

## Adsorbed Si on the Si(111)-(7×7) surface studied by scanning tunneling microscopic and molecular-orbital approaches: Stationary and diffusing Si adsorbates

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In experiments of Si deposition onto the Si(111)7×7 surface using scanning tunneling microscopy, we observe “diffusing” Si adsorbates detected as a noise-shaped pattern in addition to the previously reported “stationary” ones that remain at the same positions. The stable positions and diffusion energy barriers of Si atoms on the surface are obtained using molecular-orbital calculations. For one Si atom, the diffusion barrier is only several tenths of eV, while it exceeds 1 eV for two Si atoms. We propose some assignments: the “stationary” adsorbate for the two Si atoms and “diffusing” one for the single Si atom.

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The study of dynamical phenomena occurring at surfaces is one of the important subjects in surface physics and chemistry. As for the adsorption process, the behavior of Si atoms on Si surfaces has been investigated using scanning tunneling microscopy<sup>1,2</sup> (STM) and a recently developed atom-tracking STM.<sup>3</sup> In the early study of epitaxial growth on the Si(111)7×7 surface with STM, Köhler *et al.* observed a “stationary” Si adsorbate that remains at the same position on the Si(111)7×7 surface.<sup>1</sup> We also observed similar “stationary” Si adsorbates, after depositing Si atoms, using the atomic manipulation technique.<sup>4</sup> This technique is suitable for supplying a small number of atoms to a local area and investigating physical properties such as the atomic bonding states.<sup>5</sup> From detailed analyses of STM images together with molecular-orbital calculations, we assigned the stationary image to a single Si adsorbate located between a rest atom and an adatom of the Si(111)7×7 surface.<sup>6,7</sup> So far, this assignment seems to be accepted widely. On the other hand, in a recent observation on the adsorption of evaporated Si atoms carried out with both conventional STM and an atom-tracking one, Sato *et al.* observed a “diffusing” Si adsorbate as a noise-shaped pattern in the STM images; they also found temperature-dependent diffusing areas inside a half unit cell of the Si(111)7×7 surface.<sup>8</sup> The origin of the diffusing adsorbate image and its temperature dependence is still not understood.

In this paper, we report on the results of STM observations after depositing Si atoms onto the Si(111)7×7 surface using the atomic manipulation technique and theoretical analyses using molecular-orbital calculations. We observe not only the stationary Si adsorbate, but also the diffusing Si adsorbate. Interestingly, calculated results on the stable positions of Si adsorbates and their diffusion energy barriers give an assignment to the stationary adsorbate image, which is different from the assignment accepted to date. That is, the stationary adsorbate image corresponds to two Si atoms. The diffusing adsorbate, on the other hand, can be understood as a single Si atom.

Experiments were made using a UHV-STM (JEOL JSTM-4500XV) at room temperature. Samples cut from a wafer of

P-doped Si(111) were cleaned in UHV (base pressure of  $1 \times 10^{-8}$  Pa) by repeated flash heating at 1200 °C. The tip was a W wire with a diameter of 0.3 mm, sharpened by electrolytic etching. By applying a voltage pulse of 4.5–6 V for 10 ms between the tip and the sample, we deposited extra Si atoms on the Si(111)7×7 surface, which were previously extracted from the surface.

Using the atomic manipulation technique, we deposited stationary Si adsorbates on the Si(111)7×7 surface. As shown in Fig. 1, the stationary adsorbates were deposited (a) between the rest atom and the corner adatom and (b) between the rest atom and the center adatom; they adsorbed more frequently on the corner adatom region than on the center adatom region by a ratio of about 1.5:1. The stationary adsorbates in the STM topographic images have slightly more anisotropic shapes and somewhat larger sizes compared with

