A scanning tunneling microscopy study of hydrogen adsorption on Si(112)

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The adsorption of atomic hydrogen on Si(112) has been investigated using scanning tunneling microscopy. The clean (112) surface is reconstructed into quasiperiodic nanofacets [each composed of a (111) and (337) terrace], and we find that atomic hydrogen does not remove this nanofacet structure at room temperature or 430 °C. This result demonstrates the surprising stability of the facet reconstruction.

I. INTRODUCTION

Vicinal silicon surfaces have recently gained attention as substrates for electronic device fabrication, primarily because of their presumed high step densities. For example, a bulk-terminated Si(112) surface would consist of short (111) terraces separated by monoatomic-height steps [Fig. 1(a)]. As a result, Si(112) has been investigated as a substrate for heteroepitaxy and the growth of spatially confined structures.[1,2] Our recent scanning tunneling microscopy (STM) studies have revealed, however, that the clean Si(112) surface exhibits a novel quasiperiodic reconstruction consisting of sawtoothlike nanofacets. Each nanofacet is composed of a single unit cell wide reconstructed (111) terrace (7×7 or 5×5) opposed by a reconstructed (337) terrace.[3] Similar nanofacets are also observed on Si(335), suggesting that they are a general phenomenon for some range of vicinality towards $[\bar{1}\bar{1}2]$.

Although nanofacets occur on clean Si(112), it is not clear whether they persist on adsorbate-covered surfaces. When adsorbates interact with surface dangling bonds, the surface free energy is usually modified, sometimes leading to a gross rearrangement of the surface.[4] It is therefore possible that certain adsorbates could remove the nanofacets on Si(112). One of the simplest adsorbates to investigate is atomic hydrogen. It is known to selectively react with dangling bonds on low index Si surfaces to relax bond strain and reduce the surface free energy.[5] This study investigates the interaction of atomic hydrogen on Si(112) in order to examine the stability of the nanofacets and the bond strain associated with this reconstructed surface.

Atomic-scale details of the interaction of atomic hydrogen with both Si(001) and Si(111) have been extensively studied using STM by Boland and others.[5–7] The adsorption of hydrogen on Si(001)2×1 results in monohydride and/or dihydride phases, where the well-ordered 2×1 monohydride phase leaves the Si dimer structure intact. In the case of Si(111)7×7, atomic hydrogen interacts with the surface dangling bonds to form a variety of hydrides, eventually leading to the creation of 1×1 domains under the appropriate conditions. Hydrogen desorbs (as H_2) from low index Si surfaces in two peaks, $\beta_2 \approx 410$ °C and $\beta_1 \approx 540$ °C, corresponding to the decomposition of silicon di- and trihydrides [β_2], followed by the monohydrides [β_1].[8] Based on these results, we have focused our study on the adsorption of atomic hydrogen on Si(112) at a sample temperature of approximately 430 °C, conditions which should favor monohydride formation.

II. EXPERIMENT

The experiments were performed in ultrahigh vacuum (UHV) using Si wafers oriented to within 0.5° of (112). To obtain a clean surface, the samples were precleaned in a 1:3 boiling solution of H_2O_2 and H_2SO_4, degassed at 600 °C for 1 h in vacuum, and then flashed to ≈1150 °C for 60 s (base pressure $\leq 2\times10^{-9}$). Atomic hydrogen was produced by leaking H_2 gas into the chamber with a hot W filament located ≈2 cm from the Si sample. During high-temperature dosages, the samples were first heated to approximately 430 °C, dosed using background H_2 pressures not exceeding 2×10^{-7} Torr (langmuir$=10^{-6}$ Torr s), annealed for 15 min at the deposition temperature, and then cooled to room temperature. All STM images were acquired at room temperature with a constant current between 0.1 and 0.3 nA and bias voltages between 1.0 and 2.5 V. Although images of both the empty and filled electronic states were acquired, only filled-state images are shown here.

III. RESULTS AND DISCUSSION

Our recent STM studies have shown that Si(112) has a much more complicated surface structure than the bulk-terminated case.[3] Images of the clean surface show a novel quasiperiodic reconstruction consisting of sawtoothlike nanofacets with an approximate period of 130 Å and depth of 8 Å [Fig. 1(b)]. The shorter sides of the nanofacets are one unit cell wide 7×7 or 5×5 reconstructed Si(111) planes, while the longer sides are 60–110 Å wide terraces with prominent rows of atomic-scale features running along $[\bar{1}10]$. Using the (111) sides of the nanofacets as an absolute length calibration, we have found that the longer sides of the nanofacets are 4.0° steeper than (112) with a unit cell length of 15.7 Å along $[11\bar{1}]$, corresponding to a (337) plane. Figure 1(c) illustrates a ‘‘perfect’’ nanofacet composed of only (337) and (111) planes: there are seven unit cells of (337) for each (111)7×7 unit cell [or five units of (337) for each unit of 5×5]. This coincident structure results in the characteristic length scale of the nanofacets. We believe that these nanofacets are the equilibrium surface structure of Si(112), indi-

