Structure of the H-Saturated Si(100) Surface

John J. Boland

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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A scanning-tunneling-microscopy study of the structures produced by the adsorption of atomic H on the Si(100) surface is presented. Moderate exposures at room temperature (RT) produced the 2×1 monohydride phase. Saturation exposures at 370 K produced the mixed 3×1 phase which, following an additional RT exposure, slowly reverted to the bulklike 1×1 dihydride phase. Saturation exposures at RT produced the 1×1 dihydride phase indicating that the 3×1 phase is a H-induced reconstruction which exists only under special conditions. The etching of the Si(100) surface by H atoms was also observed and its implication for saturation coverage and the species present on the surface are discussed.

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The structure of the H-saturated Si(100) surface has been in dispute for many years. On the bulk-terminated surface each Si atom has two dangling bonds (DBs). It is now well established that this surface forms a 2×1 reconstruction in which dimers are formed between neighboring Si atoms along the $[01\bar{1}]$ direction[1,2] [see Fig. 1(a)]. As a result each Si atom has a single DB on the reconstructed surface. It is further established that moderate H doses or saturation doses at elevated substrate temperatures (~650 K) quench the DB states observed in photoemission and electron-energy-loss spectroscopy while the surface retains the 2×1 reconstruction.[3,4] This then corresponds to the monohydride phase which occurs at a coverage of 1.0 monolayer. Following saturation exposures LEED studies show a 1×1 pattern with a diffuse background.[3–5] Originally it was believed that on the saturated surface the dimer bonds are broken and the surface adopts a bulklike arrangement with two H atoms per surface Si atom, i.e., saturation is 2.0 monolayers.[3] Recently, it has been suggested on the basis of LEED and ir studies[6] that the saturated surface actually consists of a disordered 3×1 phase which involves repeated alternating monohydride and dihydride units, thus providing a natural explanation for the observed saturation value of 1.5 monolayers. There are, however, several problems with this model. First, despite the fact that the 3×1 phase involves alternating monohydride and dihydride units, the coverage associated with this phase is 1.33 monolayers, i.e., 4 H atoms for every 3 Si atoms, and not 1.5 as the authors claim[6] [see Fig. 1(a)]. Furthermore, recent estimates of the saturation coverage yield a value of 1.85 ± 0.18 monolayers,[7] substantially closer to that of the dihydride phase than previously reported. In view of these facts we have undertaken a detailed study of the structure of the H-saturated Si(100) surface.

In this work we present a scanning-tunneling-microscopy (STM) study of the nature of the H-stabilized Si(100)-3×1 phase and its role in the saturation of the Si(100) surface. The 3×1 phase was observed only on samples prepared following the procedure previously reported.[6] Additional room-temperature (RT) exposures of this phase produced an increasingly bulklike structure, demonstrating that the 3×1 phase is not fully saturated. Under the more usual RT exposure conditions a bulklike surface was obtained but with no evidence of the 3×1 phase. The saturated surface therefore consists of a bulklike structure with two H atoms per surface Si atom.

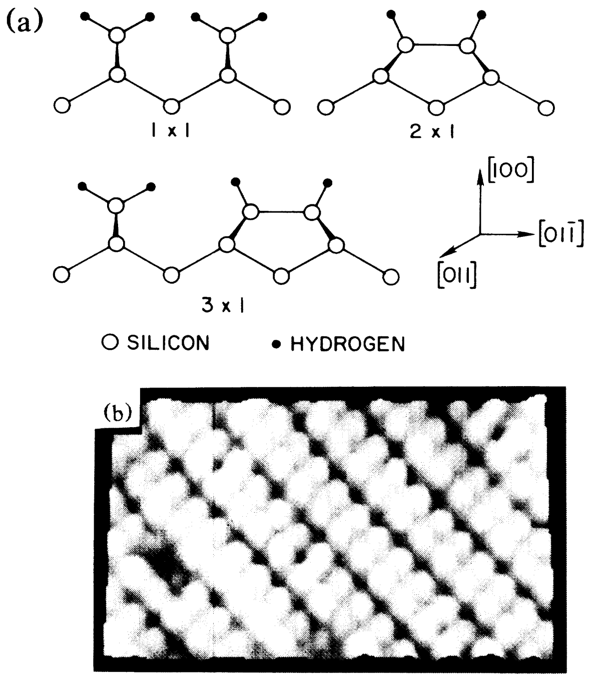

FIG. 1. (a) Schematic of the various possible hydrogenated structures present on the Si(100) surface. (b) Scanning-tunneling-microscopy (STM) topograph of the monohydride phase. The surface shown is 59×39 Å and the image was recorded at a sample bias of +2.5 V.

