids line is an exponential fit with a time constant of 2.9 ± 0.2 ms. The inset shows a time-dependent tunneling current trace taken above a corner Si adatom site. A high current level represents a Ge atom moving to an adsorption site that causes the corner Si adatom site to be brighter.

Ge coverage of about 0.01 ML in order to observe individual Ge atoms in the half-unit cells.

1. Room-temperature imaging results

Figure 2(a) shows a RT STM image of low Ge coverage on a Si(111)-(7×7) surface. We observed many fuzzy triangular patterns in both FHUC and UHUC of the surface. These noisy patterns are similar to the cases of single Pb atoms adsorbed on Si(111)-(7×7) surfaces at room temperature[21] and single noble metal atoms[22,23] and Sn atoms[24] adsorbed on the same surfaces at lower temperature. They are likely to originate from a single Ge atom hopping frequently from site to site within the half-unit cell, similar to the activity of noble metal atoms. On this sample, we did not observe any evidence of Ge atom substitution for the original Si adatoms as in the high-temperature deposition case. The inset of Fig. 2(a) shows an empty state STM image of a single Ge atom adsorbed in a FHUC, where the Si adatoms underneath the fuzzy noise can be clearly identified. This further suggests that the adsorbed Ge atom did not substitute for Si adatoms and destroy the original Si(111)-(7×7) surface lattices.

Figure 2(b) shows the filled-state STM image of single Ge atoms diffusing in FHUC obtained at a relatively slow scanning speed of 25 nm/s [vs the speed of 75 nm/s in Fig. 2(a)]. Under this slower scanning speed, it is expected that the more favorable adsorption sites will appear to be brighter than those less favorable sites due to different average residence times of Ge at different sites. In Fig. 2(c), the line profiles along the solid and dashed lines across the corner-center-corner Si adatoms [Fig. 2(b)] in two neighboring FHUCs, one with a Ge atom and the other without a Ge atom, are shown. One can easily see that the height difference between the corner Si adatoms in the two FHUCs is negligible, but the height difference between the center Si adatoms is remarkably large, at about 0.3 Å. This height difference suggests that the adsorbed Ge atoms prefer to stay at the adsorption sites near a center Si adatom than at those near a corner Si adatom during diffusion.

To obtain quantitative information about the hopping rates and residence times of Ge atoms at the adsorption sites near both a corner Si adatom and a center Si adatom, we performed a time-dependent tunneling current study on the diffusion of Ge atoms at RT. The details of this technique have been described in a previous work.[23] The inset of Fig. 3 shows a typical time-dependent tunneling current trace recorded at a bias of +2.0 V above a corner Si adatom site with feedback loop turned off. The current trace shows two distinct states with high-current and low-current values, corresponding to a Ge atom staying at an adsorption site near the corner Si adatom and hopping away to other adsorption sites, respectively. The high tunneling current pulses in the current trace represent the randomly appearing events of a Ge atom at the chosen adsorption sites. In Fig. 3, we plot the number of resident events that have a residence time longer than a given duration as a function of time, which should follow exponential decay, $P(t)=\exp(-\gamma t)$, where $P(t)$ is the probability of finding the atom remaining at this site at time t, and γ is the hopping rate out of this site. As shown in Fig. 3, a reasonable fit to this relationship gives the decay time constant of $\sim2.9\pm0.2$ ms and thus the hopping rate out of the adsorption site near the corner Si adatom is about 340 Hz. This rate is found to be affected by the sample bias to some extent (<3 fold change) and is not purely from thermal motion. The measured hopping rate of Ge within the half unit cell is much slower than that of noble metal atoms [e.g., slower than Cu by a factor of ~10 (Ref. 23)] but comparable with that of Si at room temperature, implying a similar interaction for Ge and Si with the Si(111)-(7×7) surface. The time-dependent tunneling currents recorded above the center

