Direct Observation of One-Dimensional Ga-Atom Migration on a Si(100)-(2 × 1)-H Surface: A Local Probe of Adsorption Energy Variation

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Atomic-scale surface migration of a Ga atom on a hydrogen-terminated Si(100)-(2 × 1)-H surface is studied using low-temperature scanning tunneling microscopy and first-principles calculations. The Ga atom migrates in a linear potential well confined by adjacent dimer rows and local dihydride defects, and is observed as a continuous linear protrusion (Ga-bar structure) at a narrow range of temperatures near 100 K. We point out that the height of the Ga-bar structure maps out the local variation in potential energy at individual adsorption sites.

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Understanding surface migration at an atomic scale is fundamentally important to the study of the growth processes of thin films and crystals [1,2]. Atoms adsorbed on solid surfaces exhibit a wide variety of anisotropic surface migration due to the surface atomic structures. Interaction of the adsorbates with the substrate determines the potential energy surface (PES), which is of great importance in determining the behavior of the adsorbates. Scanning tunneling microscopy (STM) provides many new studies concerning migration of adsorbates at an atomic level [3]. Much recent attention has been focused on the migration pathway on the surface before nucleation [4]. Swartzentruber used a noble atom-tracking STM and revealed that the adsorption site resolved one-dimensional migration of Si dimers on a Si(100)-(2 × 1) surface [5]. Borovsky *et al.* discussed one-dimensional to two-dimensional transition of Si-dimer migration on the Si(100) surface [6]. Although many theoretical studies exist, the atomic-scale migration paths are still unexplored experimentally. Thermally deposited Ga atoms migrate on a hydrogen-terminated Si(100)-(2 × 1)-H surface at room temperature and preferentially adsorb on the dangling bonds [7]. More detailed understanding of the migration process is needed for the study of film growth and nanostructure fabrication [7].

In this Letter, we show that a Ga atom on a Si(100)-(2 × 1)-H surface is occasionally imaged as a linear protrusion in a narrow range of temperatures near 100 K, which we call a Ga-bar structure. The observations are analyzed using first-principles theoretical calculations. We conclude that the Ga-bar structure is an image of a Ga atom, which is confined and migrating in a linear well of PES. The observed height modulation of the Ga-bar structure reflects the local variation in potential energy at individual adsorption sites (adsorption energy variation), which may be caused by the local stress made by surface defects or subsurface impurities.

A Si(100) sample (P-doped, *n*-type, 7 to 18 m$\Omega \cdot$ cm) was cut from a wafer and used as a substrate. An electrochemically etched $\langle 111 \rangle$ oriented single-crystal tungsten wire was used as the STM tip. Details of surface and tip preparation have been described previously [8]. By heating a W filament with Ga metal to 600–650 °C, Ga atoms were evaporated *in situ*. The base pressure of the STM chamber was lower than 5×10^{-11} Torr during the STM observation. Experiments were carried out at various temperatures ranging from 30 to 150 K with deposited Ga of approximately 0.002 ML [1 ML is defined as the number of Si atoms on the bulk-terminated ideal Si(001) surface: 6.78×10^{14} atoms/cm^2].

In our calculations, the Si(100)-(2 × 1)-H surface was represented by a slab model consisting of five layers of Si atoms with a periodic 4 × 2 or 4 × 4 supercell. Dangling bonds at the surface were terminated by hydrogen atoms. Relaxed atomic geometries and electronic structures were calculated within the local-density-functional approach, using the exchange correlation term of the Ceperley-Alder form [9] and ultrasoft pseudopotentials proposed by Vanderbilt [10]. Electronic and ionic degrees of freedom were optimized using the conjugate gradient method [11]. Wave functions were expanded in a plane-wave basis set with an energy cutoff of 9 Ry. In order to obtain the PES, total energy of the system with Ga adsorbates was minimized with respect to the electronic charge density and the substrate lattice. The criterion of the convergence of the geometry optimization is that all of the forces acting on each atom are within 1.0×10^{-3} Hartree/a.u.