In addition, the etching of the Si(100) surface by H atoms was observed. While this process necessarily increases the surface area we show that it does not result in an increased saturation coverage, although it may have a pronounced effect on the nature of the hydrogenated species that are present on the surface.

The microscope used in this work is similar to that discussed by Demuth *et al.*[8] and was mounted in a UHV chamber with a base pressure of $\sim 1\times10^{-10}$ Torr. The sample was a 1-Ω cm phosphorous-doped Si(100) wafer. The atomic hydrogen was produced by decomposing H_2 gas (99.9995% purity) from a glass flask on a 1800-K W filament positioned about 2 cm from the sample. The H_2 was directly collimated from the UHV side of a variable leak valve onto the sample. Baffles were positioned about the filament and sample so as to generate a stagnation volume in front of the latter. The flux of atomic H was not measured. On the Si(111)-7×7 surface, a 1-min RT exposure with an ion-pump pressure of 7×10^{-9} Torr was sufficient to saturate about 30% of the surface DBs. Pressures as high as 6×10^{-8} Torr were used to saturate the surface during which the sample temperature rose 20–30 K.

Before studying the nature of the 3×1 phase we first characterize the pure monohydride phase whose dimer units are an integral part of the proposed 3×1 structure.[6] Figure 1(b) shows an STM topograph of the Si(100)-2×1 monohydride surface. This surface was prepared by either a moderate RT H dose or a saturation dose at 650 K, with equivalent results. At positive-sample bias when imaging the unoccupied states of the sample the individuals atoms of the dimers are clearly resolved. This is due to the presence of a broad H-derived σ^* state which is located about 1 eV above the Fermi energy.[5,9] In agreement with the work of Hamers, Avouris, and Bozso[9] these atoms are also resolved in the occupied-state topographs but for reasons that will become apparent later we will restrict ourselves to a discussion of images of the unoccupied states.

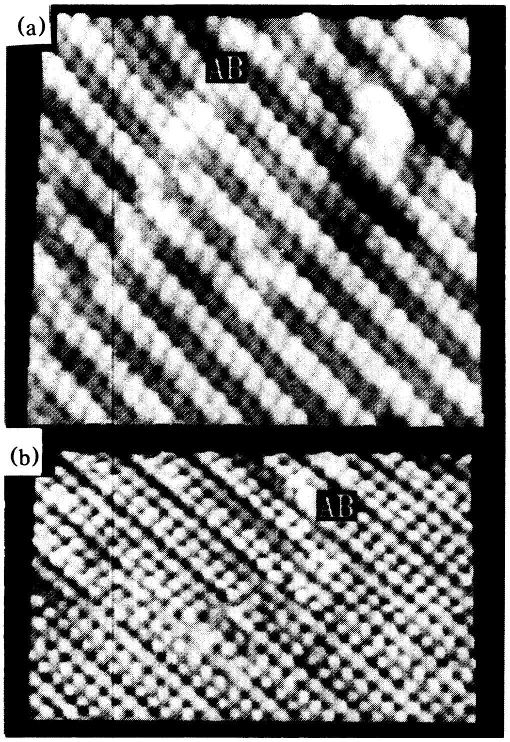

FIG. 2. (a) STM topograph of the unoccupied states (+2 V) on the 3×1 phase. The area shown is 104×107 Å. There is a slight uncorrected thermal drift in this image. (b) STM topograph of the occupied states (−2 V) on the 3×1 phase. The area shown is 108×75 Å. *AB* denotes the presence of 3×1 antiphase boundaries.