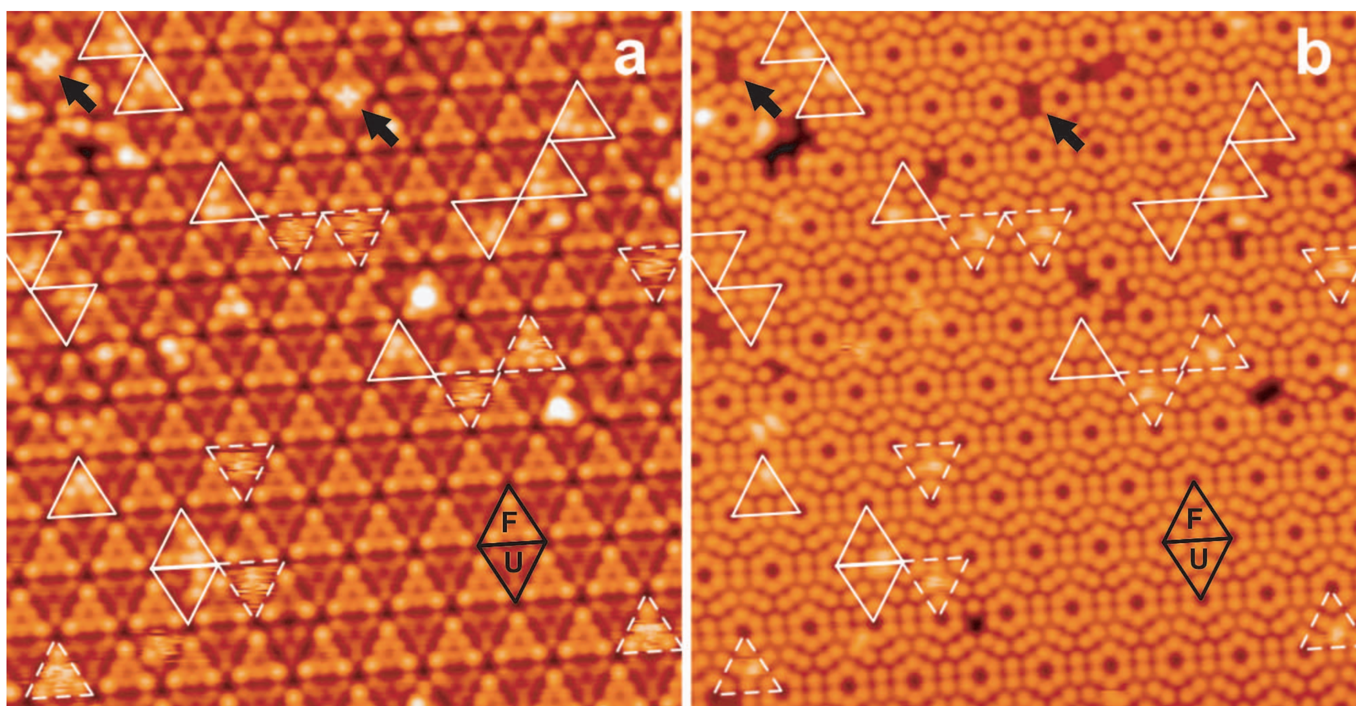

FIG. 4. (Color online) STM images of Ge atoms on the Si(111)-(7×7) surface deposited at RT but imaged at 78 K, showing two adsorption states: the stable adsorption state near a corner Si adatom (solid triangles) and the hopping state (dashed triangles) in a half-unit cell. (a) Filled state image at a bias voltage of −1.5 V; (b) empty state image at a bias voltage of +1.5 V. FHUC and UHUC are indicated by black triangles marked "*F*" and "*U*," respectively. Black arrows point out the tetramers formed by two Ge atoms and two center Si adatoms in two adjacent FHUC and UHUC.

Si adatoms are more complex (not shown here) with three to four current states at different levels, indicating that the diffusing Ge atom at more than one nonequivalent adsorption sites can contribute to the measured currents.

Our observations here are quite similar to what has been observed in the diffusion of single Si atoms on Si(111)-(7×7) at RT by Sato *et al.*[20] using atom-tracking scanning tunneling microscopy. The single Si atoms were also observed to diffuse within each half of the (7×7) unit cell and exhibit fuzzy patterns. It was found that the adsorbed Si atoms spend most of the time inside the small triangles formed by the three center Si adatoms in the half-unit cell, similar to our observations in Fig. 2(b). On the same sample, Sato *et al.* also observed many so-called center tetramers, each believed to be formed by two adsorbed Si atoms with two center Si adatoms in the two adjacent half-unit cells.[20,25] This led to special patterns being observed in two neighboring half-unit cells in their studies. We did not observe similar tetramers on our RT prepared sample when imaging at RT, and we found that two single Ge atoms in two neighboring half-unit cells can diffuse independently rather than combining together to form a tetramer.