Figure 1(a) shows a typical gray-scale filled-state STM image after the Ga deposition at 100 K (sample bias voltage $V_s = -2.0$ V, tunneling current $I_t = 20$ pA). Various types of Ga adsorption are observed: some are on dangling bonds and at the edge of missing-Si defects. We observe several characteristic one-dimensional (1D)

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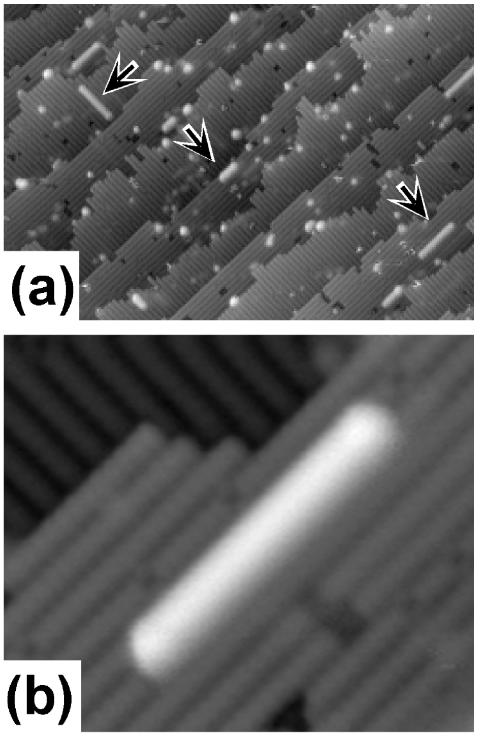

FIG. 1. (a) An STM image obtained after Ga deposition of approximately 0.002 ML at 100 K (70 nm × 40 nm, $V_s = -2.0$ eV, $I_t = 20$ pA). The arrows show examples of the characteristic Ga-bar structures. (b) Close up view of a Ga-bar structure (12 nm × 9 nm).

structures (Ga-bar structures). These are formed parallel to the Si dimer rows and are located in the trough between two neighboring Si dimer rows [Fig. 1(b)].

We first assumed that the Ga-bar structure would be a row of Ga atoms, considering the fact that the formation of ad-dimer chains on a bare Si(100)-(2 × 1) surface is quite common, as in the case of Si [12] and Al [13,14]. Those atoms form similar 1D structures of ad-dimers but are perpendicular to the dimer-row direction. We argue, however, that the Ga-bar structure is an image of a Ga atom adsorbed and migrating one dimensionally.

We performed first-principles calculations to understand the Ga-atom surface migration. Figure 2(a) shows the contour plot of calculated PES for a Ga atom in a 4 × 2 unit cell. We find that the most stable adsorption sites are located in the trough between two adjacent dimer rows and that each site is composed of two minima [A_0's in Fig. 2(a), equivalent to A_1's]. The activation barrier between two A_0 sites (34 ± 1 meV) is negligible in the present temperature range, and we regard two A_0 sites as one adsorption site throughout this Letter. The metastable B site at the pedestal site has a potential energy higher by 221 ± 1 meV than the A_0 site. A Ga adsorbate at the A_0 site has the lowest activation barrier of 215 ± 1 meV for surface migration from the A_0 site to the A_1 site (path I). The activation barrier for migration from the A_0 site to the B site (path II) is 469 ± 1 meV.

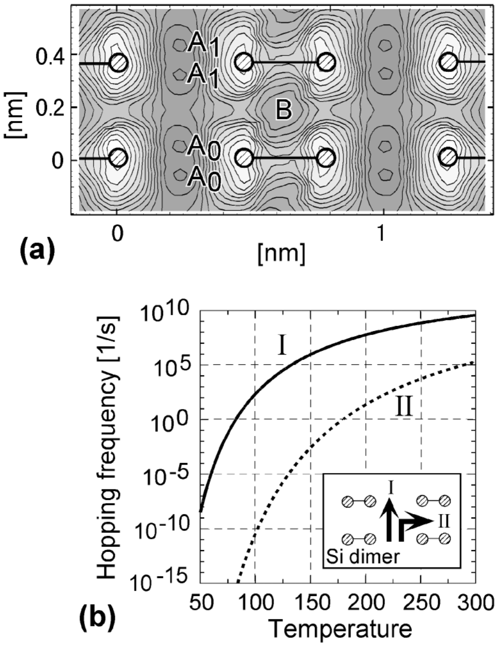

FIG. 2. (a) Calculated contour plot of the PES for a Ga atom on the Si(100)-(2 × 1)-H surface. The contour spacing is 0.1 eV. The hatched circles denote the first-layer Si atoms. (b) Temperature dependence of hopping frequency for the migration paths I and II shown in the inset.