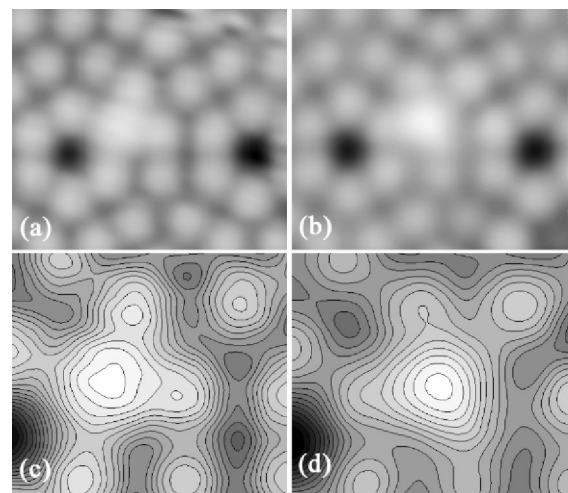


FIG. 1. STM topographic images of stationary Si adsorbates deposited (a) between the rest atom and the corner adatom and (b) between the rest atom and the center adatom on the Si(111)7×7 surface. (c), (d) Magnified contour maps of the respective stationary Si adsorbates. Images were taken at a sample bias of 2 V and a current of 0.6 nA.

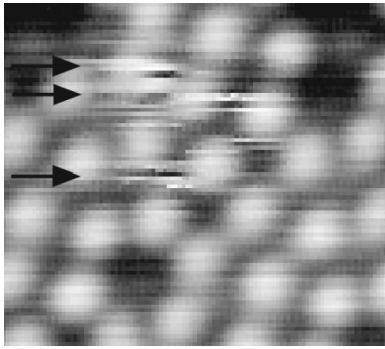


FIG. 2. STM topographic image of a diffusing Si adsorbate inside the half unit cell of the Si(111) $7\times 7$  surface. The noiselike adsorbate is indicated by arrows.

a Si adatom of the surface. In our experiments at room temperature, the stationary adsorbate did not migrate on the surface, except when a voltage pulse was applied.<sup>4</sup> Meanwhile, in the experiments for Si deposition, we occasionally observed diffusing adsorbates on the Si(111) $7\times 7$  surface (Fig. 2). The noiselike glimpse feature inside the half unit cell of the surface is very similar to the evaporated diffusing Si atom on the Si(111) $7\times 7$  surface reported by Sato *et al.*<sup>8</sup> Therefore, in our experiments at room temperature, both the stationary and the diffusing Si adsorbates existed on the surface.

To identify atomic structures of stationary and diffusing Si adsorbates, we performed molecular-orbital calculations. We used *ab initio* Hartree-Fock [6-31G basis of GAUSSIAN98 (Ref. 9)] and semiempirical [AM1 method<sup>10</sup> of MOPAC97 (Ref. 11)] methods, together with Si<sub>13</sub>H<sub>16</sub> and Si<sub>51</sub>H<sub>44</sub> cluster models. The positions of the Si atoms were taken from the optimized geometry of the dimmer-adatom-stacking fault (DAS) structure calculated by the *ab initio* molecular-dynamics method.<sup>12</sup> Hydrogen atoms were introduced to terminate dangling bonds. We adopted the semiempirical AM1 method because the method was reported to give optimized structures similar to those obtained using the *ab initio* Hartree-Fock method with the 3-21G\* basis.<sup>13</sup> In our calculations, geometries of extra Si atoms, rest atoms, and adatoms of the cluster models were optimized. Transition states for the extra Si atoms on the Si<sub>51</sub>H<sub>44</sub> cluster model were obtained using an automatic searching technique.<sup>14,15</sup>

From calculations using the Si<sub>13</sub>H<sub>16</sub> cluster model, we confirmed that the most stable and the next most stable positions of an extra Si atom obtained using the AM1 method were quite similar to those obtained using the *ab initio* method. Therefore, we decided to use the AM1 method in further calculations with the Si<sub>51</sub>H<sub>44</sub> cluster model.

With a varied number of adsorbed extra Si atoms from one to six on the Si<sub>51</sub>H<sub>44</sub> cluster model, we obtained optimized geometries and their electron-density isosurfaces. In a rough approximation, an electron-density isosurface corresponds to a topographic STM image. Figure 3 shows optimized geometries of Si cluster models with electron-density isosurfaces for (a) an adsorbed extra Si atom and (b) two extra Si atoms. With side views of the electron-density isosurfaces, representative cross sections through the observed

