Adsorption of Atomic Hydrogen on Si(100) Surface

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The interaction of atomic hydrogen (deuterium) was studied by nuclear reaction analysis and Rutherford backscattering-channeling analysis. The hydrogen coverage as a function of exposure is found to exhibit a plateau at about 2.0 monolayers. The coverage continues to increase with further exposures of atomic hydrogen (deuterium), a consequence of localized etching of the silicon surface. The channeling data show that the Si(100)-2×1 surface is highly strained. The strains parallel to the (100) surface are mostly removed on the "saturated" bulklike Si(100)-1×1-H surface.

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The adsorption of atomic hydrogen has been extensively studied in the past decade [1-8]. It is well established that H forms monohydride, dihydride, and even trihydride [9-12] on both Si(100) and Si(111) surfaces. This subject has recently attracted attention. This is largely attributed to a scanning tunneling microscope (STM) observation of atomic H etching on Si(100)-2×1 [13] and Si(111)-7×7 [14,15] at large exposures. These new STM results have challenged [13] the previously accepted H-terminated Si surface structural models, especially the hydrogen-saturated surfaces. The dispute has been focused on one physical parameter—the saturation hydrogen coverage. For example, it was originally believed [2] that the saturation coverage of H on Si(100) is 2.0 monolayers (ML, defined as 6.78×10^{14} atoms cm^{-2}), but it was then suggested [1,3,16] that saturation occurs at about 1.5 ML, and it was proposed [13] recently on the basis of STM and elastic recoil detection analysis (ERDA) [7] that saturation is close to 2 ML. However, we will demonstrate in the following text that the H coverage as a function of exposure only exhibits a plateau at about 2.0 ML. The coverage continues to increase with further ultrahigh exposure to atomic hydrogen, as a result of localized etching of the silicon surface.

To our knowledge, the most reliable experimental techniques for direct determination of absolute hydrogen or deuterium coverages on Si surfaces are nuclear reaction analysis (NRA) [6,8,17] and ERDA [7]. In this Letter, we have studied the adsorption of atomic deuterium on a Si(100)-2×1 surface by NRA, to determine the absolute deuterium coverage, and by low-energy electron diffraction (LEED) and Rutherford backscattering-channeling analysis, to study the surface structures.

The experiment was carried out in a diffusion and sublimation pumped ultrahigh vacuum chamber with a base pressure of 5×10^{-11} torr. The silicon samples were cleaned by direct-current heating to about 1200 °C as described elsewhere [17]. A sharp Si(100)-2×1 LEED pattern with no evidence of split beams was obtained after cleaning. The misalignment is less than 1°. The atomic deuterium was produced by a hot (1800 °C) W filament in front of the sample. The sample temperature rose less than 10 °C above room temperature during the exposure, as a result of thermal radiation from the W filament. The atomization rate on the W filament, at deuterium exposure pressures of 1×10^{-6} torr, is estimated [18] to be about 10^{14} cm^{-2}s^{-1}, which gives a deuterium atom flux to the sample surface of about 10^{12} atoms cm^{-2}s^{-1} in our experimental setup.

The deuterium coverage was determined by counting the yield of protons from the nuclear reaction ^{2}H(^{3}He, p)^{4}He. The protons were collected by a Si surface-barrier detector. The incident ^{3}He$^+$ beam energy was 630 keV. The absolute deuterium coverage was calibrated through the measurement of a standard Ta_2O_5 sample (placed at the same position), using the ^{16}O(d,p)^{17}O reaction. The relative cross section of these two reactions under the experimental conditions is well established [19]. The typical beam dose for each measurement was 2.5 μC/mm^2. The deuterium coverages for different exposures were measured on different spots. The total accumulated dose on each spot was around 10 μC/mm^2. This is well below 200 μC/mm^2, which has been reported [6] to leave a silicon surface with a tendency to adsorb more deuterium.

The backscattering-channeling measurements were carried out with a 2.0-MeV incident ^{4}He$^+$ beam, aligned in the ⟨100⟩ direction. The backscattered ^{4}He$^+$ particles were counted by another Si surface-barrier detector located at a scattering angle of about 115°. The absolute magnitude of the Si surface peak was determined through the measurement of a standard Bi-implanted Si sample (placed at the same position). All of the above ion beams were generated by a 2.5-MeV Van de Graaff accelerator. The beam line is coupled via two stages of differential pumping with base pressures of 10^{-7} and 10^{-10} torr, respectively, so the vacuum of the analytical chamber is not affected by admission of the beams.