The migration rate typically depends exponentially on temperature [15]. We evaluate the hopping frequency f using a simple Arrhenius equation,

$$f = \nu \exp(-Q/kT), \tag{1}$$

where ν is a preexponential factor, Q is an activation barrier for surface migration, k is the Boltzmann constant, and T is the temperature of the system. The preexponential factor ν, equal to the oscillation frequency of a Ga atom, is estimated to be $1.6 \pm 0.1 \times 10^{13}\ \mathrm{s}^{-1}$ by approximating the calculated PES near the A_0 site by a harmonic potential [16]. Figure 2(b) shows the calculated temperature dependence of hopping frequency f for the Ga migration paths I and II using the same ν. At 100 K, the hopping frequency in the trough (path I) is approximately $240 \pm 40\ \mathrm{s}^{-1}$, whereas that for across the dimer row (path II) is an order of $10^{-11}\ \mathrm{s}^{-1}$. As a result, the migration is highly anisotropic.

Our calculation predicts that Ga atoms migrate two dimensionally at higher temperatures (>130 K or so) until they arrive at stable adsorption sites such as dangling bonds and the Ga-atom migration is quenched at lower temperatures (<100 K or so). In the intermediate temperatures near 100 K, 1D migration of a Ga atom results in the Ga-bar structure. This evaluation well explains the Ga-bar structures experimentally observed in the narrow range of temperatures near 100 K (77 to 110 K). Thus, we think that the Ga-bar structure is the image of a Ga atom at the A_0 sites. Indeed, the STM image shown in Fig. 1(b) shows a small height corrugation corresponding to each adsorption site when increased contrast is used.

Two Ga atoms in the same trough would result in a Ga-bar structure. However, having two or more Ga atoms in one Ga-bar structure is not likely because of the Ga coverage (0.002 ML). The Ga-bar structures were quenched at the temperatures lower than 77 K, and we observed only stable Ga adsorption. We have been further trying to observe the one-to-one correspondence of a Ga-bar structure with a quenched Ga atom by cooling down the sample. However, a thermal drift resulting from the temperature change of even a couple of degrees prevented us from correlating these.

By applying a voltage pulse with a large tunneling current on the Ga-bar structure ($V_s = -3.0$ V and $I_t = 0.7$ nA for 200 ms, for example), the Ga atom moved out from the trough and the hydrogen-terminated surface was observed. Figure 3(b) reveals that the Ga-bar structure is terminated by two dihydride Si dimers at the ends. Similar observations were made when we repetitively scanned the Ga-bar structure at a higher temperature limit near 110 K. Figures 3(c) and 3(d) show the schematic view of a Ga-bar structure and the calculated cross section of PES along the trough. Two dihydride dimers with the migration barrier of 0.56 eV and a trough determine a linear potential well for the Ga atom. Consequently, we conclude that the Ga-bar structure is an STM image of the rapidly migrating Ga atom confined in a linear potential well.

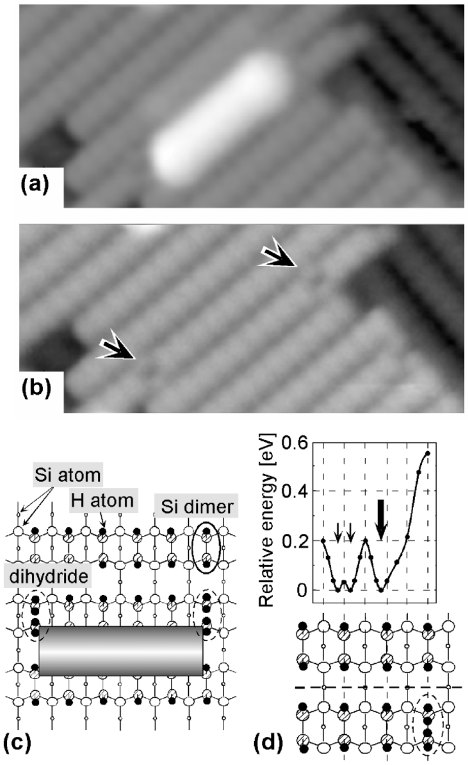

FIG. 3. (a) An STM image of a Ga-bar structure (7 nm × 3 nm, $V_s = -2.0$ V, $I_t = 20$ pA). (b) Same as (a) but after removing the Ga-bar structure by a voltage pulse (local dihydride species are shown by arrows). (c) Schematic view of a Ga-bar structure. The hatched, blank, and filled circles denote the first- and second-layer Si and hydrogen atoms, respectively. (d) Calculated cross section of the PES along the Ga-bar structure.

