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Evidence of temperature dependence of initial adsorption sites of Ge atoms on Si(111)-7×7

Zubaida A. Ansari and Masahiko Tomitori[a)]
School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan

Toyoko Arai
Department of Physics, University of Tsukuba, Ibaraki 305-8571, Japan
and PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

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Small amounts of Ge atoms are deposited on Si(111)-7×7 surfaces at room temperature (RT) and at 100 °C to clarify the initial adsorption sites using scanning tunneling microscopy. At RT Ge atoms are adsorbed at high coordination B_2 sites around the rest atoms, as predicted by Cho and Kaxiras [Surf. Sci. **396**, L261 (1998)]. On one hand, at 100 °C Ge atoms are adsorbed on corner adatom sites. With increasing Ge coverage the corner sites are gradually occupied, followed by Ge adsorption at center adatom sites, resulting in Ge cluster growth with a size of the half unit cell.
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The stable periodic structure of a Si(111)-7×7 surface with a comparatively large size unit cell (UC) offers a good template for fabricating self-assembled nanostructures.[1–4,6] For example, Si magic clusters and self-assembled metal nanostructures confined in a UC over the Si(111)-7×7 surface have been extensively studied.[3–14] In addition, there are many reports on the initial Ge growth in the UC of Si(111)-7×7 accompanied by the formation of clusters with various shapes and sizes at submonolayer coverages,[3,4,13–20] followed by Stranski-Krastanov (SK) growth mode with increasing Ge coverage owing to Si–Ge lattice mismatch.

At present, there is a considerable controversy regarding the initial Ge adsorption site and the bonding coordination over the Si(111)-7×7 surface. Dev *et al.* have performed x-ray standing wave measurements at submonolayer Ge coverage and proposed that Ge adatoms directly bond to Si adatoms and rest atoms.[12] However, using first principles density-functional theory (DFT) calculations, Cho and Kaxiras suggested that a bridge (B_2) site among the high coordination sites has the minimum energy for Ge adsorption, even compared to those of Ge adatoms bounded with dangling bond of adatoms and rest atoms.[21] On the other hand, Wang *et al.*[20] explored the Ge adsorption over Si adatom sites in detail as well as sites other than the B_2 site. They concluded that Ge atoms are replaced with Si adatoms, and the kicked-out Si atoms migrate to near B_2 sites within a basin on a half unit cell (HUC): This is in agreement with earlier reports.[3,4,15,20] In this letter we report on the initial stages of Ge adsorption on Si(111)-7×7 at room temperature (RT) and at 100 °C, which are observed by scanning tunneling microscopy (STM). The results show that Ge atoms are adsorbed over B_2 sites at RT, while they are adsorbed at corner adatom sites at 100 °C by being presumably replaced with the Si adatoms, preferably over a faulted half unit cell (FHUC).

Experiments were performed using a homemade ultrahigh vacuum (UHV) STM having a base pressure <2 $\times 10^{-11}$ Torr, equipped with a field emission microscope[22] (FEM) to evaluate STM tips, and with a resistive-type Ge evaporation source. *N*-type Sb-doped Si(111) substrates were used (thickness=375 μm, ρ=0.02 Ω cm). Clean Si(111)-7×7 surfaces were prepared by the procedure reported earlier[19] and their cleanliness was confirmed by STM. Then a submonolayer amount of Ge [<0.005–0.1 ML (monolayer)] was deposited at RT and at 100 °C at a controlled flux of ~0.005 ML/min in a vacuum better than 5×10^{-11} Torr. STM images were acquired at RT at a constant current of 0.05 nA using chemically etched [111]-oriented single crystal W tips, which were cleaned and sharpened by thermal-field treatment and checked by FEM.

