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Absorption of gas-phase atomic hydrogen by Si(100): Effect of surface atomic structures

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The atomic-scale surface structural evolution of Si(100) exposed to gas-phase thermal hydrogen atoms, H(g), has been investigated by scanning tunneling microscopy and temperature-programed desorption mass spectrometry. For the substrate temperature (T_s) between 420 and 530 K, dihydride species in 3×1 :H domains were selectively etched upon extensive exposures to H(g). As a result, etch pits grew laterally along Si surface dimer rows. The presence of these pits correlates with the absorption of H(g) into the bulk of Si(100), confirming our earlier suggestion that atomic-scale surface roughening caused by etching is a prerequisite for H(g) absorption. © 2001 American Institute of Physics. [DOI: 10.1063/1.1379989]

Hydrogen, prevalent in semiconductor device processing, deactivates dopants, and creates and passivates defects on and in crystalline silicon $(c-Si)^1$ and at Si/SiO₂ interfaces.² Passivation of defects is beneficial, but incorporation of hydrogen into c-Si epifilms or substrates can be detrimental to device performance. Although the interaction between Si(100) and gas-phase thermal hydrogen atoms, H(g), has been investigated intensively over the past several decades,³ direct H(g) incorporation into c-Si is a recent observation.4

Surface uptake of H(g), on Si(100)-2×1 leads to three different phases depending on the substrate temperature (T_s) and H coverage (θ_H): (1) a 2×1:H monohydride phase $(\theta_H = 1 \text{ ML})$ at ~600 K; (2) a 3×1:H phase with the alternating dihydride and monohydride units ($\theta_H = 1.33 \text{ ML}$) at ~400 K; and (3) a 1×1:H dihydride phase ($\theta_H = ~2$ ML) of at $\sim 300 \text{ K.}^{3-5}$

The latter two phases give two H₂ desorption peaks at 670 K (β_2) and 780 K (β_1), the recombinative desorption from surface di- and monohydrides, respectively.^{3,4} Recently, Kang *et al.*⁴ reported an additional and unsaturable H_2 temperature-programed desorption (TPD) peak (α) at 860– 900 K from Si(100) surfaces held between 420 and 530 K during H(g) exposure, which was attributed to hydrogen evolution from the c-Si bulk. They also showed TPD evidence that surface etching and microscopic surface roughening were associated with this bulk uptake.⁴

In this letter, we present atomic-scale scanning tunneling microscopy (STM) images of the etch features produced by H(g) and show a direct correlation between microscopic surface structure and H(g) incorporation into the subsurface of Si(100). This work provides interesting fundamental and technological insights.

Experiments were performed in an UHV chamber (base pressure of $< 2 \times 10^{-10}$ Torr) equipped with an OMICRON VT-STM. The Si(100) sample used was N-type (P-doped; $\leq 1 \Omega$ cm) and cut into a 2×10 mm² size for STM measurements. The clean surface was prepared by outgassing for 12 h at $\sim 900 \,\text{K}$ and flash annealing to $\sim 1350 \,\text{K}$ in vacuum without ex situ sample pretreatment. The clean and ordered Si(100)-2×1 surface was confirmed by STM. H₂ gas was introduced into the UHV chamber through a tubular doser controlled by a variable leak valve. To remove impurities such as hydrocarbons and water in the gas delivery line, a liquid-nitrogen cold trap was used. H(g) was produced by cracking H₂ molecules with a hot (\sim 1800 K) spiral W filament positioned \sim 5 cm away from the Si surface. Exposures are reported in langmuirs (1 L=1×10⁻⁶ Torr \cdot s) of H₂, not H, because more than 98% of the measured chamber pressure increment is due to H_2 . All H(g) exposures were done at a fixed T_s of 460 K lying at the center of the interval where H(g) absorption occurs. All STM images of 25 nm on a side were taken at $V_{\text{sample}} = -1.6 \text{ V}$ and $I_t = 0.1 \text{ nA}$ at room temperature using electrochemically etched W tips.

Figure 1 shows STM images of Si(100) surfaces exposed to H(g) of: (a) 3000 L; and (b) 10000 L H₂ at T_s of 460 K. The surface in Fig. 1(a) exhibits a 2×1 : H phase with few imperfections. For the surface in Fig. 1(b), a 3×1 : H phase, with its alternating parallel rows of bright monohydride dimer and *dark* dihydride units, are formed on the surface. A few atom vacancies due to slight surface etching and several anti-phase boundaries (see the boxed area) within 3×1 :H areas are also observed.⁶ Domains of 2×1 :H (see the circled area) also persist, reflecting an intermediate stage of the 2 \times 1:H to 3 \times 1:H phase transition,⁶ which is in part due to the relatively high H(g) dosing T_s of 460 K employed here.