We now look at site occupation probability p of a Ga atom at adsorption sites (A_0's). In the constant-current-mode STM operation, time-averaged tunneling current

$$pI + 2pI' + (1 - 3p)I'' = \text{const.} \tag{2}$$

Here, I is the peak tunneling current when the Ga atom is directly below the tip. The second and third terms are the contributions from the tunneling current when the Ga atom is not directly below the tip but with the same tip-Si dimer spacing, where I' and I'' are the current when the Ga atom is located at the nearest neighbor adsorption sites and when the Ga atom is farther away from the tip. The peak tunneling current I is given by

$$I = A\exp\left(-\frac{2\sqrt{2m}}{\hbar}\sqrt{\phi}\,z\right), \tag{3}$$

by the WKB approximation [17]. Here, A is a constant, z is time-averaged tip-Ga atom spacing, $\hbar$ is the Plank constant divided by 2π, and m is the electron mass. The work function ϕ when a Ga atom is directly below the tip is estimated to be 5.55 eV, by fitting the calculated z-I curve to Eq. (3).

When the Ga-bar structure consists of n adsorption sites, p is approximated by $1/n$. The difference in the tip-to-sample spacing is evaluated by taking the cross section of the Ga-bar structure perpendicular to the dimer-row direction and by measuring the height of the Ga-bar structure at the center for I''/I and at the point 0.384 nm away from the center for I'/I. We find that the second and third terms of Eq. (2) increase as n increases (because the height decreases) and are less than 5% and 3% when $n = 21$. This corresponds to the increase in the Ga-bar height by 0.003 nm at maximum. Equations (2) and (3) imply that the height variation of the Ga-bar structure can be converted to the site occupation probability p.

We analyzed cross sections of the Ga-bar structures and obtained site-averaged height $\bar{z}$. The $\bar{z}$ dependence on the length of Ga-bar structure [Fig. 4(c)] shows that the height of the Ga-bar structure decreases as the length increases. A possible mechanism of the Ga-bar structure to be a static Ga atom being pulled under the tip because of the tip-adsorbate interaction is not likely because of this dependency. When the length of potential well increases, the site occupation probability p decreases and hence the longer Ga-bar structure is observed lower in height. The site-averaged site occupation probability $\bar{p}$ is given by $1/n$. The dashed curve in Fig. 4(c), obtained using the 10-adsorption-site Ga-bar structure as a reference, fits well with the experiment.

The tip-sample interaction should be carefully considered, because it is likely that it affects the surface migration [18]. The actual PES of Ga atom should be evaluated

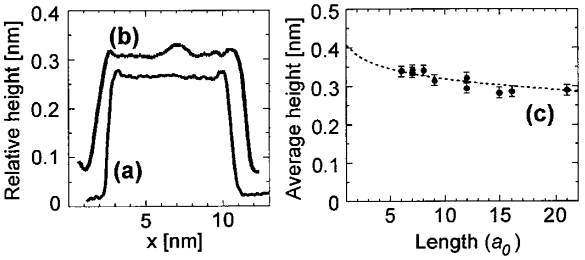

FIG. 4. (a),(b) Cross-sectional views of Ga-bar structures. (c) Averaged height $\bar{z}$ with error bars (in nm) versus length of Ga-bar structures (in a_0) obtained at $V_s = -2.0$ V, where a_0 is the unit length of Si(100):0.384 nm.

using the adsorption energy and the tip-adsorbate interaction [19]. In order to observe a continuous Ga-bar structure, the minimum hopping frequency of the Ga atom is estimated to be 100 Hz in our scanning condition. However, this value has uncertainty of up to 2 orders of magnitude, which corresponds to the temperature inaccuracy of 20 K using Eq. (1). Assuming the hopping frequency larger than 100 s^{-1} for the path I migration and smaller than 0.0001 s^{-1} for the path II migration, we obtain the calculated temperature range of 100–130 K for the Ga-bar structure. However, the experimental observation is 77–110 K. This implies 30 ± 10 K difference between theory and experiment. This result can be explained by the reduction of the activation barrier Q by 60 ± 20 meV due to the tip-adsorbate interaction. This is in good agreement with the discussion by Nakayama *et al.* [19].

