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Interplay of the monohydride phase and a newly discovered dihydride phase in chemisorption of H on Si(100)2 × 1

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We have established that chemisorption of atomic hydrogen on Si(100) forms a previously unreported dihydride phase, Si(100)1 × 1::2H, as well as the monohydride phase Si(100)2 × 1:H. The interplay of these phases as exposure and temperature are varied casts new light on surface structure and bonding, and on the kinetics of thermal desorption. These studies suggest that the reconstruction inherent in the clean Si(100)2× 1 surface is achieved by the pairing of adjacent surface rows (pairing model) rather than by surface vacancies (vacancy model).

Hydrogen chemisorption on silicon surfaces has been studied by a number of investigators as a basic system offering the possibility of both theoretical and experimental understanding of chemisorption. Recently, in the case of Si(111), experiment[1,2] and theory[3,4] agree in the conclusion that the interaction of atomic hydrogen with suitable starting surfaces can produce both a monohydride phase, Si(111) : H,[1] and a trihydride phase, Si(111) : SiH_3.[2] The observation of this trihydride phase suggested the possibility of formation of a previously unobserved dihydride phase on Si(100).

The present work demonstrates for the first time that the interaction of atomic hydrogen with the clean reconstructed Si(100)2×1 surface produces not only a monohydride phase but also a dihydride phase. We represent these phases by the symbols Si(100)2×1 : H and Si(100)1×1 :: 2H, respectively. In each symbol the portion following the low-energy-electron diffraction (LEED) symmetry designation, 2×1 or 1×1, indicates the hydrogen bonding to each surface Si atom. The formation of Si(100)1×1 :: 2H clearly indicates that atomic hydrogen can modify the geometrical structure of surface substrate atoms and leads to a conclusion concerning the nature of the reconstruction inherent in the clean Si(100)2×1 surface. The monohydride and dihydride surfaces exhibit different surface electronic structures as observed by ultraviolet photoemission spectroscopy (UPS). Variation of substrate temperature during adsorption and thermal desorption each yield results which confirm our structural conclusions and illuminate the kinetics of the interplay of the two phases.

The starting surface in these experiments is the well-ordered clean Si(100)2×1 surface[5] obtained by sputter etching with Ne^+ ions, annealing at 600°C for about 10 min, and cooling to room temperature. This surface exhibits a sharp 2×1 LEED pattern with no impurities distinguishable by Auger electron spectroscopy above noise level ($\sim\frac{1}{2000}$ of the principal Si signal at 91 eV). Hydrogenation was achieved by dissociation of H_2 to 2H at heated W filaments of our sputtering apparatus.[6] In order to maintain the sample near room temperature it is placed 6 cm distant from the W filaments and is shielded from them. In lieu of the unknown H arrival rate at the sample surface we specify the constant H_2 pressure (1.5×10^{-6} Torr) used and the constant temperature (1710°C) at which the filaments are held during the exposure. In the UPS measurements employing 21.2-eV He I radiation all emitted photoelectrons are collected and analyzed using a four-grid analyzer. This insures averaging over all diffraction effects, and a surer comparison of experimental data with theoretical calculations of local densities of states is thereby obtained.

Exposure of the clean Si(100)2×1 surface at room temperature to atomic hydrogen for increasing exposure times produced the series of spectra of curves 1–6 in Fig. 1(a). LEED pattern observations were made simultaneously. On the basis of these LEED patterns we may divide the sequence into two distinguishable parts. During the first part, curves 1–3, the nonintegral or superstructure spots, although visible and indicating a 2×1 structure, become weaker and more diffuse. In the second part, curves 4–6, the LEED pattern changes to a sharp 1×1 with complete disappearance of the nonintegral spots contrary to the observation of Ibach and Rowe.[7]

During the first stage of chemisorption the UPS spectrum develops peaks at $E - E_{VAC}$ near −10 and −12 eV. During the second stage a stronger peak at $E - E_{VAC}$ near −10 eV appears with little further growth of the peak near −12 eV. Thus both the LEED and UPS data suggest that there are two distinct hydrogenated Si(100) surfaces which differ in surface-atom position and in electronic structure. Continued exposure between 8 and 15 min did not change curve 6 of Fig. 1 nor the sharp 1×1 LEED pattern. From this we conclude that