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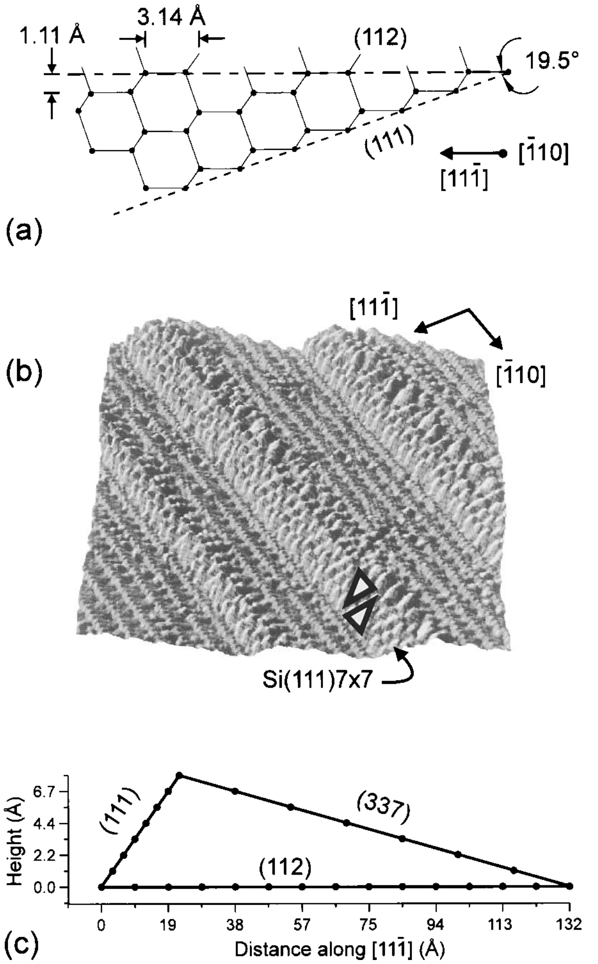

FIG. 1. (a) Model of the bulk-terminated Si(112) surface, consisting of 8.87-Å-wide (111) terraces separated by 3.14-Å-high (001)-oriented steps. The unit cell is 3.84 Å×9.41 Å in the (112) plane. (b) Rendered, filled-state STM topograph of Si(112) (320 Å×270 Å, 12 Å height range) showing a sawtoothlike nanofacet structure. One 7×7 unit cell on the shorter (111) side of a sawtooth is highlighted. (c) Illustration of an ideal Si(112) nanofacet composed of a (337) terrace and a (111) terrace one 7×7 unit cell wide. Unit cell increments of the bulk-terminated surfaces are indicated by filled circles.

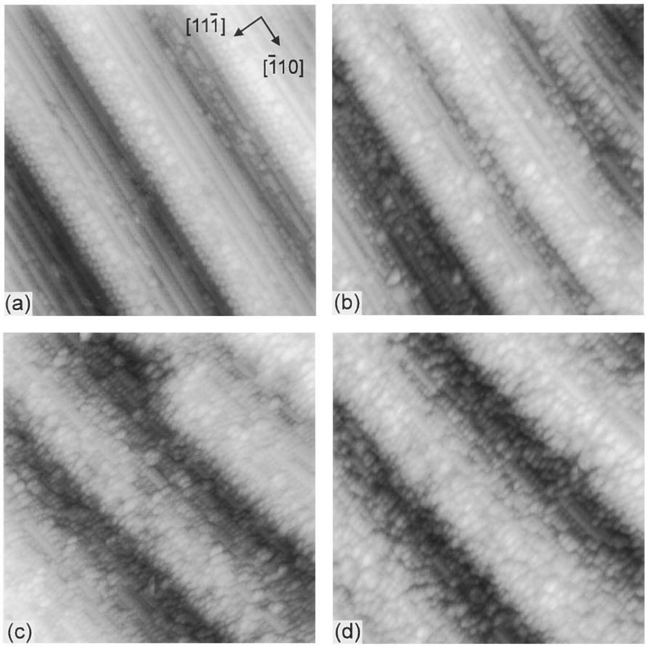

FIG. 2. Filled-state images of Si(112) (350 Å×350 Å) exposed to hydrogen with $T_{\mathrm{Si}} \approx 430$ °C: (a) 0 L, (b) 50 L, (c) 100 L, and (d) 150 L.

cating that the surface energy for the combination of reconstructed (111) and (337) planes is lower than that for a planar reconstructed (112) surface.