2. Low-temperature imaging results

Our above results on the RT-deposited Ge sample are clearly different from those on the high-temperature deposited Ge sample. While the RT STM imaging provides information on diffusion, it cannot identify the adsorption sites due to fast diffusion. This calls for experiments at low temperatures.

Figure 4 shows filled and empty state images of the same area for Ge atoms adsorbed on a Si(111)-(7×7) surface at 78 K. Two typical states were observed in both FHUC and UHUC for single Ge atoms: one is the state of stable adsorption near a corner Si adatom and the other is the state of hopping within a half-unit cell. For the hopping state, which will be discussed later in detail, the Ge atoms are observed to be diffusing around all three center adatoms in one half-unit cell at −1.5 V, but only near one center adatom at +1.5 V. The probabilities of a Ge atom in these two states are found approximately equal. In each state, the events that occur in FHUC and UHUC are also about the same. At this imaging temperature, we also observed center-tetramers on the sample [crosslike clusters in Fig. 4(a), indicated by black arrows], which were very similar to the Si tetramers formed at RT by depositing Si atoms onto a Si(111)-(7×7) surface.[20,25] Due to the similar properties of Ge and Si, it is reasonable to assume that the tetramer structure is formed by two adsorbed Ge atoms and two native center Si adatoms in the adjacent half-unit cells.

To understand and identify the precise adsorption sites of single Ge atoms, we performed first-principles calculations using the VASP code[26,27] within the framework of density functional theory (DFT) (Refs. 28 and 29) by carefully examining all the low energy sites in a 7×7 unit cell. We employed the projector augmented-wave (PAW) method[30,31] and the exchange correlation with the generalized gradient approximation by Perdew, Burke, and Ernzerhof

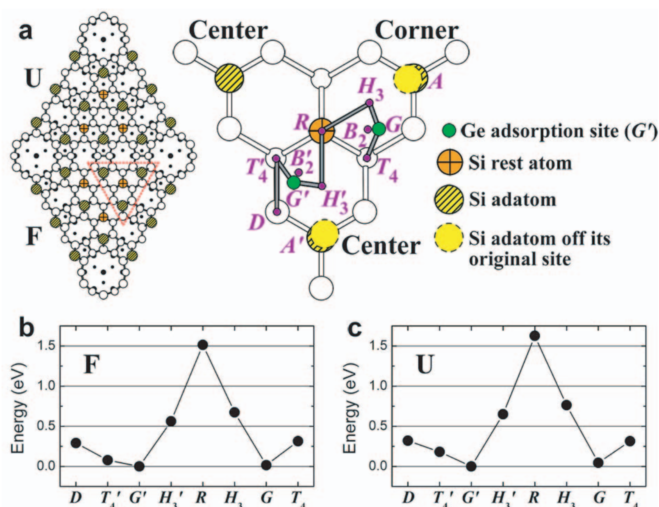

FIG. 5. (a) (Color online) The dimer-adatom-stacking fault (DAS) model and the basin on which the selected sites for adsorption are labeled. "*U*:" UHUC, "*F*:" FHUC. (b) and (c) Energies obtained from the first-principles calculations for a Ge atom at selected adsorption sites in FHUC and UHUC, respectively.

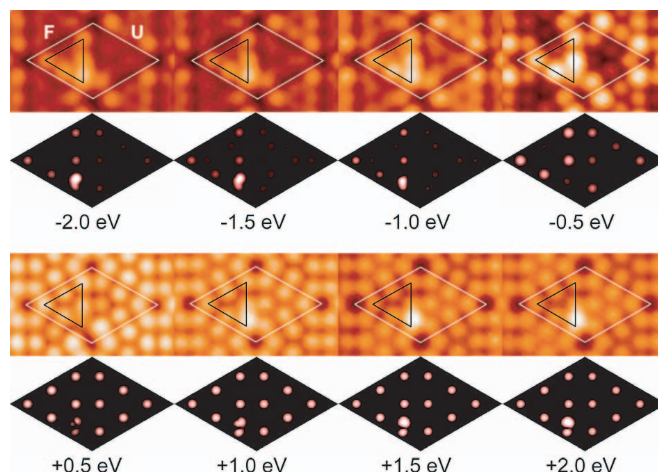

FIG. 6. (Color online) Experimental STM images (upper) and theoretically simulated STM images (lower) of a single Ge atom adsorbed at site G near a corner Si adatom in the Si(111)-(7×7) FHUC at different bias voltages. The images are taken at 78 K.