However, we point out that the tip-adsorbate interaction in the present case is considered to be almost equal for each Ga-bar structure because the Ga atom exists directly below the tip when the Ga is feeling most of the tunneling current. Indeed, the uniform height of the Ga-bar structure shown in Fig. 4(a) implies that the tip-adsorbate interaction is quite uniform within the accuracy of 1 meV in the length range discussed here ($\approx$10 nm). The fitted curve in Fig. 4(c) agrees well with the experiment and supports the argument.

From this point of view, we again review our data. Equations (2) and (3) can be applied to each adsorption site. For the system at thermal equilibrium, the hopping frequency f and the site occupation probability p follow the relation $pf =$ const. for each adsorption site. By assuming that the preexponential factor ν is constant for all the adsorption sites, we can derive local adsorption energy variation ΔQ from the local height variation.

We here look into only two examples. Both ends of the Ga-bar structure protrude by 0.020 ± 0.003 nm in Fig. 4(a). In our calculation, the edge site of the Ga-bar structure [large arrow in Fig. 3(d)] has $\Delta Q =$ 4 meV lower potential energy than the adjacent adsorption site [small arrows in Fig. 3(d)]. This energy difference gives the ratio of site occupation probability of $\exp(-\Delta Q/kT) = 1.59$ at 100 K. The height difference is then evaluated to be 0.018 nm. This value should be compared with the experiment.

Another example of the cross section in Fig. 4(b) has a local maximum around the middle of the Ga-bar structure, which is approximately 0.03 nm and corresponds to the adsorption energy difference of 6 meV. We found that the position of the local maximum agrees with the position of a missing dimer defect on the substrate $3a_0$ away from the Ga-bar structure (to the direction perpendicular to the dimer-row direction). We believe that there is a local PES distortion in this region because of the defect. In this way, we can map out a local adsorption energy variation by using the height variation in the Ga-bar structure. Detailed examination of this distortion will be discussed elsewhere [16].

In conclusion, we directly observed anisotropic surface migration of a Ga atom on the Si(100)-(2 × 1)-H surface. The Ga-bar structure is an image of the migrating Ga atom and the observed height reflects a site occupation probability of the Ga atom under the STM tip. We claim that the local height variation of the Ga-bar structure can be used to map out the local adsorption energy variation.

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[1] W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. London. Ser. A **243**, 299 (1951).
[2] *Epitaxial Growth,* edited by J. D. Mathews (Academic Press, New York, 1975); *Kinetics of Ordering and Growth at Surfaces,* edited by M. G. Lagally (Plenum, New York, 1990).
[3] Y.-W. Mo *et al.*, J. Vac. Sci. Technol. A **8**, 201 (1990).
[4] G. Brocks, P. J. Kelly, and R. Car, Phys. Rev. Lett. **66**, 1729 (1991).
[5] B. S. Swartzentruber, Phys. Rev. Lett. **76**, 459 (1996).
[6] B. Borovsky, M. Krueger, and E. Ganz, Phys. Rev. Lett. **78**, 4229 (1997).
[7] T. Hashizume *et al.*, Jpn. J. Appl. Phys. **35**, L1085 (1996).
[8] T. Hitosugi *et al.*, Jpn. J. Appl. Phys. **36**, L361 (1997).
[9] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[10] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[11] J. Yamauchi *et al.*, Phys. Rev. B **54**, 5586 (1996).
[12] Y. M. Mo *et al.*, Phys. Rev. Lett. **66**, 1998 (1991).
[13] J. Nogami, A. A. Baski, and C. F. Quate, Phys. Rev. B **44**, 1415 (1991).
[14] G. Brocks *et al.*, Phys. Rev. Lett. **70**, 2786 (1993).
[15] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).
[16] Y. Suwa *et al.* (unpublished).
[17] J. G. Simmons, J. Appl. Phys. **35**, 2472 (1964).
[18] J. Li *et al.*, Phys. Rev. Lett. **76**, 1888 (1996).
[19] T. Nakayama, D.-H Huang, and M. Aono, Microelectron. Eng. **32**, 191 (1996).