Increasing the exposure by factors of 5 and 10 [Figs. 2(a) and 2(b)] indicates significant etching. Images of

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FIG. 1. Filled-state STM images of Si(100) exposed to H(g) of (a) 3000 L H_2 ; and (b) 10 000 L H_2 at T_s of 460 K. An antiphase boundary (boxed) and 2×1 :H domain (circled) are indicated.

300 000 and 500 000 L H₂ (not shown) do not differ much from the 100 000 L H₂ image of Fig. 2(b). Figure 2(a) shows that atom vacancies and vacancy lines are clearly evident and located mainly along dihydride rows, in contrast to previous reports that the 3×1 :H phase is stable to extended H(g) exposures.⁵ Unlike a previous suggestion,⁶ our results show no preferential etching of dihydrides at antiphase boundaries. 3×1 :H domain sizes in Fig. 2(a) are much smaller than those in Fig. 1(b), a result attributed to complicated local surface reconstructions forced by atom vacancies and strain introduced by etching.⁶ The terraces formed within larger etch pits retain the 3×1 :H domain structure and contain etch vacancies, Fig. 2(b).

Surface trihydride species, $SiH_3(a)$, produced by H insertion into $SiH_2(a)$, can be hydrogenated by H(g) and removed as $SiH_4(g)$. The random distribution of atom vacancies observed in Fig. 2 is in accord with the Eley–Rideal



FIG. 2. Filled-state STM images of Si(100) exposed to H(g) of (a) 50 000 L H₂; and (b) 100 000 L H₂ at T_s of 460 K. Etch pit lines (circled) occurring in local (1×1) regions are indicated.

mechanism for initiating the surface etching reaction.⁷ Most of surface vacancies are located on dihydride rows, and etch pit lines are mostly observed in local 1×1 :H regions (see the circled areas in Fig. 2). Figure 2(a) shows that most of etch pit lines occur between two dihydride rows reflecting this repulsion-enhanced etching within 1×1 :H domains. Compared with adjacent dihydride units in 3×1 :H domains, those in 1×1 :H domains experience increased steric repulsion,⁵ and are more vulnerable to H(g) attack.

The linear and rectangular pits are a result of initiation by selective dihydride etching, subsequent branching and, finally, coalescence of adjacent linear pits.⁸ The total etch pit area after 100 000 L H₂, measured by summing missing atoms in single atom vacancies and etch pits from the STM images, is 30% of the total surface area [Fig. 2(b)]. For a five-fold larger exposure (not shown), the pit area is 35% of che total, indicating that 100 000 L H₂ is close to steady-state



FIG. 3. H_2 (solid) and SiH₄ (dashed) TPD spectra from Si(100) exposed to H(g) of 500 000 L H₂ at 460 K. Also displayed as a reference is a H₂ TPD spectrum (dotted) from Si(100)-3×1:H prepared by a H(g) dose 1500 L H₂ at T_s of 430 K. The α peak is unsaturable and attributed to H absorbed into bulk Si(100).

concentration of missing atoms and, by inference, steadystate etching rate. Kang *et al.*⁴ showed that etching rates at $T_s < 400$ K overwhelm H(g) absorption rates while for $T_s > 600$ K, removal of surface hydrogen, H(a) via abstraction by H(g) dominates etching and surface roughening, and therefore H(g) is not absorbed.

In Fig. 3, we show H₂ and SiH₄ TPD spectra from a Si(100) surface exposed to H(g) of 500 000 L H₂ at T_s of 460 K. Consistent with previous work, there is a strong α peak from bulk H.⁴ There is also measurable SiH₄ desorption reflecting surface SiH₃(a), which is also confirmed by bright protrusions in STM images after large H(g) doses at T_s between 420 and 530 K. From comparison with the reference 3×1 :H β_1 plus β_2 intensity of H₂, we estimate that the surface area has increased by ~30% as result of the etching-induced roughening, in agreement with the STM image

analysis. Confirming our earlier suggestion,⁴ the TPD and STM results provide solid evidence for the correlation between H(g) absorption into bulk Si(100) and surfaces roughened with atomic-scale etch vacancies and lines. Further support occurs from preliminary results showing that roughening induced by Ar^+ bombardment also facilitates H(g)absorption.

In summary, our STM results show that H(g) dosing of Si(100) at T_s of 460 K etches the 3×1 :H domain structure creating atom vacancies and atomic-scale etch pits. These atomic-scale etch features provide a low activation-energy path for H(g) to incorporate into bulk Si(100).

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