(PBE-GGA).[32] A repeated-slab geometry is used, with six Si layers separated by a 12 Å vacuum. The unit cell has 298 Si atoms and 49 H atoms to terminate the bottom Si layer. The wave functions are expanded on a plane wave basis with an energy cutoff of 250 eV, and only Γ point is used in the summation of the Brillouin zone of the simulation cell. The Si atoms on the bottom layer are fixed in position and all the other atoms are fully relaxed until the forces are less than 20 meV/Å. As shown in Fig. 5, in both FHUC and UHUC, we found that the lowest energy sites are the high-coordination G' sites near the center Si adatoms, and the second lowest energy sites are the G sites near the corner Si adatoms, where the $G'(G)$ site is laterally close to the $B_2'(B_2)$ bridge sites but has a lower symmetry. The energy difference between the G' and G sites is 16 meV for FHUC and 46 meV for UHUC, respectively. Energies of a Ge atom at some other sites are also presented in Figs. 5(b) and 5(c) for comparison. In a previous work, we studied the adsorption sites for Ag, Cu, and Au on Si(111)-(7×7) surfaces.[22] We found that the adsorption sites of Au, Cu, or Ag atom are also high coordinated but shift slightly away from those of Ge.[22] Ge adsorbed on a $G(G')$ site also chemically bonds with the nearby three Si atoms and pulls the Si adatom slightly off its original position to lower the total energy.

In Wang *et al.*'s work,[17] they used a 4×4 unit cell and found two lowest-energy configurations: Ge atom at the B_2 site and an S_4-type configuration in which the Ge atom substitute for a Si adatom (S_4 site) and the replaced Si atom adsorbs at a B_2 site near a neighbor Si adatom. Their calculations showed that the energy difference between these two configurations is essentially negligible (less than 20 meV). However, by using a 7×7 unit cell, we found up to nine nonequivalent S_4-type configurations, in contrast to the 4×4 unit cell in which only three nonequivalent S_4-type configurations exist. In six of them, a Ge atom substitutes for one Si adatom (corner or center) and the replaced Si atom adsorbs at the $G(G')$ site near a neighbor Si adatom. In the other three configurations, a Ge atom substitutes for one Si adatom and the replaced Si atom adsorbs on the $G(G')$ site near the Ge atom, i.e., a simple permutation structure of our calculated lowest energy $G(G')$-type configurations in Fig. 5(a). The lowest energy of these S_4 configurations is still higher than that of the Ge atom at $G(G')$ site adsorption. The energy difference between the lowest-energy S_4 configuration and the Ge atom at G' site is 98 meV for FHUC and 152 meV for UHUC, respectively. Therefore, we believe that at RT deposition substitution of Si adatoms by Ge atoms is highly unlikely due to the energy cost of breaking three strong σ type covalent bonds that are connected to a Si adatom from other Si surface atoms. Our experimental data in the inset of Fig. 2 also support the assertion that the Ge atom has not substituted for the Si adatom; otherwise, different contrasts among the six Si adatoms in the half unit cell would have been seen at different sample bias voltages. It is not surprising that the RT deposition of Ge onto the Si(111)-(7×7) is different from the deposition at an elevated temperature. At a high temperature, it is possible that the adsorbed Ge atom can break the Si backbonds and replace the Si adatom, followed by the diffusion of the replaced Si atom away to a step edge, resulting in a very different configuration with lower energy, as described by Wang *et al.*[17]

To verify the consistency between the theoretically calculated adsorption sites and experimental observations, we simulated STM images from the first principles calculations using the model by Tersoff and Hamann.[33] Figures 6 and 7 show the low-temperature STM images at a number of biases for single Ge atoms adsorbed near a corner Si adatom in FHUC and UHUC, respectively, together with the corresponding theoretically simulated STM images with Ge at the G sites. The adsorbed Ge atoms manifest themselves as larger bright spots near the corner Si adatoms at high biases, both positive and negative, but make the corner Si adatoms dim at lower biases. In particular, the adsorption of a Ge atom brightens the two neighboring center Si adatoms at all