The effects of atomic hydrogen adsorption on the nanofacets are illustrated in Fig. 2, which shows a sequence of images as a function of hydrogen exposure at high temperature (≈430 °C). Although the atomic-scale features become disrupted with increasing hydrogen exposure, the nanofacets remain intact. This is clearly evident in the rendered image displayed in Fig. 3. (Note: The nanofacet reconstruction was still observed following the highest exposures, ~250 L.[9]) We also adsorbed hydrogen on surfaces held at room temperature, where different surface chemistry is expected (dominated by silicon di- and trihydride formation), and found no evidence for the removal of the nanofacets. These results demonstrate the surprising stability of the Si(112) nanofacet structure with respect to atomic hydrogen adsorption.

Although atomic hydrogen does not remove the nanofacet reconstruction, it significantly disrupts the atomic-scale structure on the top surface layer of the nanofacets. Since the nanofacets contain (111)7×7 terraces, previous STM studies of the H:Si(111) system are particularly relevant to this work. Boland has proposed a model for hydrogen adsorption on Si(111)7×7 involving the selective reactivity of hydrogen with Si bonds having different degrees of bond strain.[5] At low temperatures and saturation conditions, backbond relaxation occurs by the formation of trihydride adatom species. As the temperature is increased, these trihydrides diffuse and combine to form bulklike islands, exposing H-terminated "rest-layer" regions. Above approximately 225 °C, hydrogen mediates the insertion of Si atoms from the adatom layer into the rest-layer dimer bonds, resulting in the formation of H-terminated 1×1 domains. When the surface is annealed to

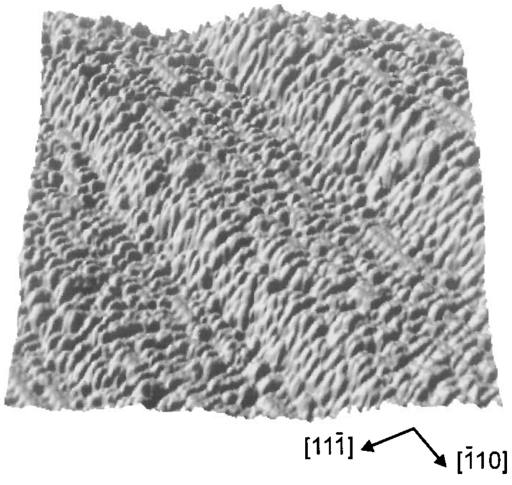

FIG. 3. Rendered topograph of Si(112) following a high-temperature 150 L hydrogen exposure. The nanofacet reconstruction is still apparent. Note that this image is the same as that shown as a gray scale in Fig. 2(d).

temperatures between the β_1 and β_2 desorption peaks (similar to our preparation conditions), higher surface hydrides such as the adatom trihydrides decompose. Another STM study by Owman and Mårtensson[6] reports that H-terminated 1×1 domains form at sample temperatures above the β_2 desorption peak, suggesting that higher hydrides still play a role at these higher surface temperatures.

Since our (112) surfaces were exposed to atomic hydrogen at ≈430 °C, we expect monohydride formation to dominate the surface chemistry. With increasing hydrogen exposure the adatoms on the (111) reconstructed terraces of the nanofacets become disordered and sometimes disappear in the filled-state STM images. Some of these ''missing'' adatoms may be monohydride-terminated adatoms that appear dark in the STM images for the bias voltages used.[5] Other missing adatoms could be due to the formation of trihydride adatoms which then diffuse away from the (111) terrace. In contrast to the H:Si(111) system where large (111) terraces are present, trihydrides cannot combine to form bulk-like islands on the nanofaceted surface. Instead, we speculate that they diffuse and bond in a disordered manner on the (337) terraces of the nanofacets, appearing as large, bright protrusions in the STM images. Since adatoms and remnants of the subsurface dimers are still visible on the (111) terraces at the largest exposures, the conditions used in this study do not fully convert the reconstructed (111) terraces to H-terminated 1×1 domains, as can occur on a Si(111)7×7 surface.

