Bonding Configurations and Collective Patterns of Ge Atoms Adsorbed on Si(111)-(7 × 7)

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We report scanning tunneling microscopy observations of Ge deposited on the Si(111)-(7 × 7) surface for a sequence of submonolayer coverages. We demonstrate that Ge atoms replace so-called Si adatoms. Initially, the replacements are random, but distinct patterns emerge and evolve with increasing coverage, until small islands begin to form. Corner adatom sites in the faulted half unit cells are preferred. First-principles density functional calculations find that adatom substitution competes energetically with a high-coordination bridge site, but atoms occupying the latter sites are highly mobile. Thus, the observed structures are indeed more thermodynamically stable.

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Semiconductor nanostructures have been mostly fabricated using compound semiconductors, benefiting from a continuous variation of one or more elements. The Si/Ge system is more limited but has the advantage that it is naturally compatible with Si technology. Indeed, Ge is currently incorporated in Si structures to fabricate strained Si layers with enhanced mobility. There is, therefore, renewed activity in Ge-based nanostructures grown on Si [1–8]. The Si(111)-(7 × 7) surface offers unique potential for the self-assembly of diverse structures because of the large number of distinct bonding sites. "Magic" Si islands and metal nanoclusters were recently grown on this surface [9–11]. Yet, 20 years of studies have not led to definitive conclusions about the initial bonding structures of Ge atoms on this surface, impeding further understanding and potential control of the growth process.

Submonolayer Ge adsorbates on Si(111)-(7 × 7) were investigated using x-ray standing-wave (XSW) measurements at 300 °C by Patel *et al.* in 1985, but it was not possible to determine the precise Ge sites and the bonding structure [12]. Using XSW measurements, Dev *et al.* proposed in 1986 that, at low coverages (< 0.5 ML), Ge atoms would prefer to occupy the on-top sites and to bond directly to the Si adatoms and rest atoms (see Fig. 1 for a schematic of the Si(111)-(7 × 7) surface and pertinent terminology) [13]. Reflection electron microscopy and transmission electron diffraction investigations by Kajiyama *et al.* in 1989 on Ge/Si(111)-(7 × 7) prepared at 640 °C found evidence that Ge atoms randomly substituted any Si atoms at the top layers [14]. Then, core-level photoemission spectroscopy measurements by Carlisle *et al.* in 1994 provided indirect evidence that there was some preference for Ge to replace the Si adatoms in the case of annealed Ge/Si(111)-(7 × 7) samples [15]. More recent measurements using near-edge x-ray absorption spectroscopy and scanning tunneling microscopy (STM) did not provide conclusive descriptions of Ge bonding sites on the Si(111)-(7 × 7) surface [7,16,17]. Very few theoretical calculations have been reported on Ge bonding sites on Si(111)-(7 × 7). Early work was semiempirical with limited predictive capabilities, but it provided support for the notion that Ge atoms bond directly to Si rest atoms or adatoms [18,19]. In 1998, Cho and Kaxiras reported a limited exploration of bonding possibilities using first-principles calculations and found that the most stable adsorption position for Ge on Si(111) is the high-coordination bridge (B_2) site, a bonding site that had not been proposed as likely on the basis of experimental data [20].

In this Letter, we report STM observations and first-principles calculations for the structure of the Ge/Si(111)-(7 × 7) surface at low Ge coverages. Direct

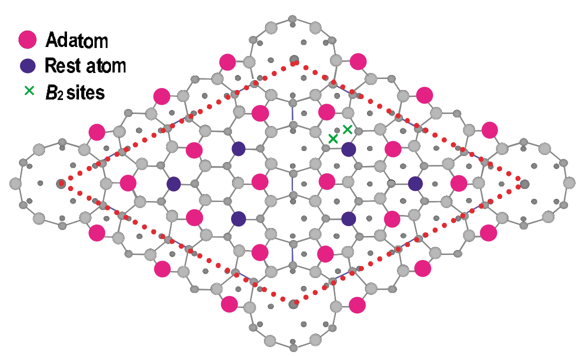

FIG. 1 (color). Schematic top view of the Si(111)-(7 × 7) reconstruction. The outlined is the 7 × 7 unit cell with the faulted and unfaulted half unit cells located on the left and right sides, respectively.