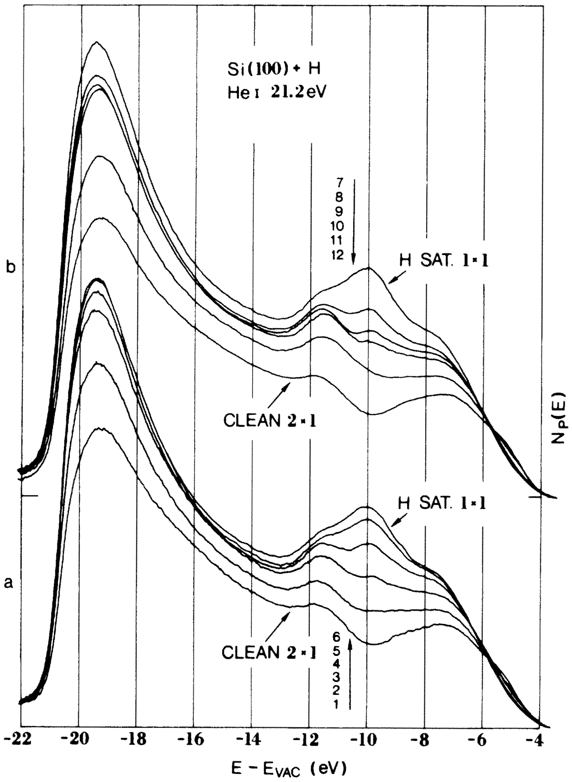

FIG. 1. (a) Curves 1–6 present UPS spectra $N_p(E)$ using He I (21.2 eV) radiation for the Si(100) surfaces produced during atomic hydrogen exposure at room temperature. Exposure times in minutes are: curve 1, 0 (clean surface); curve 2, 0.5; curve 3, 1; curve 4, 2; curve 5, 5; curve 6, 8 and 15 (H-saturated surface at room temperature). (b) Curves 7–12 present He I UPS spectra $N_P(E)$ obtained during thermal desorption of atomic hydrogen from the H-saturated surface. Curve 7 (identical to curve 6) is for the H-saturated surface at room temperature. The temperature at which the sample had been held for 1 min prior to each of the other curves are: curve 8, 320 °C; curve 9, 400 °C; curve 10, 460 °C; curve 11, 500 °C; curve 12, 700 °C (clean surface).

the surface at room temperature has been saturated with hydrogen.

We believe that the sequence of events just described can be given a convincing explanation if the 2×1 structure of the clean surface results from the alternate moving together of adjacent rows of surface atoms as suggested originally by Schlier and Farnsworth.[5] This is the so-called pairing model illustrated schematically at the left of panel b in Fig. 2. Another model of the clean 2×1 surface is the vacancy model suggested by Phillips.[8] A calculated density of states for the pairing model[9] has been shown to agree better with the measured photoelectron energy distribution[7] than does a calculated density for the vacancy model.