In Fig. 1 we show the deuterium coverage on the Si(100) surface as a function of exposure of molecular deuterium in units of langmuirs (L; defined as 10^{-6} torr s). For practical reasons, the exposure is given at three different deuterium pressures of 1×10^{-6}, 1×10^{-5}, and 5×10^{-5} torr. The atomization rate of hydrogen

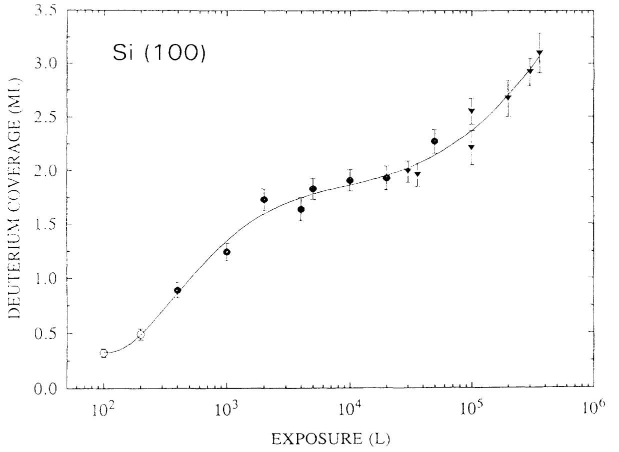

FIG. 1. The deuterium coverage as a function of the logarithm of the exposure. The exposure was made at a pressure of 1×10^{-6} torr (open circles), 1×10^{-5} torr (solid circles), and 5×10^{-5} torr (solid triangles). The exposure is the calculated molecular deuterium exposure. The actual atomic deuterium exposure is estimated to be at least 2×10^{3} times smaller.

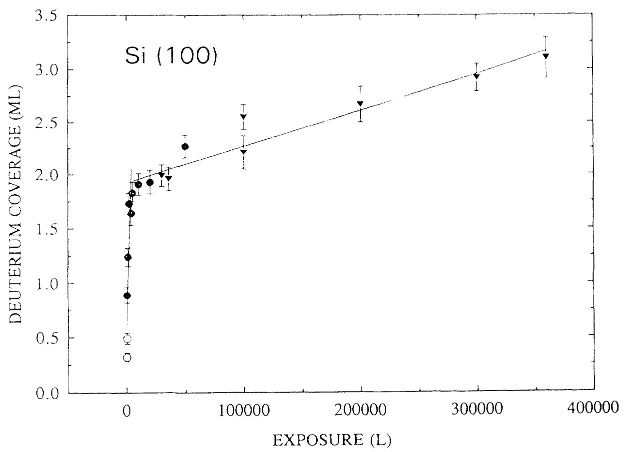

FIG. 2. The deuterium coverage as a function of exposure on a linear scale. The exposure was made at a pressure of 1×10^{-6} torr (open circles), 1×10^{-5} torr (solid circles), and 5×10^{-5} torr (solid triangles).

(deuterium) on the W filament has been found [18] to increase linearly with molecular hydrogen (deuterium) pressure. For convenience, we will discuss the adsorption in two different stages. Stage I corresponds to deuterium coverages up to 1.93 ML, and stage II to that above 1.93 ML. This classification is more apparent as we plot the coverage as a function of exposure on a linear scale, as shown in Fig. 2.

The mechanism of the adsorption process in stage I has been extensively studied [1-7], and has been thought of as due to adsorption by the dangling bond (DB) formation of the Si(100)-2×1-H monohydride phase at coverages up to 1.0 ML, and gradual formation of the Si(100)-1×1-H dihydride phase as Si-Si dimers are broken by further adsorbed hydrogen. However, our previous data [17] for low H coverage show no obvious break point around 1 ML, while other reported ERDA data [20] indicated a break point at about 0.6 ML. These results suggest that breaking of the Si dimer may occur at submonolayer H coverages. In fact, it has been found by Northrup [21] in a recent first-principles total-energy calculation that (3×1) alternating monohydride and dihydride is more stable than separated (2×1) monohydride and (1×1) dihydride phases. Furthermore, it is not clear whether the deuterium (hydrogen) coverage on a "saturated" dihydride-terminated silicon surface is 1.5 ML [1,13,16] or close to 2 ML [2,7,13]. According to present results, there is no evidence of saturation or even an inflection point near 1.5 ML, and a value of about 2 ML may be reasonable if the plateau visible in Fig. 1 corresponds to the completion of adsorption as distinct from etching, which we might consider as an independent physical event. Certainly there are two regions distinguished by their kinetics.

The adsorption in stage II may be interpreted as the breaking of dihydride Si-Si backbonds, and consequent formation of trihydride and then gaseous silane, i.e., a process of H etching. The NRA data do not directly indicate where the onset of etching occurs. The plateau region as displayed in Fig. 1 might be due to offsetting roughness and DB density effects of the type suggested by Boland [13]. However, the abrupt change in slope (reaction probability) suggests that stage II is not simply an extension of stage I. Local effects (e.g., defects) will play roles in the onset of etching, and such effects might cause variations in the coverage at which a plateau is observed on different samples. Despite these reservations, it is clear that the previously assigned saturation coverage of 2 ML is associated with a change of reaction rate rather than "true" saturation. The etching has also been observed by several groups using different techniques such as (1) real-space STM observation of localized H etching on Si(100) surface [13]; (2) observation of trihydride species on both Si(100) and Si(111) surfaces by various surface analytical techniques [9-12]; and (3) real-time observation of silane produced by atomic hydrogen with a beam flux of 10^{16}-10^{17} cm^{-2}s^{-1} [22] and 10^{15} cm^{-2} s^{-1} [23]. Localized H etching will produce a rough surface and this has been observed by Boland [13]. A rough surface that has an enlarged surface area, however, was believed [13] to have no effect on the "saturation" coverage of 2 ML assuming that the coverage of trihydride is negligible. This is certainly not consistent with our observations. The arguments used by Boland for a maximum coverage of 2 ML are based on the assumption of ledges with (111) facets surrounding etched regions. The (111) facets, as suggested in Ref. [13], contain one dangling bond (DB) per surface atom, while the surface area of these ledges scales as $1/\cos(\theta)$, where θ is the angle between the (100) and (111) planes. Since $\cos(\theta)$

