Diffusion of Single Hydrogen Atoms on Si(111)-(7 × 7) Surfaces

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Adsorption and diffusion of single hydrogen atoms on Si(111)-(7 × 7) surfaces at elevated temperatures have been studied using scanning tunneling microscopy. Hydrogen atoms adsorb preferentially atop rest atoms. An adsorbed H atom can hop between two neighbor rest atoms via an adatom, i.e., via a metastable intermediate state. Below 340 °C, the hopping is mostly confined within a half-cell, but at higher temperatures, they can hop across the cell boundary. The activation energies for different hopping paths were measured. The binding energy difference between rest-atom and adatom sites and that between corner and edge adatom sites were also determined to be ~0.2 and ~0.05 eV, respectively. [S0031-9007(98)06382-0]

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The interaction of hydrogen with silicon surfaces is a subject of considerable importance in surface and materials sciences. Hydrogen adsorption can unreconstruct surfaces and passivate surface dangling bonds, and thus can change the surface properties dramatically. Formation of various hydrides in chemical vapor deposition processes plays a dominant role in the thin film structures and surface morphologies. From theoretical considerations, hydrogen atoms represent the simplest adsorbate possible for first-principles calculations. There have been numerous experimental and theoretical studies of the reaction of hydrogen with silicon surfaces. However, many questions regarding the reaction kinetics and paths remain unsolved. One of the fundamental issues is the role of surface diffusion of hydrogen atoms. For example, it has been speculated that surface diffusion plays a crucial role in the recombinative desorption of hydrogen from silicon surfaces [1]. Surface diffusion of chemisorbed species is, of course, an important process in catalysis.

Previously, the activation energy for diffusion of atomic hydrogen on Si(111)-(7 × 7) was measured by Reider *et al.* using optical second-harmonic diffraction to be ~1.5 eV [2]. Based on density functional calculations, Vittadini and Selloni [3] proposed that the most stable adsorption site for H atoms on Si(111) is the rest-atom (R) site. They also predicted that hydrogen atoms can hop from an R site to a neighboring R site via an adatom (A) site. The rate-determining process, $R \rightarrow A$, has an activation energy of ~1.3 eV. In this work, we study diffusion of single hydrogen atoms on Si(111)-(7 × 7) surfaces with a variable-temperature scanning tunneling microscope. In agreement with calculations by Vittadini and Selloni, hydrogen atoms are found to occupy preferentially the R site, and the hopping between two neighboring R sites is indeed via an A site intermediate state. However, H atoms are also found to hop to a neighboring half-cell at higher temperatures, which should be the rate-determining process for diffusion of atomic hydrogen across the surface. Hopping across a cell boundary over the dimer was studied by Sorescu *et al.* [4] using variational phase-space theory methods, though the stable adsorption sites were taken to be the adatom sites. In this study, we also measure the relative binding energies between different adsorption sites and the activation energies for different hopping paths. In other words, our data are both adsorption-site and hopping-path specific.

Si(111)-(7 × 7) is a very complicated reconstruction. According to the DAS (dimer-adatom-stacking fault) model of Takayanagi [5], there are 19 dangling bonds for every 7 × 7 unit cell: 12 for the adatoms, 6 for the rest atoms, and 1 for the corner hole. Each 7 × 7 unit cell consists of faulted and unfaulted half-cells. These half-cells are separated by dimer rows and corner holes. Each half has six Si adatoms, with three occupying the corner sites and the other three the edge sites. The rest atoms with a dangling bond are located at the center of three surrounding adatoms. It has been reported that H atoms, rather than H_2 molecules, are reactive with Si(111)-(7 × 7) at room temperature [2,6–12]. Previous room-temperature scanning tunneling microscopy (STM) studies showed that the point defects induced by hydrogen adsorption on Si adatoms appear dark at ±1 V, but the image spots reappear as bright as Si adatoms at ±2 V [9–12]. Rest-atom dangling bonds were also found to react with H atoms at room temperature using I-V measurements of STM [10,11]. However, no STM images of this defect were reported, and very little was known about it in previous experimental studies.

In our experiment, we exposed a clean Si(111)-(7 × 7) surface to a very small amount of atomic hydrogen, ~0.008 monolayer or less, at the variable-temperature STM stage. The operation of this STM and the preparation of clean Si(111)-(7 × 7) surfaces has been described earlier [13]. The atomic hydrogen is produced by decomposing H_2 on a 1500–1600 °C tungsten filament positioned ~5 cm from the sample. The temperature reading was obtained by an optical pyrometer with accuracy ~10 °C and precision ~2 °C. Our room temperature result is consistent with previous STM studies. Therefore we report only the high temperature result in this Letter.