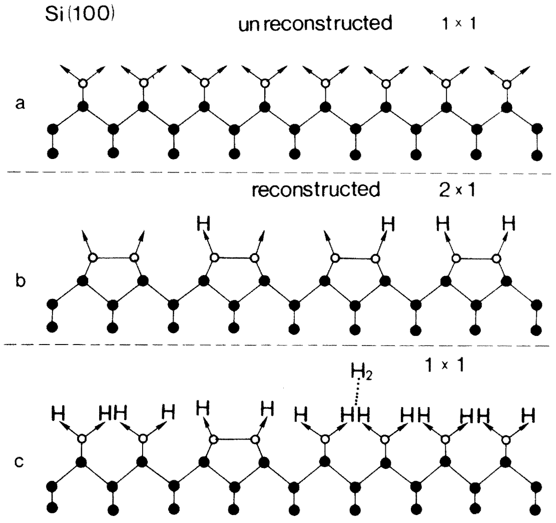

FIG. 2. (a) Schematic of the clean Si(100) surface if it were unreconstructed with two dangling orbitals per surface atom. (b) Reconstructed surface based upon a pairing model yielding a 2 × 1 LEED pattern and having one dangling orbital per surface atom. We suggest in this panel that atomic hydrogen can bond to the dangling orbitals without changing the 2 × 1 superstructure. Bonding of H to all available orbitals of this surface produces the Si(100)2 × 1 :H monohydride phase. (c) In this panel we suggest that atomic hydrogen adsorption beyond the saturated Si(100)2 × 1 :H phase breaks the Si-Si lateral surface bonds and attaches two H atoms to each surface Si atom to produce the dihydride phase, Si(100)1 × 1 :: 2H. We further suggest the model that thermal desorption of hydrogen most likely occurs by the formation of H_2 from two neighboring H atoms of the dihydride phase when it is present.

The initial stages of H adsorption are then to be attributed to the bonding of H to these orbitals without alteration of the 2×1 structure to produce Si(100)2×1 : H shown at the right of panel b of Fig. 2. Appelbaum, Baraff, and Hamann[9,10] expect chemical bonding of an adsorbate atom to dangling π states to be possible without rupture of the dimerization bond between the surface Si atoms. Adsorption of more atomic hydrogen we believe does result in the rupture of the lateral Si-Si bonds accompanied by the bonding of H atoms to each of the additional dangling orbitals thus produced. The terminal UPS spectrum at room temperature is reasonably associated with an unreconstructed 1×1 surface having two H atoms attached to each surface Si atom in the Si(100)1 ×1 :: 2H structure shown at the left of panel c of Fig. 2.

Since the adsorption sequence of Fig. 1(a) occurred at room temperature it is not surprising that only the initial clean and final saturated structures are sharply defined. The intermediate structure is diffuse because of some disorder associated with the coexistence of monohydride and dihydride phases on the surface.

The model we have presented of the adsorption sequence at room temperature would assign the peak at $E - E_{\mathrm{VAC}} \sim -12$ eV principally to the monohydride phase and the peak at $E - E_{\mathrm{VAC}} \sim -10$ eV to the dihydride phase. We recognize that the electronic structure of each phase may be extended in energy as a result of two-dimensional banding effects in the adsorbed layer.

The model we have presented is confirmed and extended by the results of stepwise thermal desorption from the room-temperature H-saturated condition [curves 7–12 of Fig. 1(b).]. The sample was heated sequentially for 1-min duration to the temperatures 320, 400, 460, 500, and 700°C as indicated in the figure caption. Note that the peak in the spectrum near −10 eV, which we have associated with the dihydride phase, drops rapidly as the result of a single heating for 1 min to ~320°C. At the same time the LEED pattern has developed diffuse nonintegral spots corresponding to the 2×1 superstructure. The second heating for 1 min to ~400°C produced a much sharper 2×1 pattern and a UPS spectrum [curve 9 of Fig. 1(a)] which is very similar to curve 3 in the room-temperature adsorption sequence at which 2×1 LEED features are still visible. As a result of further heatings to 460 and 500°C (curves 10 and 11), the spectral features we have attributed to the Si(100)2×1 : H surface diminish in intensity reversing the adsorption sequence of curves 1–3 while the LEED pattern is maintained at 2×1. Finally, heating to ~700°C recovers the original spectrum of the clean surface (curve 12 is equal to curve 1).

The UPS spectral behavior during thermal desorption agrees well with the model we have presented for the nature of the hydrogenated surface phases and their interplay. The initial rapid decline of the peak at $E - E_{\mathrm{VAC}} \sim -10$ eV indicates that the thermal desorption occurs from the dihydride phase, which it depletes. This suggests that the mechanism of desorption with the dihydride present consists of the association of two neighboring H atoms in the dihydride structure to form molecular H_2 which desorbs. This returns the adsorption phase of the two surface Si atoms involved to the monohydride phase as suggested in panel c of Fig. 2. Neighboring H atoms in the dihydride phase (separation ~1.5 Å) are more likely to combine to form H_2 under thermal agitation than neighboring H atoms in the monohydride phase.