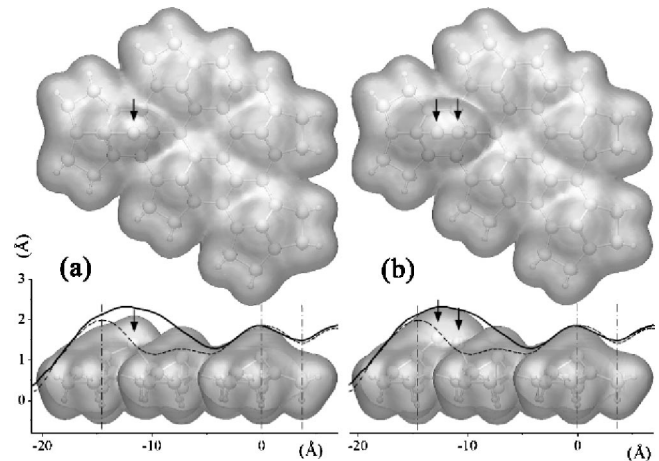


FIG. 3. Electron-density isosurfaces of the Si<sub>51</sub>H<sub>44</sub> cluster model with cross sections of the observed stationary Si adsorbate (a solid line) and the equivalent intrinsic Si surface (a dashed line) shown in Fig. 1(a). (a) The next most stable structure for an extra Si atom and (b) the most stable configuration for two extra Si atoms. Adsorbed extra Si atoms are indicated by arrows.

stationary adsorbate and an equivalent intrinsic Si surface (Fig. 1(a)) are also shown. The shape of the isosurface for the two Si adsorption is much closer than that for one Si adsorption to the stationary Si adsorbate in the STM image. In cases where more than two extra Si atoms adsorbed, the electron-density isosurfaces around the extra Si atoms became much wider.

Figure 4(a) shows the stable positions for an extra Si atom on the Si<sub>51</sub>H<sub>44</sub> cluster model obtained by the semiempirical AM1 method. Stable positions are located between the rest atom and the adatom: the most stable position (labeled 1b) and the next most stable position (1a) are on the corner adatom region. A more detailed description of stable positions for an extra Si atom is given elsewhere.<sup>7</sup> The stable positions for an extra Si atom are in close agreement with other calculated results by the density-functional method with a plane-wave basis.<sup>16,17</sup> A potential-energy surface for an extra Si atom is shown in Fig. 4(b). The energy barrier on the diffusion path from the most stable position (1b) on the corner adatom region to the stable positions (1c-1g) on the center adatom region A was 0.78 eV; that from the stable position (1c) on the center adatom region A to the stable position (1h) on another center adatom region B was 0.59 eV. These energy barriers inside the half unit cell were considered reasonable values in comparison with the activation energy<sup>8</sup> of 1.14 eV for hopping across the boundary of the half unit cell (obtained from experimental data using an Arrhenius plot). This is because the diffusing Si atom stayed for a long time within the half unit cell of the Si(111) $7\times 7$  surface.

Stable configurations and a potential-energy surface for two extra Si atoms on the Si<sub>51</sub>H<sub>44</sub> cluster model are shown in Figs. 4(c) and 4(d). The most stable configuration (2a) is located on the corner adatom region. The two extra Si atoms form a pair on the cluster model. The second most stable configuration (2i) is on the center adatom region A. In addition to these, there are many stable configurations between the rest atom and the adatom (2b-2d, etc.), and over the two