To prepare the 3×1 phase a clean Si(100) surface was exposed to atomic H while the sample temperature was held at 370 K.[6] The results are shown in Fig. 2. Figure 2(a) shows the surface to consist of rows of alternating monohydride and dihydride units corresponding to the 3×1 phase reported earlier.[6] The darker dihydride units are readily distinguished from those of the brighter monohydride, despite the fact that the individual atoms of the dimers are resolved in these images. The monohydride units are identical to those observed on the pure monohydride phase in Fig. 1(b). The well-ordered 3×1 phase shown in Fig. 2(a) was found to exist over large regions of the surface and was routinely observed on samples dosed at 370 K. Since this 3×1 phase is formed at low temperatures, we rarely observe the presence of large 3×1 domains. Typically several domains are observed on a given (100) terrace and where these domains meet there is a 50% probability that an antiphase boundary will be formed. This reflects the fact that each surface atom has an equal probability of forming a dimer with the atom on the right or the left along the $[01\bar{1}]$ direction. The presence of such domains is consistent with a 2×1 → 3×1 transformation which involves only a local bonding rearrangement. One such boundary is labeled *AB* in Fig. 2(a). Note that in one instance this boundary is accommodated by the formation of a double row of dihydride units, demonstrating that the inter-H interaction between dihydride units is not as unfavorable as has been suggested.[6] However, more typically this is accomplished by cleaving a dimer unit at one side of the boundary and allowing one of the dimer atoms to form a dihydride unit while the other dimerizes in the opposite direction in registry with the dimer rows of the other domain.

Figure 2(b) shows a topograph of the occupied states of the 3×1 surface. There is a pronounced minimum between the atoms which make up the dimers, consistent with the earlier results of Hamers, Avouris, and Bozso.[9] However, the dihydride rows are still distinguishable, being in general wider and less well resolved in the [011] direction, i.e., along the direction of the rows. The former is due to the large separation between monohydride units reflecting the existence of the dimer bonds within these units while the latter is likely due to the presence of Si backbonds along the [011] direction [see Fig. 1(a)]. Antiphase boundaries, although present [see Fig. 2(b)], are not easily identified in topographs of the occupied states. Furthermore, since the presence of dimers is most readily detected in topographs of the unoccupied states, we shall restrict future discussion to these images.

To determine whether the 3×1 phase corresponds to the saturated Si(100) surface, a further RT exposure of the well-ordered 3×1 phase shown in Fig. 2 was performed. The result is shown in Fig. 3. Note that the surface gradually adopts a more bulklike structure although remnants of the original 3×1 phase remain. One such remnant is denoted by *R* in Fig. 3. These regions of 3×1 structure slowly revert to the 1×1 structure with further H exposures, although obtaining good-quality topographs of these highly dosed surfaces becomes increasingly difficult. This slow H uptake beyond the monohydride coverage has been noted in several earlier studies.[4,7] However, we observe that the incorporation of additional H into the 3×1 phase appears to be more difficult than for the simple monohydride phase.

In contrast to our earlier work on the Si(111) surface,[10] the (100) surface is readily etched by H atoms. This occurs at relatively localized sites on the surface with exposed regions of the bulk, when observable, exhibiting an unreconstructed 1×1 structure. The enhanced etch rate of the (100) surface is presumably due to the prominent Si backbonds on this surface. It is yet unclear what surface species act as precursors which nucleate this etching process. However, there is a strong correlation between the commencement of etching and the occurrence of the bright white features which are now present on the surface. These features are in general adjacent to the etched regions of the surface suggesting that they may be products of this etching process.

To determine the nature of the saturated surface obtained under more typical exposure conditions, a clean 2×1 surface was given a large RT dose of atomic H, the results of which are shown in Fig. 4. In contrast to the surface shown in Fig. 3, this surface has almost completely adopted a bulklike 1×1 structure. Remnants of the intermediate 2×1 structure were occasionally observed. Here, too, we observe etching of the bulk by H atoms. However, in contrast to the data shown in Fig. 3, we find no evidence for either an ordered or disordered 3×1 phase. This demonstrates that the saturated surface has a bulklike structure and that the 3×1 phase is a H-induced surface reconstruction which occurs at subsaturation coverages and only under the special exposure conditions described earlier.

