Scanning tunnelling microscopy study of atomic hydrogen adsorption on the Si(111) 7x7 surface

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Abstract. We studied initial atomic hydrogen adsorption onto Si(111) 7x7 adatoms by scanning tunnelling microscopy in an ultrahigh vacuum. Adatom reaction probabilities were measured as a function of atomic hydrogen exposure time for room-temperature and high-temperature surfaces. Hydrogen uptake was well represented by Langmuir adsorption at 361 and 414 K, while depression of uptake was seen at 481 K after one of six adatoms was terminated by hydrogen. Hydrogen adsorption had positive adsorption correlations between adjacent centre adatoms and corner adatoms across the 7x7 half unit. These correlations were enhanced at 481 K. In accordance with the positive reaction correlation between these adjacent adatoms, the average number of reacted adatoms in adjacent 7x7 half units was also enhanced as the number of reacted adatoms increased in the half unit.

1. Introduction
Since the invention of scanning probe microscopy (SPM), a wide variety of clean and adsorbate surfaces have been resolved by this technique with subatomic spatial precision. The reaction of such gaseous species as hydrogen and oxygen with semiconductor surfaces is crucial for the development of new fabrication technology for mature semiconductor devices. Therefore, many studies have focused on the reactions of these process gases [1]. In particular, after the birth of scanning tunnelling microscopy (STM), hydrogen interaction with clean reconstructed silicon surfaces, such as Si(100) 2x1 and Si(111) 7x7 reconstructions, have been extensively studied [1,2]. These early studies showed that clean surfaces are intact for molecular hydrogen exposure, whereas thermally cracked hydrogen, or hydrogen radical (H), is reactive to these surfaces, and H is chemisorbed by terminating the surface dangling bond. H adsorption reaction is thought to be direct (the Eley-Rideal mechanism), and thus the evolution of the adsorption is characterized as Langmuir adsorption. However, our recent study of H reaction on adatom sites of the Si(111) 7x7 surface [3] showed that even though the apparent hydrogen uptake was well represented by a Langmuir adsorption form and no preferential adsorption among inequivalent adatoms was seen, positive reaction correlations between particular adatom combinations, adjacent centre adatoms and corner adatoms across the dimer row, were observed for room-temperature adsorption. In addition, the number of reacted adatoms in the half unit showed a binominal distribution suggesting a pure random process in 7x7 half units, but there was a positive

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adsorption correlation between adjacent 7x7 half units, i.e., clustering of H adsorption or autocatalytic reaction over the 7x7 half unit.

In this report, to investigate the origin of these H adsorption correlations for adjacent adatoms and adjacent half units and to explore the adsorption and/or desorption mechanism for H adsorption in detail, we studied the substrate temperature effect on the H adsorption on the 7x7 adatom. Substrate temperatures were elevated between 361 and 481 K where no hydrogen diffusion has ever been seen [4,5]. We found that apparent initial H uptake decreased at 481 K and adsorption correlations were enhanced. In addition, the number of reacted adatoms in adjacent half units was also enhanced as the number of reacted adatoms increased in the half unit.

2. Experiment

Since details of the apparatus and experimental procedure were described previously [3], here we briefly mention the essential points of the experiment. A commercial UHV-STM (JEOL JSTM-4500VS) with a base pressure of 7x10^-9 Pa was employed. Samples were flashed in UHV to expose clean 7x7 reconstruction with a mean 7x7 domain size of ~500×500 nm². Hydrogen produced by water electrolysis was backfilled in the chamber at 1.8x10^-4 Pa by a leak valve during exposure. Hydrogen was thermally cracked by a hot tungsten filament located ~6 cm from the samples, which were held at room temperature or heated to a specific temperature by direct current through them. Sample temperatures were estimated with a thermocouple attached behind the sample by applying the same voltages as the H adsorption experiment in a separate experiment. STM topographies were acquired during heating samples or after cooling them to room temperatures. No significant difference was recognized between hot and cold surfaces. STM images were acquired with a sample voltage of +1.6 V, imaging the empty surface states where the contrast between reacted and unreacted adatoms was most enhanced. Tunneling currents were chosen between 0.1-0.3 nA. Since we could not discriminate the H adsorption at the rest atom sites in particular for higher H coverages [6], we only studied H reaction at the adatom sites.

3. Results and discussion

A typical evolution of surface morphologies by H adsorption is depicted in figure 1. Each image was taken after a specified period of H exposure. As previously demonstrated [3], reacted adatoms are depressed in all STM images and increased for longer H exposures. Reacted adatoms were counted for several STM images for each exposure, and reaction probability was extracted as a function of

![Figure 1](image_url)

**Figure 1.** Series of STM images of Si(111) 7x7 surfaces exposed to atomic hydrogen, acquired with sample bias of +1.6 V. Exposure time is indicated in inset of each image. Scanning areas are 16 nm × 10 nm for all images.
Figure 2. Reaction probabilities as a function of hydrogen exposure time for adatoms in unfaulted (a) and faulted (b) halves of Si(111) 7x7 surfaces. Filled and open symbols denote corner and centre adatoms, respectively. Langmuir adsorption for room-temperature surface is represented by broken lines.