Figure 1 shows filled-state STM images of two Si(111)-(7 × 7) surfaces which have been exposed to atomic hydrogen. On a clean Si(111)-(7 × 7) surface, adatoms in the faulted half appear slightly brighter than those in the unfaulted half; rest atoms are also imaged though the image intensity is reversed [14]. As can be seen from the parts enclosed in triangles, when an H atom is adsorbed at the surface, a rest atom becomes invisible, while the adatoms surrounding it become brighter than usual. From a consideration of the image symmetry, one easily arrives at the conclusion that the H atom is adsorbed atop the rest atom, similar to H-atom adsorption on Ge surfaces [15]. Above 280 °C, an H-adsorbed R site can hop to a neighboring R site within its own half as shown in Figs. 1(a) and 1(b). If the temperature is raised above ~320 °C, an H adsorbed R site can hop across the cell boundary over a dimer to the next half as seen in Figs. 1(c) and 1(d).

On Ge(111)-$c(2 \times 8)$, Klitsner and Nelson [15] found that reaction with atomic hydrogen produces a symmetric triangle and an asymmetric rectangle of bright adatoms in filled-state STM images. According to their first-principles calculation, the defects are caused by adsorption of a hydrogen atom at the rest-atom sites that originally had a dangling bond. It was proposed that the reverse charge transfer from rest atoms to neighboring adatoms makes the surrounding adatoms appear brighter than those in the clean region [15]. Similar to Ge(111)-$c(2 \times 8)$, there is a charge transfer from adatom dangling bonds to rest-atom dangling bonds on Si(111)-(7 × 7) [16]. Reaction of rest atoms with hydrogen atoms would cause a reverse charge transfer from the reacted rest atoms to surrounding adatoms, and thus makes those adatoms appear brighter and the rest atom darker.

In our continuous-time imaging, we find that the hopping of the H-induced defect is via an intermediate state. Figure 2(a) shows an STM image of two H-induced defects, taken at 310 °C. At 9.3 s later [Fig. 2(b)], the defect on the left has changed. Now an edge adatom site appears darker in both filled-state and empty-state images. In the

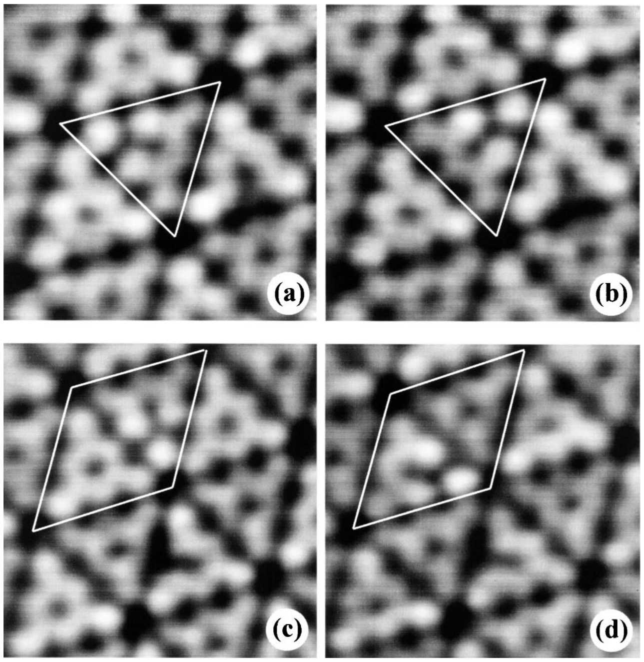

FIG. 1. STM images of an H-exposed Si(111)-(7 × 7) surface. (a) and (b) show hopping of one point defect, H adsorption on a rest-atom site, within an unfaulted half. (c) and (d) show hopping of one point defect from an unfaulted half to a neighbor faulted half.