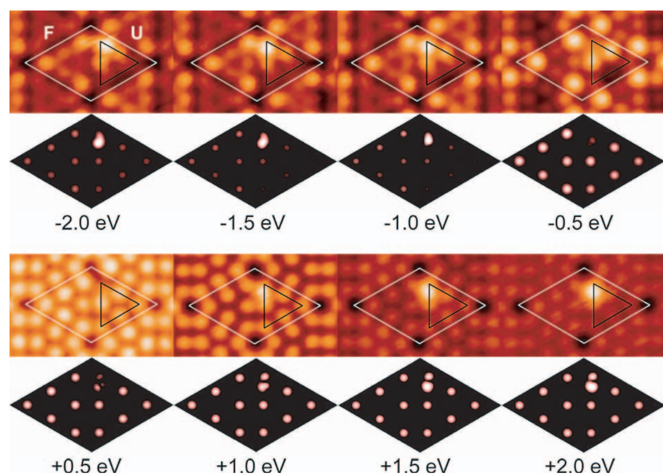

FIG. 7. (Color online) Experimental STM images (upper) and theoretically simulated STM images (lower) of a single Ge atom adsorbed at site G near a corner Si adatom in the Si(111)-(7×7) UHUC at different sample biases. The images are taken at 78 K. Between the first two experimental STM images, the Ge atom has hopped from one G site to another equivalent G site near the same corner Si adatom.

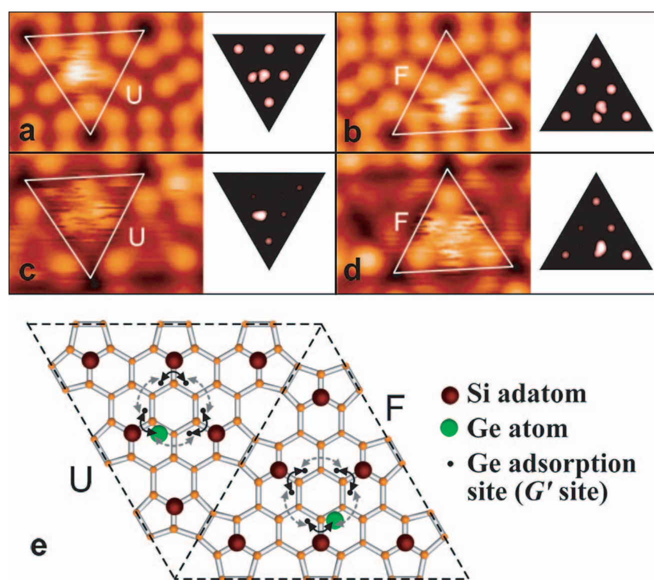

FIG. 8. (Color online) Empty state STM images (a, b) (sample bias +1.0 V) and filled state STM images (c, d) (sample bias −1.0 V) showing that the single Ge atoms were hopping near the center Si adatoms in the UHUC (a, c) and FHUC (b, d) of the Si(111)-(7×7) surface at 78 K. The simulated STM images for Ge at site G' at the corresponding biases are placed next to the experimental STM images for comparison. (e) A schematic model of adsorption sites and hopping paths. The green (light) balls and dots stand for the six G' adsorption sites; the solid arrows indicate the hopping paths between two nearest adsorption sites (corresponding to the empty state cases) and the dashed arrows indicate the hopping paths between sites next to different center Si adatoms.

negative biases. In contrast to high temperature deposition (Fig. 1), where the bright protrusion exactly sits at the Si adatom positions, the bright spot in all the experimental images for the RT deposition at different biases is off from the corner Si adatom site. The simulated STM images reproduce the main features of the experimental images well at all biases and thus are consistent with the experimental evidence. None of the simulated STM images for the S_4-type and other configurations reproduce the observed STM images. Thus, our results on the RT-deposited Ge sample support the theoretical calculation results by Cho and Kaxiras[18,19] but with fine adjustments to the exact adsorption sites.