STM observations clearly show that, at low coverages, Ge atoms reside at the Si adatom sites. Profile measurements rule out the possibility of coexistence of a Ge atom and a Si adatom underneath it, thus revealing that the Ge atoms substitute for the Si adatoms. Initially (up to 0.02 ML), the occupation of adatom sites is random with a slight preference for corner adatoms in the faulted half unit cell (FHUC). As coverage is increased, the preference for the FHUC corner adatom sites is enhanced. At 0.08 ML, a distinct triangular pattern of Ge atoms at the corners of the FHUC is dominant. At a slightly higher coverage (0.1 ML) other distinct patterns become more visible and tiny islands start to appear. The above observations are complemented with first-principles calculations. We find that the high-coordination B_2 configuration of adsorbed Ge has roughly the same energy as the configuration in which a Ge atom replaces a Si adatom, with the latter occupying the lowest-energy nearby site. However, we also find the atoms at the B_2 sites are highly mobile, whereas Ge atoms that replace Si adatoms are very stable against diffusion.

The experiments were conducted in an ultrahigh-vacuum STM system (Omicron UHV-STM, Germany) with a base pressure $\sim 5 \times 10^{-11}$ mbar. The samples were cut from an antimony-doped n-type Si(111) wafer (resistance: $\rho \sim 0.03\ \Omega$ cm; thickness: $\sim$0.5 mm). Before it was introduced into the vacuum chamber, the sample was cleaned by ethanol in an ultrasonic bath and rinsed thoroughly by deionized water. Inside the chamber it was degassed for several hours at $\sim$600 °C. The sample was annealed by direct current heating while the pressure was kept below 5×10^{-10} mbar. An annealing cycle consisted of flashing the sample to 1200 °C for 20 s and lowering the temperature fast to about 900 °C and then at a slow decreasing pace rate of 1–2 °C/s to room temperature. The Si(111)-(7×7) reconstructed surface was finally obtained. Ge (99.9999% purity) was deposited onto the as-prepared Si(111)-(7×7) surface by resistive evaporation, and the substrate temperature was 150 °C by irradiation. During evaporation the pressure in the chamber was lower than 5×10^{-10} mbar. A typical deposition rate of $\sim$0.01 ML/min was routinely achieved. One monolayer is defined as the atomic density of the unreconstructed Si(111) surface (1 ML $= 7.83 \times 10^{14}$ atoms/cm^2). All the STM images were acquired in a constant-current mode with an electrochemically etched tungsten tip at room temperature.

Figure 2 shows STM topographic images of the Si(111)-(7×7) surface with Ge coverages of 0.02, 0.08, and 0.10 ML, respectively. These images show that the surface lattice retains the original 7×7 reconstruction. The dimers and the Si adatoms are visible. The FHUC and the unfaulted half unit cell (UHUC) of the 7×7 reconstruction are distinguished due to the different contrast [Fig. 2(a)]. The deposited Ge atoms appear as bright protrusions. Three significant features are present in the STM images. First, the deposited Ge atoms are clearly resolved as a single atom. Second, the adsorbed Ge atoms reside on the sites that were occupied by the Si adatoms on Si(111)-(7×7). Finally, more Ge atoms occupy the corner adatom sites in the FHUC than the other adatom sites. No Ge atoms are found at either the rest atom or the high-coordination surface sites. Furthermore, profile lines through the bright dots in the STM images show that the height difference between the Ge atom and the original Si adatoms is about 0.2 Å, as shown in Fig. 3. These data clearly show that the Si adatom does not stay in its original position which is just below the Ge atom (the Si adatom occupies a T_4 site just above a second-layer Si atom on a clean surface [21–23]). We conclude that Ge would prefer to substitute the Si adatoms in its initial adsorption stages.