The observation of pronounced H-atom etching on the Si(100) surface calls into question the very concept of saturation coverage on this surface. Clearly, much Si has been lost in the formation of products, presumably silanes. On the (100) terraces this etching process is likely initiated by the rupture of one of the Si-Si backbonds. This process proceeds radially, exposing the (100) surface beneath. Since the etched surface still has a bulklike structure consisting mainly of dihydride units, the overall saturation coverage will be close to 2 monolayers. As this process continues a significant number of monohydride species are generated which are associated

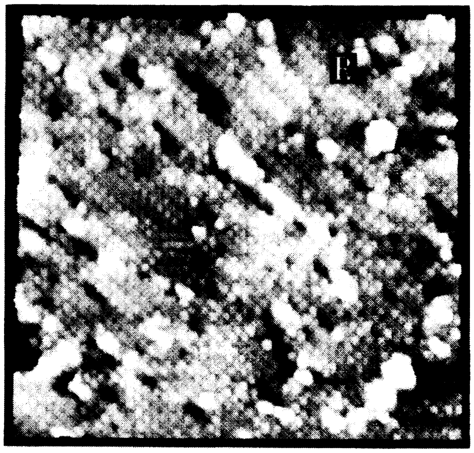

FIG. 3. STM topograph of the unoccupied states (+3 V) of the 3×1 surface following a RT exposure to atomic H. *R* denotes remnants of the 3×1 phase. The area shown is 181×194 Å.

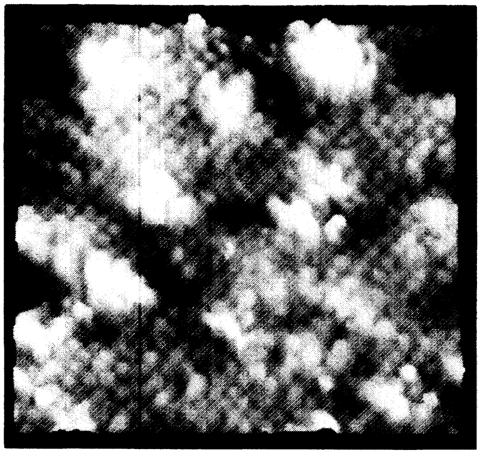

FIG. 4. STM topograph of the unoccupied states (+2 V) of a clean 2×1 surface following a large exposure to atomic H. The area shown is 102×103 Å.

with the ledges surrounding these etched regions of the surface. Despite this, the maximum saturation coverage on the Si(100) surface, including these ledge species but excluding possible Si adspecies such as SiH_3, etc., is still 2 monolayers. This is because these ledges consist of (111) facets which contain one 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 $\cos(\theta) = \cos(60°) = \frac{1}{2}$, the increased surface area due to etching is completely offset by the reduced DB density on the (111) surface. This explains why saturation coverages above 2 monolayers have never been reported on this surface and why such surfaces may exhibit 1×1 LEED patterns and yet contain a significant population of monohydride species.[6] The existence of this etching process underscores the difficulty in interpreting ir measurements performed on this surface.

We have observed that etching occurs at a rate which is comparable to the rate of insertion of H into the dimer bonds, suggesting that the dimer bonds on the monohydride surface are not highly strained. This is consistent with a recent theoretical study which shows that the dimer bond length in the monohydride phase is close to the bulk value and that the Si dimer atoms have an sp^3 bulklike hybridization.[11] On the other hand, we are unable to address the significance of the inter-H interaction known to exist on the dihydride surface.[5,6] Evidently, this repulsive interaction is not sufficient to prevent the formation of the dihydride phase. However, it is not possible to determine whether the recently proposed rotated dihydride phase actually exists.[5]

In conclusion, the 3×1 phase exists only on specially prepared surfaces and does not correspond to the structure of the saturated Si(100) surface. Further RT exposures of this 3×1 phase produced an increasingly bulklike structure demonstrating that the 3×1 phase is not fully saturated. Under normal exposure conditions the Si(100) surface adopted a bulklike structure with some remnants of the intermediate monohydride phase. No evidence for the 3×1 phase was ever observed in these latter studies. On this basis we conclude that the saturated Si(100) surface has a bulklike structure with two H atoms per surface Si atom. In addition, etching of the Si(100) surface was observed at high exposures. While this etching process increases the surface area, we show that it does *not* result in an increased saturation coverage, although it may significantly enhance the population of the ledge monohydride species on the surface.