For the initial growth of Ge on Si(111) at RT, we deposited a Ge amount of ~0.005 ML. A typical STM image at a sample bias voltage of 2.0 V is shown in Fig. 1(a). We found prominent bright spots near the center of FHUC with a faint triangle feature over the HUC. A high-resolution STM image at 0.7 V, shown as an inset of Fig. 1(a), exhibits the fine protruded structure of the spot slightly distorted from the center. These features are extremely different from those in STM images of the Ge initial adsorption at higher temperatures, as described later in detail, although the atomic structure is unclear from the images. The atoms may migrate within the HUC at RT; further study is required to determine it, for example, by bias dependent STM imaging or low temperature observation. Theoretical calculations indicate that rest atom site has a high energy barrier for a Ge atom to diffuse and approach it, compared to high coordination sites such as B_2, H_3, and T_4,[20,21] denoted in Fig. 1(b). A potential well is formed around the rest atom surrounded by three Si adatoms and acts as a basin of attraction for an adsorbed atom. Thus, the spots possibly correspond to a Ge adatom moving at RT around T_1, i.e., rest atom site, or change in the electronic state distribution around T_1 owing to the stress induced by Ge atom adsorption near T_1. According to the calculation by Cho and Kaxiras,[21] the potential minimum for a Si and a Ge atom appears at a lowest symmetrical bridge site, i.e., B_2 with the adsorption energy of −3.94 and −5.91 eV, respectively. Consequently, it is plausible that a

[a)]Electronic mail: tomitori@jaist.ac.jp

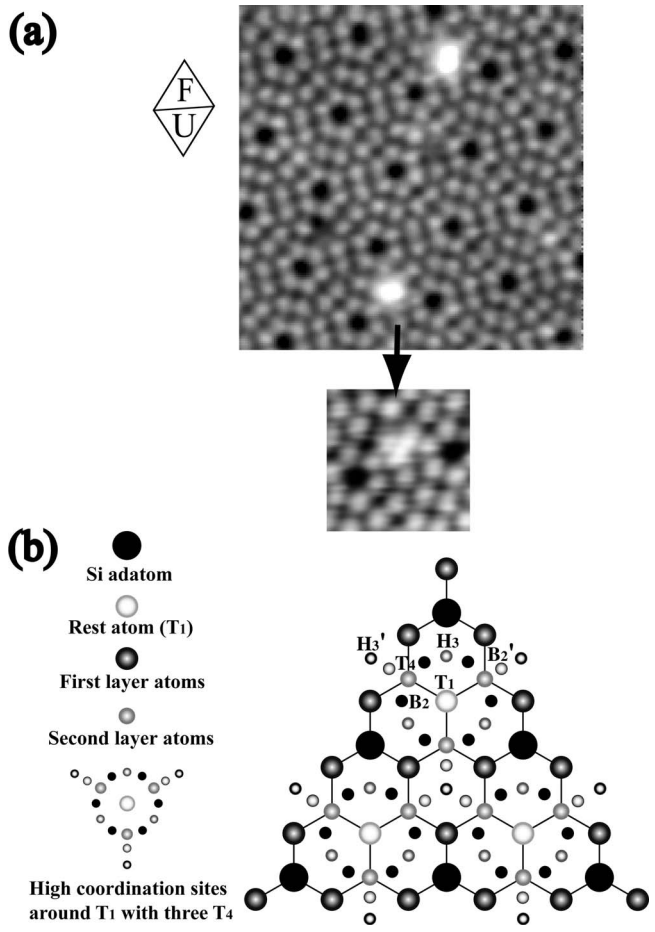

FIG. 1. (a) Empty state STM image of ~0.005 ML Ge deposited Si(111)−7×7 at RT at I_t=0.05 nA and V_s=+2.0 V, scanning area: 10×10 nm^2. Inset exhibits a STM image at V_s=+0.7 V in the region denoted by an arrow. (b) Schematic top view of the atomistic model of a half unit cell of Si(111)−7×7.