Our model of the interplay between the monohydride and dihydride phases suggests the following test experiments. First, atomic hydrogen exposure holding the substrate at a temperature high enough to desorb H_2 from the dihydride phase but not from the monohydride phase should produce an H saturated 2×1 surface having only the characteristics of the monohydride. Second, after achieving this surface we should be able to convert from the monohydride completely to the dihydride by lowering the substrate temperature while continuing to expose to atomic hydrogen. We have successfully performed these experiments as the data of Fig. 3 show.

The first exposure of clean Si(100)2×1 to atomic hydrogen was performed holding the substrate at 225°C. As is seen in Fig. 3(a) the spectrum we have associated with the monohydride develops monotonically as a function of exposure time. After 8 min H exposure the terminal monohydride spectrum is achieved with no tendency to shift to the terminal room-temperature (dihydride) spectrum. In further contrast to the room-temperature adsorption the LEED pattern remained a

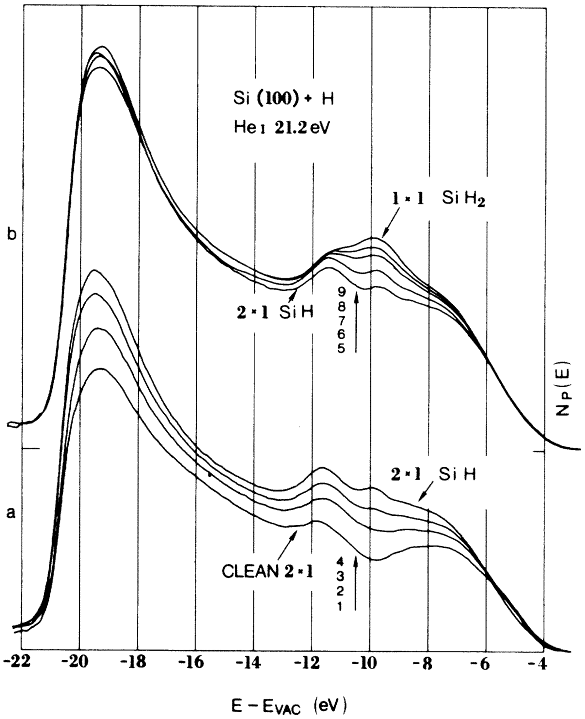

FIG. 3. (a) Curves 1–4 present He I UPS spectra $N_P(E)$ for the Si(100) surfaces produced during atomic hydrogen exposure holding the sample at 225°C. Exposure times in minutes are: curve 1, 0 (clean surface); curve 2, 0.5; curve 3, 1; curve 4, 4 and 8 (H-saturated 2×1 surface). (b) Curves 5–8 present He I UPS spectra $N_P(E)$ obtained by further atomic hydrogen exposure holding the target at room temperature. Additional exposure times in minutes are: curve 5 (H-saturated 2×1 surface), 0; curve 6, 0.5; curve 7, 1; curve 8, 2; curve 9, 4 and 8 (H-saturated 1×1 surface).

sharp 2×1.

We then experimented with substrate temperature reduction. H exposure for 15 min at 150°C substrate temperature produced no change at all in the UPS spectrum or LEED pattern. Reduction of the substrate temperature to 100°C during H exposure resulted in some diffuseness of the 2×1 superstructure spots and a minor change in the UPS spectrum near $E - E_{\mathrm{VAC}} \sim -10$ eV. Warming the surface to 225°C for 5 min in the presence of atomic hydrogen recovered the sharp 2×1 LEED pattern and the monohydride UPS spectrum.

Exposure of the H-saturated 2×1 surface to additional atomic hydrogen after cooling to room temperature resulted in the series of UPS spectra of Fig. 3(b). The expected shift to the dihydride occurred with the terminal spectrum (curve 9, Fig. 3) being almost identical to the terminal spectrum (curve 6, Fig. 1) of the room-temperature sequence starting with the clean surface.

We conclude that we have been able to demonstrate the existence of both monohydride and dihydride phases of adsorbed hydrogen on Si(100) by experiment alone without recourse to theoretical identification of the UPS spectra. We further conclude that the interplay of these phases on the surface clearly suggests that the 2×1 structure of the clean surface and of the monohydride adsorption phase is the result of the dimerization or pairing of adjacent rows of Si atoms. Finally, we have identified the dihydride phase as that from which desorption preferentially occurs when the two phases coexist on the surface.

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