TABLE I. Surface peak measured with a 2.0-MeV $^4\mathrm{He}^+$ ion beam in units of atoms/row. 1 atom/row corresponds to a surface atomic density of 2.72×10^{15} atoms cm^{-2} for the ⟨100⟩ direction.

^{2}H coverage (ML)	0	1.0	1.7	1.93	3.0
Surface peak	5.34 ± 0.15 5.43 ± 0.16[a]	5.30 ± 0.15	4.89 ± 0.15[a]	4.67 ± 0.14	5.20 ± 0.15

[a]From Narusawa and Gibson [8].

$=\cos(60°)=\frac{1}{2}$, the increased surface area due to etching is completely offset by the reduced DB density on the (111) surface. This is true only if a Si(111) surface atom cannot be etched; otherwise, the DB density will be tripled. However, H etching of Si(111) has been observed by STM [14,15], although the etching reaction is much slower. We have carried out measurements on the Si(111)-7×7 surface and found an adsorption curve [24] similar to that shown in Figs. 1 and 2. The high coverages, > 2 ML, measured can therefore be interpreted as a consequence of increased surface area produced by localized H etching.

As we can see from Fig. 2, the breaking of a Si-dimer bond by atomic deuterium occurs at a much faster rate than the breaking of a Si-Si backbond. This suggests that a Si-dimer bond is highly strained compared to a Si-Si backbond. The existence of strains on the dimer can also be seen in various theoretical calculations [25–27].

In Table I we show the Si(100) surface peak measured in the ⟨100⟩ channeling direction as a function of deuterium coverage at about 300 K. For a clean Si(100)-2×1 surface, we find that the surface peak is 5.34 ± 0.15 atoms/row. For the Si(100) ⟨100⟩ direction, 1 atom/row is equivalent to 4 ML or 2.72×10^{15} atoms cm^{-2}. The large surface peak observed by ion channeling was interpreted as due to subsurface distortion [16]. Based on the comparison of experimental results and simulation of a bulklike surface, Feldman, Silverman, and Stensgaard [16] concluded that at least a total of four Si layers must be out of registry with the bulk. The large distortion of subsurface layers caused by the surface dimer reconstruction on a Si(100)-2×1 surface was also reported recently by Craig and Smith [27], who found in a theoretical calculation that significant reconstruction and charge transfer occurs down to five layers below the surface.

For the surface coverage with 1.0 ML of deuterium, we found no change in the surface peak area within our precision. For the surface covered with 1.93 ML of deuterium, i.e., the Si(100)-1×1-H phase, we found that the ⟨100⟩ surface peak has been significantly reduced to 4.67 ± 0.14 atoms/row, a value close to the theoretical value for bulklike Si(100) surface peak (calculated for a 2.0-MeV $^4\mathrm{He}^+$ ion beam) of about 4.4 atoms/row [16]. This clearly indicates (1) the breaking of the dimer bond and the formation of silicon dihydride, and (2) at least partial restoration of previously distorted subsurface layers with respect to lateral distortions, although for normal incidence channeling, vertical displacements would be undetected.

For the surface covered with 3.0 ML deuterium, we find a surface peak of 5.20 ± 0.15 atoms/row, a 0.53-atom/row increase from the "saturated" 2-ML surface. This can be attributed to the roughness of the surface. On a rough surface, reconstruction and relaxation at ledges, microfacets, etch-induced defects, etc., could contribute to a large surface peak.

In summary, we have measured the absolute deuterium coverages on Si(100) exposed to various doses of atomic deuterium. The adsorption process can be seen as (1) adsorption by the Si DBs at coverages ≤ 1 ML, (2) the breaking of the Si dimers to form Si dihydride at coverages between 1 and 1.93 ML, and (3) the breaking of Si-Si backbonds to form trihydride and then gaseous silane, i.e., etching of silicon with further exposures of atomic deuterium. Processes (2) and (3) might overlap to some extent; i.e., etching might begin below 1.93 ML. We are currently attempting to correlate STM, NRA, and RBS experiments to address this question. We found that the "saturated" Si(100)-1×1-H surface is covered with 1.93 ± 0.11 ML deuterium. Channeling studies show that the Si(100)-2×1 surface is highly strained with a surface peak of 5.34 ± 0.15 atoms/row. For a "saturated" Si(100)-1×1-2H surface, the ⟨100⟩ Si surface peak is found to be reduced to 4.67 ± 0.14 atoms/row.

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