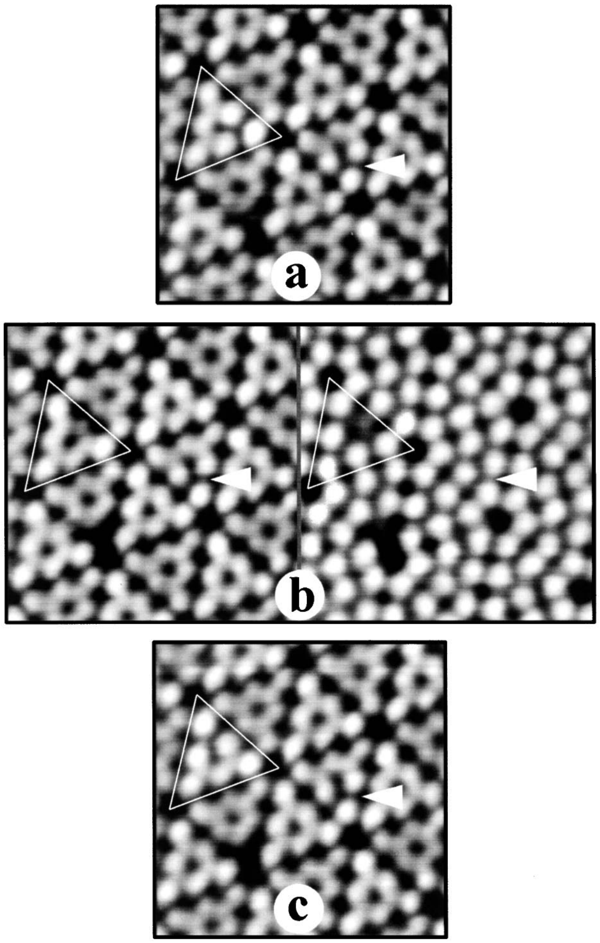

FIG. 2. Three successive STM filled-state images (enclosed in triangles) show the hopping pathway $R \rightarrow A \rightarrow R$ of an H atom inside a faulted half cell at 310 °C. (b) Shows dual polarity, filled state at left and empty state at right, images with the same bias voltage. The acquisition time for each image is 9.3 s. The tunneling current is 0.2 nA and bias voltage 1.5 V. An H adsorbed R site in an unfaulted half that did not move during this time is pointed out by arrows. One notices that an H-adsorbed R site cannot be seen in empty-state images, but the intermediate A site appears darker in both the filled- and empty-state images.

filled-state image, the image spot related to the reacted rest atom reappears. In Fig. 2(c), the H-induced defect changes sites. We think the H atom hops from an *R* site [Fig. 2(a)] to a neighboring *R* site [Fig. 2(c)] via an intermediate *A* site [Fig. 2(b)]. The *A* site appears darker probably due to saturation of its dangling bond by the H atom, which is consistent with previous STM observations.

Hydrogen atom adsorption on the *A* site is a metastable state. Although its lifetime is much shorter, this state can be directly observed below 320 °C. Above that, the lifetime is too short to be imaged by STM. From thousands of continuous-time STM images taken below 320 °C, we can estimate the binding energy difference between *A* and *R* sites using the relation $P_R/P_A = \frac{1}{2}\exp(E_A - E_R)/k_BT$, where the statistical weight $\frac{1}{2}$ accounts for the fact that the number of the available *A* sites is twice that of the *R* sites. On the 7×7 surface, $E_A - E_R$ is found to be $\sim$0.2 eV for both the faulted and unfaulted halves. At temperatures above 320 °C, we start to see the hopping of H atoms across a dimer row to a neighboring half cell. We have taken many continuous-time STM images from 280 to 380 °C. From the hopping rates, the activation energies for hydrogen atoms to hop between *R* sites within a half cell and those to hop across the cell boundary are derived using Arrhenius plots (see Fig. 3). In addition, from the relative frequencies of observing two different intermediate states, i.e., H atoms at corner adatom sites and those at edge adatom sites, we derive the relative binding energies of H atoms at these sites in both halves. The corner sites in both halves are found to have a slightly larger binding energy of $\sim$50 meV than the edge sites. Combining the energy data we have measured, a potential energy diagram shown in Fig. 4 is obtained which provides the energetics of understanding diffusion of H atoms by different pathways on Si(111)-(7×7) surfaces. The effect of the scanning tip is checked by examining, at 290 °C, how the hopping rate changes with the scanning time which varied from 2.4 to 18.5 s. The lifetimes of the *R* site and the *A* site adsorption increase by a factor of 1.4 and 1.8, respectively. This effect is relatively small if one considers that the activation energy is derived from the slope of a semilogarithmic plot. However, the true experimental errors are expected to be larger than the statistical errors indicate. A conservative estimate places the accuracy of our measurement to be no *worse* than ± 0.1 eV in activation energies and $10^{\pm 1.5}$ in preexponential factors.