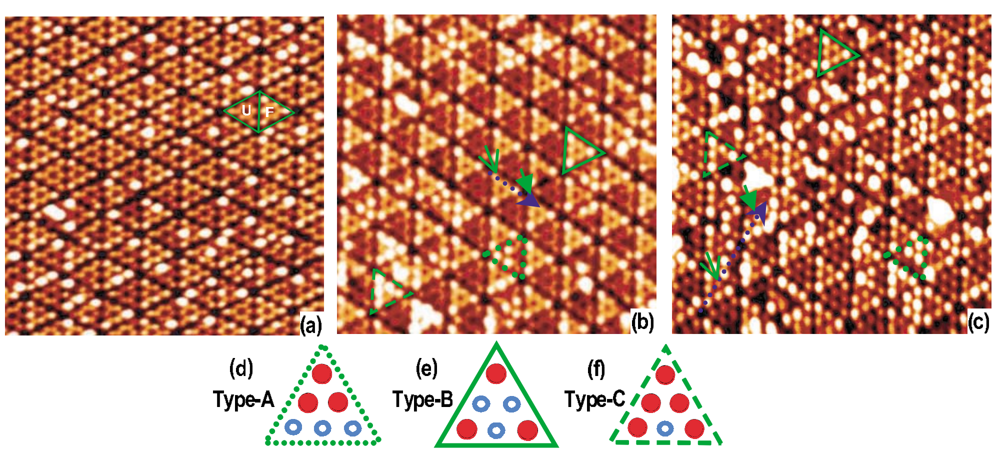

FIG. 2 (color). Filled state STM images of the Si(111)-(7×7) surface with Ge coverages of (a) 0.02 ML, (b) 0.08 ML, and (c) 0.10 ML. A 7×7 unit cell is marked by two triangles in (a), where F and U represent the FHUC and UHUC, respectively. Sample bias: -2.2 V in (a) and -1.5 V in (b) and (c); tunneling current: 0.5 nA in (a) and 0.2 nA in (b) and (c). The scanning area is 20 nm $\times$ 20 nm. Three different configurations of Ge protrusions distributions are denoted in (b) and (c) by the dotted-line triangle, the solid-line triangle, and the dashed-line triangle, respectively. The schematics for the three typical Ge protrusions, named type A (d), type B (e), and type C (f), are also shown.

As shown in Figs. 2(b) and 2(c), there are three types of collective Ge patterns that appear on Si(111)-(7 × 7). The schematics of these Ge protrusions, named type A, type B, and type C, are given in Figs. 2(d), 2(e), and 2(f), respectively. Type A illustrates three Ge atoms locating at one corner adatom site and two adjacent center adatom sites in a HUC. Type B indicates the configuration with three Ge atoms occupying corner adatom sites in a HUC. Type C refers to the adsorption structure with five Ge atoms residing on the sites of three corner adatoms and two center adatoms in a HUC. Type B and type C distribute preferentially in the FHUCs, as shown in Figs. 2(b) and 2(c). The contrast difference between the Ge adatoms in the type-C protrusions is attributed to both their difference in occupation of the dangling bond states and different heights (corner adatoms transfer less charge to the rest atoms and reside higher than center adatoms). Table I shows the site distribution of the Ge atoms. At the coverage of 0.02 ML, the site preference ratio is about 5.6:4.4 for the FHUC to the UHUC, and 6.1:3.9 for the corner to the center adatom sites, respectively. When the coverage increases to 0.08 ML the site preference ratios are about 9:1 for the FHUC to the UHUC, and 4:1 for the corner to the center adatom sites. The site distribution for the coverage of 0.10 ML is similar to that for the coverage of 0.08 ML. The overall conclusion is that after an initial random occupation of Si adatoms sites, corner adatom sites in the FHUC are preferred and gradually type-B patterns become dominant. Type-A and type-C patterns are more discernible at slightly higher coverages, and, finally, small islands begin to appear [Fig. 2(c)].

Earlier theoretical studies employing semiempirical methods suggested that Ge atoms bond directly to Si adatoms and rest atoms and reside at the on-top sites [18,19]. The studies also concluded that substitution of Ge for the Si adatom was not possible [19]. On the other hand, earlier first-principles calculations based on a 4 × 4 supercell showed that Ge would prefer to bond at the bridge site (B_2-type) between a rest atom and a first-layer Si atom [20]. While these theoretical conclusions are inconsistent with our experimental observations, we note that the possibility that Ge atoms may replace Si adatoms was not considered in the previous first-principles calculations [20].

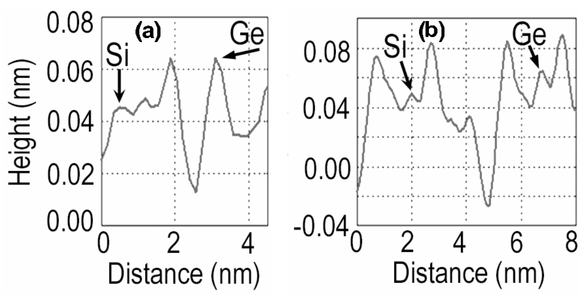

FIG. 3. The profile lines corresponding to the dashed-arrow lines in the STM images of Figs. 2(b) (a) and 2(c) (b), respectively.