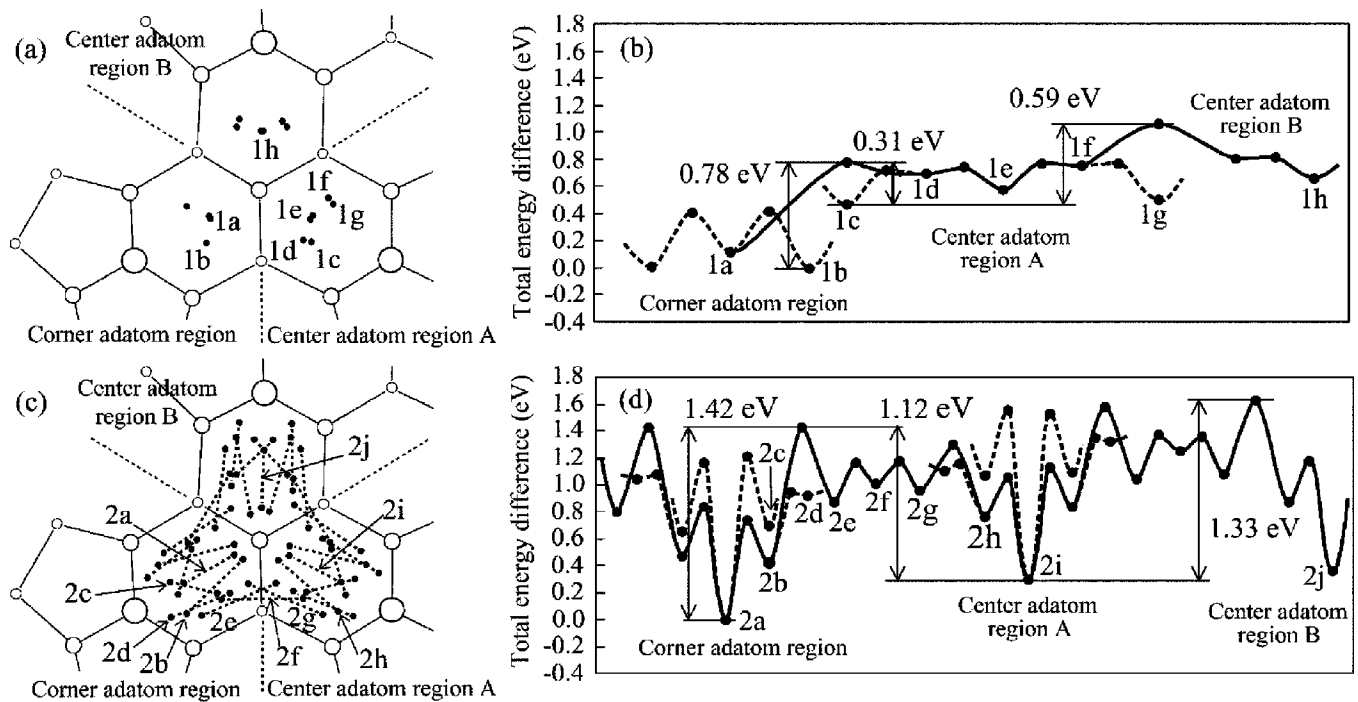


FIG. 4. (a) Stable positions and (b) potential-energy surface for an extra Si atom on the Si<sub>51</sub>H<sub>44</sub> cluster model. (c) Stable configurations and (d) potential-energy surface for extra two Si atoms. Representative stable positions are labeled as 1a to 1h for an extra Si atom, and stable configurations for two extra Si atoms are labeled as 2a to 2j. (b), (d) Solid circles on the potential-energy surfaces show total-energy differences for stable structures and transition ones.

adatom regions (2e-2g, etc.). The energy barrier on the diffusion path from the most stable configuration (2a) on the corner adatom region to the stable configuration (2i) on the center adatom region A was 1.42 eV; the barrier from the stable configuration (2i) on the center adatom region A to the stable configuration (2j) on the center adatom region B was 1.33 eV. The dominant diffusion barrier of 1.42 eV for the extra two Si atoms are 1.8 times higher than the corresponding dominant barrier for the extra one Si atom around the rest atom, while the Si adsorbates have two symmetrical diffusion paths with the same dominant barriers from the corner adatom region to both the two center adatom regions.

In addition, we found that the total energy increased when extra two Si atoms adsorbed separately around the same rest atom on the cluster model: that is, one Si atom at position (1a) and the other at position (1e). The total energy of this structure, denoted hereafter by (1a+1e), was 1.81 eV higher than the energy of the most stable structure (2a). Although the transition state between the structures (2a) and (1a+1e) could not be obtained by the automatic searching technique because of the existence of another transition state [between (2e) and (2f)] with a lower energy barrier near (1a+1e), the energy barrier on the path from (2a) to (1a+1e) must certainly be more than 1.81 eV. This is much higher than other barriers [Figs. 4(b) and 4(d)]. Therefore, once a Si pair forms, diffusions breaking the pair are considered to be more difficult than diffusions maintaining the pair.

From the above calculated results, the stationary adsorbate and the diffusing one can be assigned to a pair of Si atoms and a single Si atom, respectively. Although the above assignment for the stationary adsorbate differs from the

widely accepted previous interpretation that the stationary adsorbate is a single Si atom, the proposed assignment is more plausible for the following reasons. First, the dominant diffusion barrier of 1.42 eV for two Si atoms [Fig. 4(d)] is large enough to prevent Si pair migration at room temperature, while migration of a single Si atom is possible, judging from the dominant diffusion barrier of 0.78 eV for this process [Fig. 4(b)]. Second, the shape of the stationary Si adsorbate in the STM topographic image [Fig. 1(a)] is very close to that of the calculated electron-density isosurface for two Si adsorption, as shown in Fig. 3(b).