In our previous work, we investigated the geometric structures of Ag, Cu, and Au adsorbed on Si(111)-(7×7) surfaces.[22] Since the Ag atom frequently hops between the two equivalent adsorption sites near a corner Si adatom at 78 K due to the very low barrier (~50 meV) between them, the observed STM image was actually the superposition of the two equivalent sites and the experimental image exhibits a pattern with a mirror symmetry along the axis through this corner Si adatom to the opposite center Si adatom. In contrast to Ag, the image of a single Ge in a Si(111) half-unit cell is obviously asymmetric. This configuration strongly indicates that the Ge atom resides only at one of two high-coordination sites near the corner Si adatom. This is not surprising since the Ge atom bonds more strongly with the coordinated Si atoms and the barrier for hopping between the two equivalent G sites near a corner Si adatom must be large,

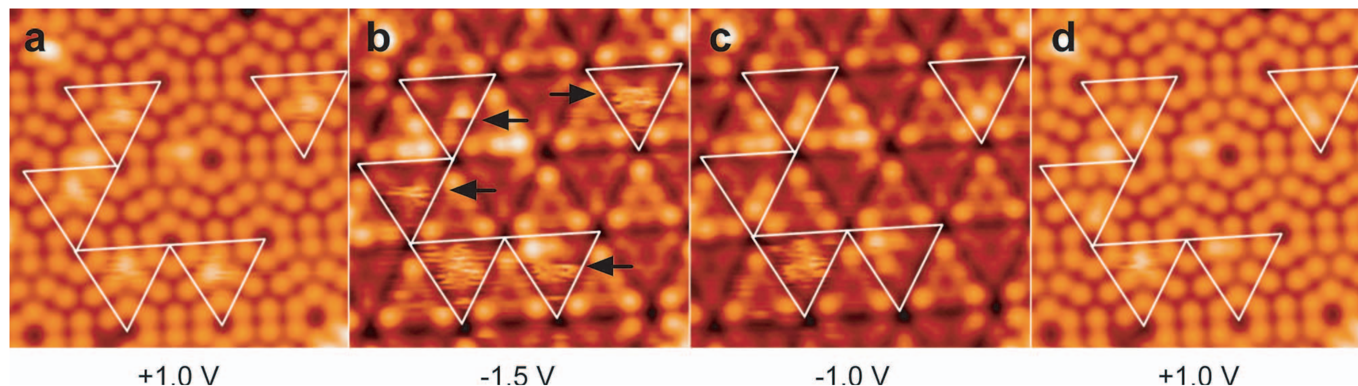

FIG. 9. (Color online) A sequential set of STM images at 78 K showing the displacement of Ge atoms from adsorption sites near center Si adatoms to adsorption sites near corner Si adatoms by an electric field. The black arrows in (b) indicate the time when the Ge atoms made the transition during scanning at a sample bias of −1.5 V. (c) and (d) confirm the change of the adsorption states.

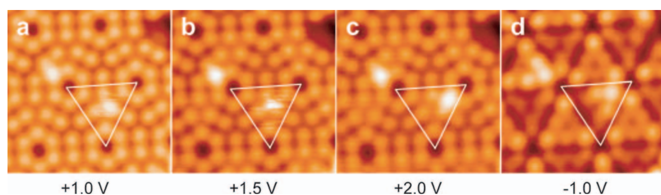

FIG. 10. (Color online) Similar to Fig. 9, except the bias voltage that induces the adsorption state change is +2.0 V.

although this hopping still occurs as observed in the first two images in Fig. 7.

Unlike the stable adsorption near the corner Si adatoms, the Ge atom adsorbed near the center Si adatoms is still hopping at 78 K (Fig. 8), which seemingly contradicts with the theoretical results that predict that the G' site is a more stable adsorption site than is the G site. For this state, we found that there is an obvious electric-field effect. At positive sample biases, the Ge atom hops near one of the three center Si adatoms in a half-unit cell [Figs. 8(a) and 8(b)]. At negative sample biases, the Ge atom was found to hop around all three center Si adatoms in a half-unit cell [Figs. 8(c) and 8(d)]. These observations can be understood by considering that there are six possible stable G' adsorption sites near the three center Si adatoms that form a triangular basin [Fig. 8(e)]. At positive biases, the Ge atom is believed to hop between the two G' sites near a given center Si adatom, as indicated in Fig. 8(e) by the solid arrowed lines. This explains why the fuzzy bright spots in Figs. 8(a) and 8(b) are mirrored around a center Si adatom. At negative bias voltages, the Ge atom may hop among all six G' sites near the three center Si adatoms, as indicated by the arrowed solid and dashed lines. Thus, the observed fuzzy STM pattern in Figs. 8(c) and 8(d) roughly have a threefold symmetry. Although the G' site is calculated to be the lowest energy adsorption site, the barrier between two adjacent G' sites may be low to allow the Ge atom to hop between them [likely via D or $T_4{}'$ sites in Fig. 5(b)], resulting in nonstationary adsorption. In contrast, the stability of the G adsorption site in the STM images is perhaps kinetically originated due to a high diffusion barrier to its neighboring equivalent G site (likely via H_3 site) or to a neighboring G' site (likely via T_4 and $H_3{}'$ sites). The calculated energies in Figs. 5(b) and 5(c) indeed support this conjecture and thus no real conflict with theoretical results exists.