Figure 3. Normalized reaction probabilities between adjacent centre (filled squares) and corner (filled circles) adatoms across the 7x7 half unit as a function of hydrogen exposure time. Broken lines at unity indicate no correlation.
exposure time, as shown in figure 2. Our previous study showed that for room temperature, reaction probability is well represented by a single Langmuir form among four inequivalent adatoms, i.e., corner and centre adatoms in the faulted and unfaulted of the 7x7 half unit, respectively [3]. In figure 2, room-temperature H uptake curve is overlaid as broken lines in both figures. At 361 and 414 K, H uptake curves (circles and squares) are almost identical with room temperature. However, at 481 K, H uptake (triangles) is considerably depressed for exposures more than 100 s, and the depression is larger for the unfaulted side of adatoms rather than their faulted counterparts. Suppression from Langmuir adsorption begins around 1/6, therefore, after one of six adatoms in the half unit is reacted, further H uptake is suppressed. H does not desorb at this temperature, so the adsorbed H atom will be transferred from the adatom site to the rest atom site. Preadsorbed H displacement was previously observed for much higher temperatures [4,5], however, because a covalent bond formation between Si adatom and impinging H is an exothermal reaction, energy release drives the H displacement from the adatom site to the energetically more stable rest atom site [7]. At room temperature, this displacement does not take place, possibly because adsorbed H does not have enough energy to surmount a potential barrier between the adatom and the rest atom. Note also that, as shown in figure 2, this potential barrier is somewhat lower for the unfaulted half, resulting in higher apparent uptake depression.

For room temperature exposures, we find that the adjacent corner-corner and centre-centre adatoms across the 7x7 half unit had positive adsorption correlations [3], i.e., when one of the adatoms in the 7x7 reconstruction is terminated by impinging H, reactivity of the adjacent adatom across the dimer is enhanced. As shown in figure 3, this positive correlation was also seen for elevated temperatures. In this figure, pair adsorption probability divided by respective one site adsorption probabilities is plotted as a function of H exposure time. Therefore, when the normalized reaction probability is unity (indicated as broken lines in figure 3), there is no correlation between the adatom pairs, whereas more than or less than unity mean positive or negative adsorption correlation, respectively. Because the event of pair adsorption for adjacent adatoms is small for shorter exposures, significant error exists for the reaction probabilities, even though for all exposure times the normalized reaction probabilities showed positive correlation behavior for elevated temperatures, particularly increasing at 481 K (fig. 3(c)). This enhancement is counterintuitive because the thermal migration will conceal minor potential differences among H adsorption sites, which weakens pair correlation. An example of an STM image for initial H adsorption is shown in figure 4. Reacted corner-corner and centre-centre adatoms are indicated as ellipsoids in the image to highlight the distribution of reacted pairs.

In addition to the reaction correlation between adatoms, it was also investigated between 7x7 half units. Figure 5 shows a typical example of the average number of reacted adatoms in the adjacent half units as a function of the number of reacted adatoms in the 7x7 half unit. If there is no correlation between half units, the average number of reacted adatoms at adjacent half units should be identical for all numbers of reacted adatoms in the half unit. Figure 5 shows, however, a clear trend that when

![Figure 4. Si(111) 7x7 surface exposed to atomic hydrogen for 25 s at 481 K. 7x7 unit is represented by thin solid lines. Reacted centre and corner adatoms are respectively indicated as ellipsoids with solid and broken lines. Scanning area is 28 nm × 28 nm.](image-url)
the number of reacted adatoms increased, the number of reacted adatoms at the adjacent half units increased in accordance with the previous room-temperature surface. For shorter exposures such as 25 and 50 s, no or only slightly negative correlation was observed. Referring to the positive reaction correlation between adjacent centre adatoms and corner adatoms even for shorter exposures, lack of correlation between half units means a negative correlation in other adatoms. However, because this negative correlation would be distributed among five other adatoms, we could not discriminate it within our experimental error.

4. Conclusion

We studied atomic hydrogen reactions on clean Si(111) 7x7 surfaces, particularly focusing on the adatom reaction for room and elevated temperatures. In accordance with previous room-temperature results, H uptake was represented by Langmuir adsorption for 361 and 414 K, but apparent uptake depression was seen for the surface temperature of 481 K, caused by H displacement from adatom to rest atom sites. Reaction correlations between adjacent corner adatoms and centre adatoms were respectively seen and increased at 481 K. The enhancement of the correlations also suggests H displacement between adatom and rest atom sites. The adsorption correlation between the 7x7 half unit also showed a positive reaction correlation for longer H exposures, in agreement with room-temperature adsorption.

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