To further confirm the first point above, we estimate the hopping frequencies  $R$  for the adsorbed one and two Si atoms using the Arrhenius equation,  $R = \nu \exp(-E_a/kT)$ , where  $\nu$  is the frequency factor,  $E_a$  is the activation energy,  $k$  is the Boltzmann constant, and  $T$  is the temperature. The frequency factor  $\nu$  for the adsorbed one Si atom on the Si(111)7×7 surface was reported to be  $10^{14.5} \text{ s}^{-1}$  using the Arrhenius plot.<sup>8</sup> Using the dominant diffusion barriers of 0.78 eV for one Si atom and 1.42 eV for two as the activation energies, the hopping frequencies of the adsorbates at 300 K are estimated to be about  $10 \text{ s}^{-1}$  and  $10^{-9} \text{ s}^{-1}$ , respectively. Because the line-scan frequency in our experiments is about  $10 \text{ s}^{-1}$ , the adsorbed single Si atom could migrate to other stable positions on the half unit cell after line scanning, while the adsorbed two Si atoms would keep stationary at the same position.

One may think that the above interpretation can be reached easily because the fact that the migration of the two Si atoms would be more difficult than that of a single Si

atom is well known for a Si(100) surface.<sup>3</sup> We would like to emphasize, however, the possibility of interpreting the stationary Si adsorbate on the Si(111)7×7 surface as two Si atom adsorption has not been pointed out at all, though more than a decade has passed since it was first observed.<sup>1</sup>

The stationary Si adsorbates were deposited more frequently on the corner adatom region than on the center adatom region, by a ratio of about 1.5:1. This tendency of Si adsorption agrees well with the calculated result that the most stable configuration (2a) for two Si atoms was located on the corner adatom region [Fig. 4(d)]. Meanwhile, the stacking fault of the unit cell did not affect the adsorption ratio. In our experiments where Si atoms were supplied from an STM tip at random locations, Si atoms were deposited on faulted and unfaulted halves with equal probability. Therefore, the two deposited Si atoms should adsorb at stable positions without diffusing over the boundary of the half unit cell of the Si(111)7×7 surface.

Our calculated results for an extra single Si adsorption [Figs. 4(a) and 4(b)] is consistent with the atom-tracking STM experiment at low temperature,<sup>8</sup> showing that a diffusing Si atom was located in an area between the rest atom and the corner adatom. However, a diffusing area in an atom-tracking image at room temperature,<sup>8</sup> around three center adatoms on the half unit cell, was inconsistent with the results of our calculation. This can be understood as follows. With increasing temperature, the hopping speed of an atom on a surface increases exponentially.<sup>18</sup> Then, at room temperature, an extra Si atom may hop to the position around the three center adatoms. Accordingly, a conventional STM, and

even an atom-tracking one, may take time-averaged images of the hopping Si atom. The possibility of observing such time-averaged images was recently suggested for the case of the Si(111) $\sqrt{3}\times\sqrt{3}$ -Ag surface on the basis of a Monte Carlo simulation.<sup>19</sup> However, the reason why the diffusing Si atom, in particular, prefers the position around the three center adatoms is still unclear. The electric field between the tip and the sample may also play a role in the STM configuration. To fully understand the behavior of the diffusing Si atom on the Si(111)7×7 surface, further calculations, including thermal energy and electric field, should be required.

In conclusion, we have investigated the stationary and diffusing Si adsorbates inside the half unit cell of the Si(111)7×7 surface. To identify the atomic structures of these Si adsorbates, we apply the molecular-orbital approach to Si atoms on the Si cluster model. As the result, we propose assignments to these adsorbates: the stationary and diffusing Si adsorbates correspond to a pair of Si atoms and a single Si atom, respectively. Although recently observed STM images are often interpreted by comparing them with theoretical calculations on stable structures and electronic states, the present study shows that even this procedure is insufficient in some cases. The present results reveal that STM images should be interpreted paying attention to the possibility of transitions among stable structures.

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