It is clear from Fig. 3 that hopping across the cell boundary requires a higher activation energy than site hopping within a half-cell; the former is what is measured by Reider *et al.* using an optical second-harmonic diffraction method [2]. The former hopping should be responsible for the mass transport of H atoms across the surface. The latter hopping, on the other hand, is more closely related to the theoretical calculations of Vittadini and Selloni [3]. The activation energies we have measured in this study are slightly higher than those from two previous studies. The small discrepancies are not surprising, since our study provides more detailed site specific data. In the measurement by Reider *et al.,* the optical method observes diffusion over a distance of $\sim$1000 Å. Effects of step edges and other surface defects on surface diffusion have been averaged out. Also, the hydrogen concentration in their study is much higher than in ours. Their result includes effects of interactions among H atoms which can affect the diffusivity. What they studied is the so-called chemical diffusion, while ours is the tracer diffusion, or single atom diffusion. In our study, the coverage is so low that the measurement was effectively done on diffusion of single hydrogen atoms, and the parameters we obtained are both site specific and hopping path specific. As for the comparison between our data for site hopping within a half-cell and the calculations by Vittadini and Selloni, very good agreement can be seen for the preferential adsorption of hydrogen atoms at the *R* site over the *A* site, the hopping pathway, and the relative binding

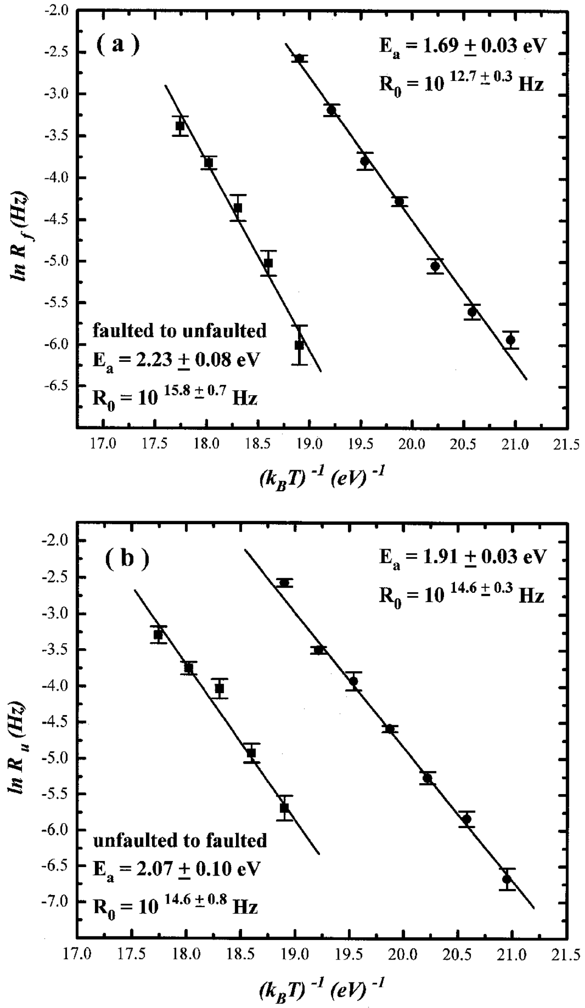

FIG. 3. Arrhenius plots for hopping within the half-cell at low temperatures and diffusion across the cell boundary at high temperatures for adsorbed H atoms. (a) and (b) show, respectively, data from faulted and unfaulted halves.

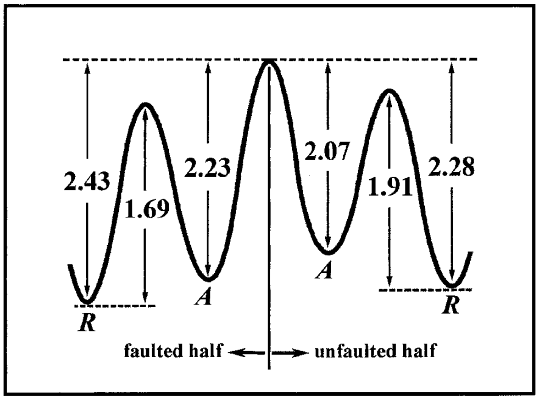

FIG. 4. A potential energy diagram showing the relative binding energy at different adsorption sites, and the activation barrier for different hopping paths. Energies are expressed in eV, and *R* and *A* represent, respectively, rest-atom and adatom sites.

energy. There is a small difference in the activation energies between our measurements and their calculations. This difference may come from the fact that in their calculations the slab of two primitive (2×2) unit cells is used rather than a true Si(111)-(7×7) crystal. Thus, there is no difference between the faulted and unfaulted halves in their calculations. The activation energies for hopping over a dimer across the cell boundary we measured are also higher than those obtained by Sorescu *et al.* [4], but again in their calculation the more stable adsorption sites are *A* sites, in disagreement with our result. The power of variable temperature atomic resolution microscopy in the study of atom dynamics of surfaces is that not only the energetics can be clarified, but also that the mechanisms and reaction paths can be identified. We believe that with much more detailed experimental data becoming available for this system, it may be worthwhile to perform new detailed first-principles calculations to compare with these experimental data.

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