The electric-field effect of the diffusion can be further observed at higher bias voltages. When the bias voltages are $V > 1.5$ V or $V \leq -1.5$ V, the hopping Ge atoms near the center Si adatoms can be pushed into a stable and stationary adsorption state near a corner Si adatom. Figures 9 and 10 show two sets of sequential STM images obtained at different bias voltages, demonstrating that the Ge atoms can be manipulated from the adsorption sites (G') near the center Si adatoms to the adsorption sites (G) near the corner Si adatoms. In Fig. 9, the image taken at +1.0 V shows that initially there are five Ge atoms each hopping in one UHUC. In the image taken at −1.5 V, four out of the five Ge atoms were transported into the stable and stationary adsorption states near the corner Si adatoms. The black arrows in Fig. 9(b) indicate when the Ge atoms changed their states. As shown in Fig. 10, a similar phenomenon was observed when the bias voltage was set to +2.0 V. While the electric field effects are clearly demonstrated experimentally and the results can be understood with reasonable assumptions about the diffusion barriers, a full theoretical understanding is beyond the scope of the present study.

The adsorption of single Ge atoms on a Si(111) surface at a low temperature is quite different from that of Si atoms. Sato *et al.*[34] studied the adsorption of single Si atoms on a Si(111)-(7×7) surface at low temperatures (from 210 K down to 80 K) using STM with the atom-tracking technique. They found that at 210 K, the Si atoms were still diffusing and the adsorption site was identified to be the H_3 site near the corner Si adatoms. When the sample was cooled to 80 K, there were two coexisting states, one with stationary adsorption at the site near the T_4 site, which is adjacent to the corner Si adatom, and the other diffusing over a small area between the corner Si adatom and the nearby rest atom. In our experiments at 78 K, in the stationary adsorption state, Ge atoms adsorbed at the G sites near the corner Si adatoms instead near the T_4 sites; in the diffusing state, the Ge atoms were found to diffuse over areas near the center Si adatoms, instead of near the corner Si adatoms.

IV. CONCLUSION

In summary, we have studied the initial stages of single Ge atoms adsorbed on a Si(111)-(7×7) surface prepared at RT and an elevated temperature using scanning tunneling microscopy and time-dependent tunneling currents. There is a strong contrast in the behavior of Ge atoms on the two samples. When the deposition is at a high temperature, Ge atoms do not diffuse but randomly substitute for Si adatoms, which is in agreement with previous works. At RT deposition, there is no evidence showing substitutions of Ge atoms for Si adatoms. Both theory (Fig. 5) and experiment (Fig. 2) indicate that G' is the most stable adsorption site and G is the secondary stable adsorption site. During RT imaging, single Ge atoms are found to rapidly diffuse in the half-unit cell of the reconstructed surface. When the imaging temperature is reduced to 78 K, these Ge atoms are found to reside at the G sites near the corner Si adatoms or still hop among the G' sites near the center Si adatoms. The stationary image for Ge at G site is caused by a high diffusion barrier that limits its diffusion to nearby adsorption sites. The fuzzy image for Ge at G' sites is due to fast diffusion over the low barriers among them. Our results also clearly demonstrate that thermodynamically stable states is for Ge atoms to substitute for Si adatoms on Si(111)-(7×7) surfaces, although sufficient thermal energy is required for the system to reach this stable state. Metastable states can exist if Ge is deposited at RT. The predictions of theoretical calculations, either earlier ones or the present ones, with B_2 or $G(G')$ agree quite well with the experiments.

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