We performed first-principles density functional calculations using the pseudopotential method and a plane-wave basis set [24]. The Si(111) surface was modeled by repeated slabs with four layers of Si atoms and four Si adatoms, separated by a vacuum region of 12 Å (each layer contained 16 Si atoms, corresponding to a 4 × 4 surface unit cell, which is a small piece of the 7 × 7 cell; as in Ref. [20], this cell is adequate for the present purposes). Two of the four rest atoms were saturated by hydrogens, so that the ratio of the number of the adatoms to that of the rest atoms is the same as for the 7 × 7 surface. Except for the Si atoms in the bottom layer, which were fixed and saturated by H atoms, all the atoms were relaxed until the forces on them were less than 0.05 eV/Å. Exchange-correlation effects were treated with the generalized gradient-corrected exchange-correlation functionals given by Perdew and Wang [25]. We adopted the Vanderbilt ultrasoft pseudopotentials [26]. A plane-wave energy cut-off of 14.7 Ry and the Γ point for reciprocal space sampling were used for all the calculations.

All the possible configurations with a Ge atom near an adatom and/or a rest atom were calculated. Two lowest-energy configurations, shown in Fig. 4, were found to have essentially the same total energy (the difference in total energy is smaller than 0.02 eV). The first configuration consists of Ge at a B_2 site [Fig. 4(a)], as identified earlier by Cho and Kaxiras [20]. In the second configuration [Fig. 4(b)], the adsorbed Ge atom substitutes for a Si adatom and the Si adatom occupies a nearby B_2 site. We refer to the Ge position in the second configuration as S_4 (a substitutional site with four nearest-neighboring silicon atoms). The total energies of the configurations with Ge bonded at the on-top positions of adatoms and rest atoms are significantly higher (2.3 and 1.6 eV, respectively) than the B_2 and S_4 configurations, clearly ruling out the possibility of such configurations, which were suggested previously on the basis of semiempirical calculations [13,18,19]. For both lowest-energy configurations (B_2 and S_4), the atom (Si or Ge) at a bridge site may diffuse within a basin (to occupy any of the six B_2 sites near the rest atom) and across basins (to occupy the B_2 sites near different rest atoms). The diffusion barriers within a basin and across basins are about 0.5 (0.6) and 1.0 eV (1.0 eV) for the Ge (Si) atoms, respectively, in agreement with previous first-principles calculations [20,27]. On the other hand, the

TABLE I. Site distribution of Ge at various adatom sites at coverages of 0.02, 0.08, and 0.10 ML, respectively.

	0.02 ML	0.08 ML	0.10 ML
Faulted corner sites	40%	76%	65%
Faulted center sites	17%	12%	13%
Unfaulted corner sites	24%	4%	8%
Unfaulted center sites	19%	8%	14%

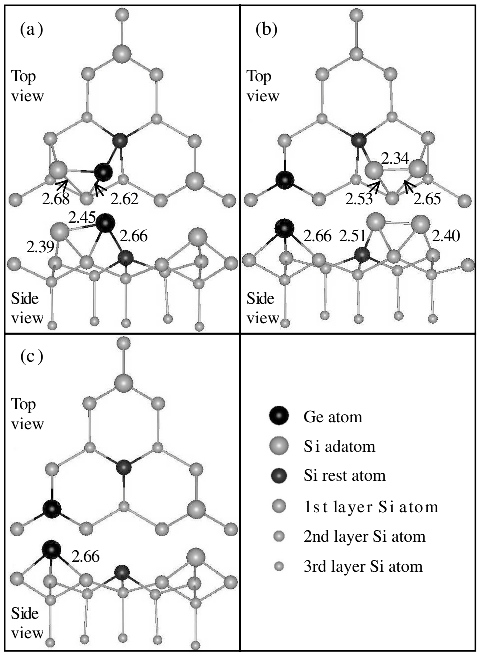

FIG. 4. Schematics of the minimum-energy configurations for a Ge atom on the Si(111) surface: (a) Ge at a B_2 site and the nearby Si adatom at the position off its original site, (b) Ge at a substitutional S_4 site and the Si adatom at a B_2 site, and (c) Ge at an S_4 site with the substituted Si adatom diffused away. The bond lengths are shown in Å.