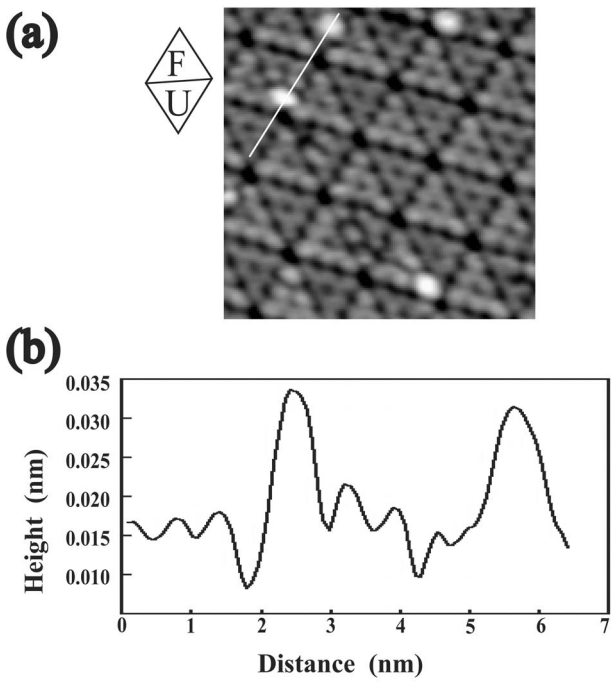

FIG. 2. (a) Filled state STM image of ~0.005 ML Ge deposition at 100 °C. Scanning area: 15×15 nm^2, obtained at I_t=0.05 nA and V_s=−2.0 V. Ge atoms are adsorbed preferably on corner adatom sites. (b) Line profile along a line in (a).

Ge atom is located at or near B_2 (one among six B_2 sites) in the potential well, resulting in a protrusion near the center in a HUC in STM images. In addition, we estimated that the number of Ge atoms in a cluster on the HUC in Fig. 1(a) was less than 3. Here we divided the number of deposited Ge atoms by the number of clusters in the image; the Ge deposition amount was evaluated by using a calibrated quartz thickness monitor for Ge deposition.[19] It is also clear that Ge atoms are preferably adsorbed to FHUC at low coverages in agreement to the results reported for different metals.[5–10] The preference is possibly attributed to the adsorption energy difference between the faulted and the unfaulted halves, which is reported as 0.05–0.1 eV.[2,11,20,21,23,24]

Figure 2(a) shows a STM image of ~0.005 ML Ge deposited at 100 °C. We found clearly resolved single bright spots at corner adatom sites, in contrast to the initial adsorption at RT as mentioned above. The adsorbed Ge atoms look to chiefly preserve the dimer-adatom-stacking fault (DAS) structure of 7×7.[1] The preferential adsorption on the corner adatom site seemed to be reasonable due to the reduction of the number of dangling bonds over the site. From the line profile shown in Fig. 2(b), we estimated the height difference between the top position of Si and Ge adatoms to be ~0.2 Å, which is lower than the bond length of Si–Ge, ~2.4 Å.[21] This strongly suggests that the Ge atom is replaced with a Si adatom than attached to the Si adatom. This configuration of Ge adsorption agrees with the calculation by Wang *et al.*;[20] Ge adsorption at the corner adatom site is thermally more stable than Si adsorption, and the Si adatom is replaced with Ge, resulting in Si atom migration around B_2 within the potential well. Although it is difficult to differentiate the migrating Si from our STM images, the Si atom may correspond to a slight contrast change in the image because of the Si atom diffusion or change in the electronic states around B_2 having the lowest energy for Si and Ge.[20,21].

By comparing the obtained results of Ge deposition at RT and at 100 °C, we have reached a conclusion that Ge atoms preferably occupy B_2 sites at RT and adatom sites at 100 °C, respectively. Both the adsorption sites for Ge atoms should have local minimum energies with high occupation probability. The crucial temperature dependence of adsorption site can be attributed to the difference in activation energy of 0.02 eV between the calculations by Wang *et al.*[20] and by Cho and Kaxiras;[21] the thermal energy is required to replace a Si atom with a deposited Ge atom at the adatom site. It is noted that we have found no change in the configuration of protrusion at the adatom sites even after annealing at 200 °C and that the stability of Ge occupancy at the site is different from the homoepitaxy case of Si on Si(111)-7×7 as reported using STM.[5,6]

On one hand, shown in a series of STM images in Figs. 3(a)–3(c) with increasing Ge deposition at 100 °C, the number of the protrusions at the corner adatom sites increased. For example, less than ten protrusions at the sites are found in an area of 15×15 nm^2 at a Ge coverage of ~0.005 ML in Fig. 3(a), and the number increases to more than 10 at ~0.008 ML in Fig. 3(b). Bright protrusions are partly found on unfaulted half unit cells (UFHC) in Fig. 3; the ratio of the number of protrusions over FHUC with respect to UFHC is approximately 13:1. Furthermore, up to a Ge coverage of <0.1 ML deposited at 100 °C, as shown in Fig. 3(c), Ge