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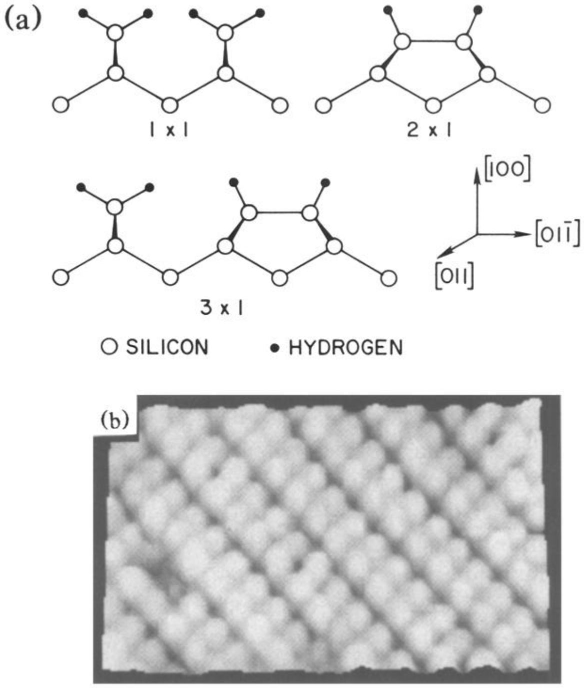

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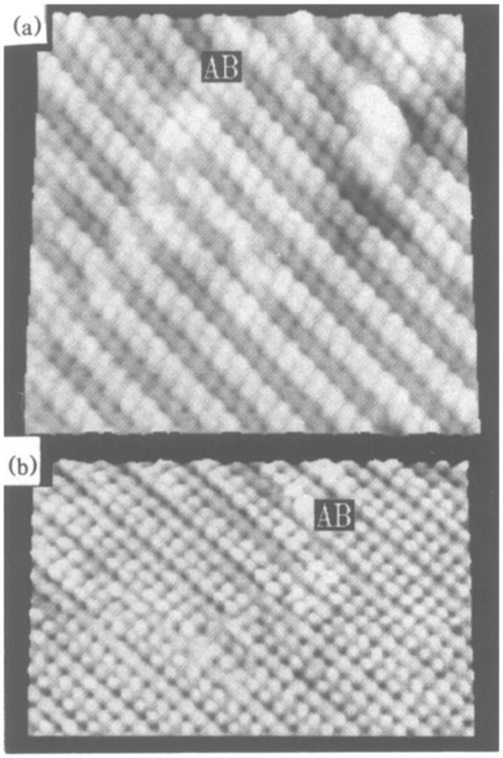

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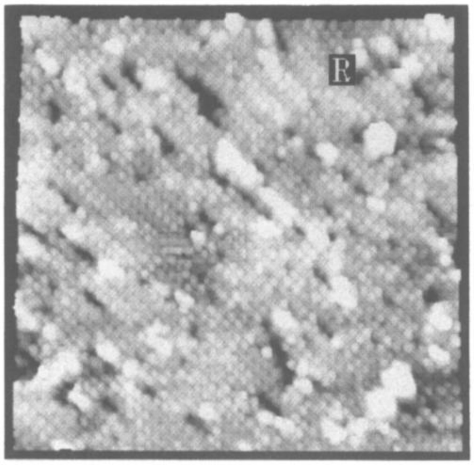

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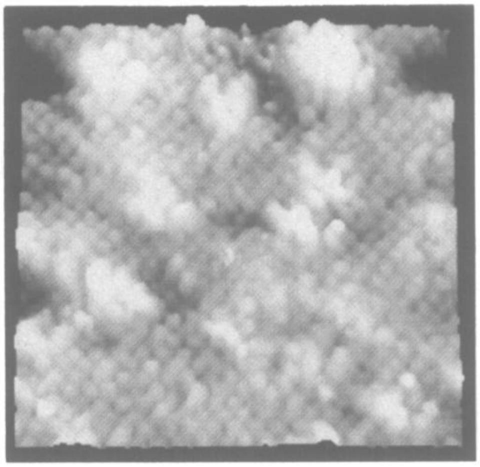

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