Ge atoms at the S_4 sites are not able to diffuse on their own. Therefore, the Ge atom in an S_4 configuration is thermodynamically more stable than in a B_2 configuration. In particular, after the atoms initially bonded at the B_2 sites migrate to step edges and/or to form islands, the surface exhibits a stable Ge-S_4 configuration in which Ge atoms substitute for some of the Si adatoms and no atoms are bonded at any of the B_2 sites [Fig. 4(c)], as shown by our STM observations. Small islands, which accommodate the substituted Si adatoms, were observed in the STM images with larger scanning areas.

It is known that the backbonds of the Si adatoms on the Si(111)-(7 × 7) surface are under considerable strain [21,22,28]. It is therefore expected that the adsorbed Ge atoms are able to break the backbonds and replace the Si adatoms at elevated temperatures. Previous studies have established that the corner adatoms in the FHUCs are under more strain than the other adatoms, implying that backbonds of the corner adatoms in the FHUCs are broken easier than those of the other adatoms [22,28]. When Ge atoms are deposited on the surface, in addition, the chance for the Ge atoms occupying the B_2 sites near a center adatom is larger than that near a corner adatom (the center adatom has two nearby rest atoms while the corner adatom has only one). Thus, the Ge-S_4 bonding structure tends to be preferentially formed at the corner adatom sites and in the FHUCs. Note that Ge adsorption does not result in appreciable surface-atom relaxations, suggesting that it does not cause strain relief.

Finally, the relaxed Ge-S_4 configuration obtained from our calculations shows that the Ge atom resides at the position higher by ~0.24 Å along the direction of the surface normal than the original Si adatom that has been replaced by Ge, in good agreement with our STM data.

In summary, the bonding structure of Ge atoms on Si(111)-(7 × 7) at low coverages was investigated with STM and first-principles calculations. We found that individual Ge atoms reside on the Si adatom sites and occupy preferentially the Si corner adatom sites in the faulted half unit cells on Si(111)-(7 × 7). STM measurements and first-principles calculations for the geometrical structures, together with energetics from the first-principles theory, demonstrate substitution of Ge atoms for the Si adatoms on the Ge-adsorbed Si(111)-(7 × 7) surface.

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[1] T. P. Pearsall, Mater. Sci. Eng. B **9**, 225 (1991).
[2] L. J. Schowalter, MRS Bull. **21**, 18 (1994).
[3] A. P. Alivisatos, Science **271**, 933 (1996).
[4] C. Westphal, Surf. Sci. Rep. **50**, 1 (2003).
[5] Y. P. Zhang *et al.*, Appl. Phys. Lett. **79**, 3317 (2001).
[6] A. Lobo *et al.*, Appl. Surf. Sci. **173**, 270 (2001).
[7] L. Yan *et al.*, Surf. Sci. **498**, 83 (2002).
[8] F. Ratto *et al.*, Appl. Phys. Lett. **84**, 4526 (2004).
[9] B. Voigtländer *et al.*, J. Phys. Condens. Matter **16**, S1535 (2004).
[10] J.-L. Li *et al.*, Phys. Rev. Lett. **88**, 066101 (2002).
[11] K. Wu *et al.*, Phys. Rev. Lett. **91**, 126101 (2003).
[12] J. R. Patel *et al.*, Phys. Rev. B **31**, 6884 (1985).
[13] B. N. Dev *et al.*, Phys. Rev. Lett. **57**, 3058 (1986).
[14] K. Kajiyama *et al.*, Surf. Sci. **222**, 47 (1989).
[15] J. A. Carlisle *et al.*, Phys. Rev. B **49**, 13 600 (1994).
[16] P. Castrucci *et al.*, Phys. Rev. B **60**, 5759 (1999).
[17] G. H. Takaoka *et al.*, Thin Solid Films **405**, 141 (2002).
[18] M. Grodzicki and M. Wagner, Phys. Rev. B **40**, 1110 (1989).
[19] L. Stauffer *et al.*, Surf. Sci. **371**, 63 (1997).
[20] K. Cho and E. Kaxiras, Surf. Sci. **396**, L261 (1998).
[21] K. Takayanagi *et al.*, J. Vac. Sci. Technol. A **3**, 1502 (1985).
[22] S. Y. Tong *et al.*, J. Vac. Sci. Technol. A **6**, 615 (1988).
[23] S. Wang *et al.*, J. Chem. Phys. **114**, 436 (2001).
[24] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[25] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[26] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[27] K. Cho and E. Kaxiras, Europhys. Lett. **39**, 287 (1997).
[28] P. Avouris, J. Phys. Chem. **94**, 2246 (1990).