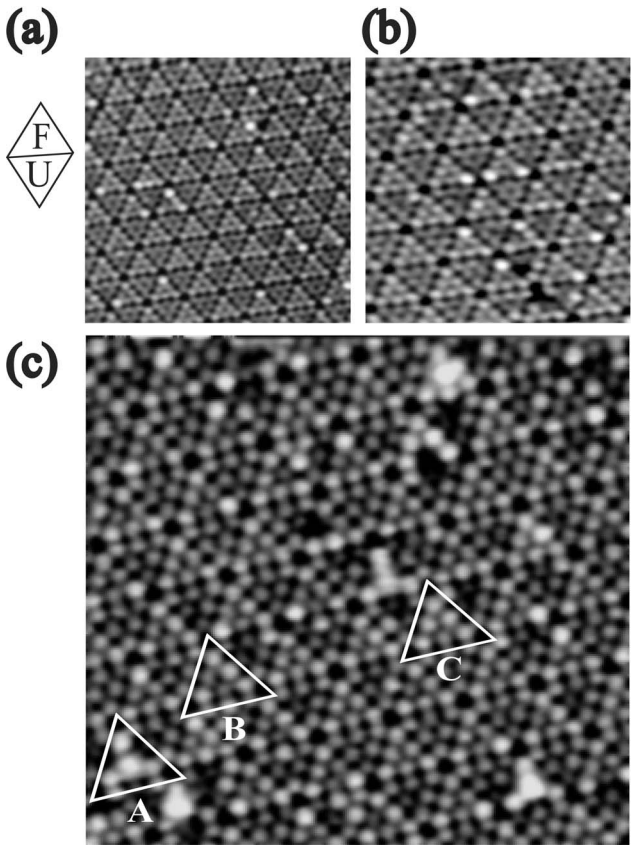

FIG. 3. Filled state STM images with different Ge coverages deposited at 100 °C, obtained at I_t=0.05 nA and V_s=−2.0 V. (a) Ge coverage of ~0.005 ML, scanning area: 20×20 nm^2. (b) with ~0.008 ML, scanning area: 15×15 nm^2. (c) <0.1 ML, scanning area: 20×20 nm^2. Some Ge atoms arranged in different configurations in FHUC are denoted by A, B, and C.

adatoms start to occupy the center adatom sites and form a triangle-shaped protrusion on FHUC, leading to the nucleation of small Ge clusters having a size within HUC. The clusters are possibly formed by adsorption of extra Ge atoms to the same potential well through the weak Ge–Ge interaction. Similar phenomena have been reported for various metals,[5–11] and, in particular, for Pb (Ref. 8) and Au (Ref. 9) with preferential adsorption on FHUC. Distinct patterns are also found in Fig. 3(c). For example, a center of the HUC and three corner sites appear protruded, denoted by A, and, in other case, protrusions at corner sites with a protrusion at their adjacent center site, denoted by B. In the third case, five adatom sites appeared protruded except a corner site, denoted by C. The increase in the deposition amount gradually leads to the growth of Ge clusters with a HUC size because of a diffusion barrier along the dimer row in the 7×7 DAS model.[1] It is estimated that the further increase in Ge deposition will form a hexagonal arrangement of Ge clusters on a template of Si(111)-7×7 as we reported.[19]

In summary, we have experimentally presented that two different adsorption sites for Ge at the initial stage can be dominant depending on the growth temperature: B_2 sites at RT and corner adatom sites at 100 °C, respectively. By depositing Ge at RT with low coverages we found clusterlike triangular features around the center of FHUC while at 100 °C bright protrusions at the corner adatom sites preferentially on FHUC, where Ge atoms are possibly replaced with Si adatoms. At higher Ge coverages at 100 °C, the number of protrusion at the adatom sites increased, leading to the growth of Ge clusters within HUC.

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