In addition to bonding with adatoms on the (111) terraces, atomic hydrogen also interacts with atoms associated with the reconstructed (337) terraces of the nanofacets. The clean (337) terraces are dominated by row structures running along $[\bar{1}10]$ with a $1a$ ($a = 3.84$ Å) atomic corrugation along each row [Fig. 2(a)]. We are presently investigating possible atomic models for these $1a$ rows and speculate that they represent either a rebonded step edge reconstruction[10] or some variation of a Π-bonded chain-type reconstruction.[11] A number of other structures can also be observed on the (337) terraces, but they will be addressed in detail in a separate publication.[12] As the clean surface is incrementally dosed with atomic hydrogen, the $1a$ row structures gradually become disrupted and eventually disappear entirely. In regions where the $1a$ rows are missing, a new type of structure occasionally occurs. These new structures consist of oblong protrusions (7.7 Å×10 Å) spaced $2a$ apart in rows running along $[\bar{1}10]$, where each row is displaced ≈4.3 Å in the $[111]$ direction from the original $1a$ rows [Fig. 4(b)]. Dual-bias images (not shown) reveal that each protrusion has one maximum in the filled electronic states and two maxima oriented along the row direction in the empty states. This result suggests that the new $2a$ rows may result from a hydrogen-induced dimerization of the original $1a$ rows; however, the disordered arrangement of the $2a$ rows presents difficulties in analyzing and modeling these structures. What is apparent from the images is that the (337) terraces are comparable in reactivity to the (111) terraces, indicating that the reconstructed (337) terraces have a density of dangling bonds similar to that on Si(111)7×7.

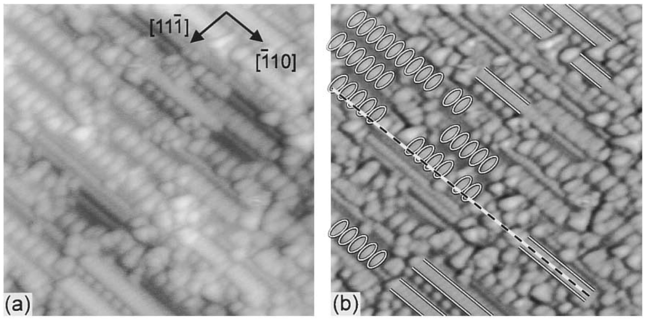

FIG. 4. (a) Filled-state image of a 100 L H-dosed surface (175 Å×175 Å) showing the disrupted top surface layer of the nanofacets. (b) High-pass filtered version of (a) with superimposed outlines showing remaining segments of (337)-type bright rows and newly created oblong protrusions. The dashed line bisects one unreacted row of the (337) structure (with $1a$ period), highlighting the relative position of the ordered H-induced oblong structures (with $2a$ period).

IV. CONCLUSIONS

We have studied the interaction of atomic hydrogen with the relatively complicated surface structure of Si(112). Our previous STM study of the clean surface showed that Si(112) forms quasiperiodic, sawtoothlike nanofacets composed of short reconstructed (111) and (337) terraces. When exposed to atomic hydrogen, the top surface layer of these nanofacets becomes disordered, but the underlying ''sawtooth'' structure is very stable and remains intact. It is possible that a kinetic limitation prevents the removal of the nanofacets by atomic hydrogen. The mass transport required for such a gross rearrangement of the surface may not be possible below the hydrogen desorption temperature (≈540 °C). It should be noted, however, that it is possible to remove the nanofacets using an adsorbate other than hydrogen: we have preliminary results showing that adsorbed Ga removes the underlying nanofacet structure at sample temperatures as low as ~500 °C.[12]

Although this study has demonstrated the stability of the nanofacet reconstruction on Si(112) with respect to hydrogen, further experiments and calculations are necessary to determine the atomic-scale structure of both the clean and reacted surfaces. On the top surface layer, hydrogen reacts with adatoms on the reconstructed (111) terraces, and creates new ''dimerized'' row structures on the (337) terraces. It would be interesting to examine whether atomic hydrogen ''dimerizes'' the Π-bonded chains present on the Si(111)2×1 surface, indicating whether the rows observed on the (337) terraces of the nanofacets are similar in structure to those seen on Si(111)2×1. Further experiments and calculations to determine the structure of the (337) terraces are in progress.

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[1] L. Fotiadis and R. Kaplan, Thin Solid Films **184**, 415 (1990).
[2] T. M. Jung, R. Kaplan, and S. M. Prokes, Surf. Sci. **289**, L577 (1993).

[3] A. A. Baski and L. J. Whitman, Phys. Rev. Lett. **74**, 956 (1995).

[4] E. D. Williams and N. C. Bartelt, Science **251**, 393 (1991).

[5] J. Boland, Adv. Phys. **42**, 129 (1993); Surf. Sci. **244**, 1 (1991), and references therein.

[6] F. Owman and P. Mårtensson, Surf. Sci. **303**, L367 (1994).

[7] R. J. Hamers, Ph. Avouris, and F. Bozso, Phys. Rev. Lett. **59**, 2071 (1987).

[8] C. M. Greenlief, S. M. Gates, and P. A. Holbert, J. Vac. Sci. Technol. A **7**, 1845 (1989).

[9] For reference, a hydrogen exposure of a few langmuirs in our system is sufficient to produce a monohydride-terminated Si(001) surface.

[10] D. J. Chadi, Phys. Rev. B **29**, 785 (1984).

[11] K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981).

[12] A. A. Baski and L. J. Whitman (unpublished).