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H-induced surface restructuring on Si(100): Formation of higher hydrides

C. C. Cheng and J. T. Yates, Jr.
Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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H-induced surface structures on Si(100) were studied using temperature-programmed-desorption mass spectroscopy and low-energy electron diffraction. It is shown that the (3×1) phase consists of mainly monohydride and dihydride structures, while the (1×1) phase is composed of a mixture of monohydride, dihydride, and trihydride surface species. The trihydride surface species is associated with the phase transition between the (3×1) and (1×1) surface phases, and liberates SiH_4 and β_3-H_2 during thermal desorption, beginning at ~200 K. For the fully saturated Si(100) surface, a saturation surface coverage of 1.9 monolayers (ML) H has been established at a Si(100) adsorption temperature of 210 ± 10 K. These results suggest that the 1.9-ML saturation coverage of H on Si(100) involves the presence of $SiH_3(a)$ species, which leads to a $(3\times1)\rightarrow(1\times1)$ LEED pattern change. This is contrary to a model for the (1×1) surface involving a uniform $SiH_2(a)$ overlayer.

I. INTRODUCTION

In this paper, we examine the H-induced surface structures—the (1×1) and (3×1) phases on the Si(100) surface—and show that the formation of surface trihydride species $[SiH_3(a)]$ during H adsorption at $T<400$ K causes the conversion of the (3×1) phase into a (1×1) phase. The H-saturated (1×1) phase at room temperature has previously been considered as a *uniform* dihydride phase (two H per Si atom) with each surface Si atom relaxing to the bulklike arrangement.[1–7] However, an ordered (3×1) phase has been recently observed by saturating the Si(100)-(2×1) surface with atomic hydrogen at a substrate temperature of 380 ± 20 K.[8] Based on the results of low-energy electron diffraction (LEED) and high-resolution infrared (ir) spectroscopy, the (1×1) phase was reassigned as a disordered phase made up of (3×1) units, where each (3×1) unit cell consists of alternating monohydride and dihydride species.[8] It is also possible that the (1×1) phase as seen by LEED is caused by the Si (1×1) underlayer as viewed through a disordered selvedge layer.

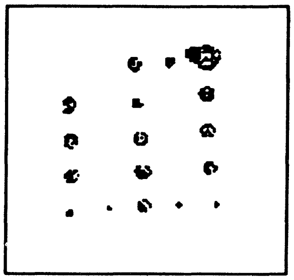
Absolute-coverage measurements of adsorbed hydrogen were expected to answer this dispute. Saturation coverages of 1.5 to ~2 monolayers (ML) for H/Si(100) have been reported at adsorption temperatures between 300 and 373 K (Refs. 7, 9, and 10) [1 ML is defined as 6.8×10^{14} H cm^{-2}, corresponding to the ideal surface Si atom density on the (100) plane]. However, simply based on the coverage measurements no detailed structural model can be provided due to lack of knowledge about the relationships between the hydrogen coverages and the populations of specific adsorbed species.

In this work, temperature-programmed-desorption (TPD) mass spectrometry has been used to differentiate different binding states existing on the surface, and to determine the surface coverages after H adsorption. It is shown that the saturated (3×1) phase consists of mainly monohydride (one H per Si atom) and dihydride structures, while the (1×1) phase is associated with a surface containing a mixture of monohydride, dihydride, and trihydride species. Moreover, the temperature dependence of the extent of formation of $SiH_3(a)$ provides the explanation for the discrepancies between the measured hydrogen saturation coverages reported by others.[7,9,10] The saturation coverage of a (1×1) phase formed by H adsorption at 210 ± 10 K is 1.9 ML, while the saturation coverage of a (3×1) phase formed at 400 ± 10 K is ~1.4 ML. These results give new insights into the H-induced reconstruction on covalent surfaces, where surface reordering and disordering involving the formation of higher hydride species is found, in contrast to hydrogen behavior on metal surfaces.[11]

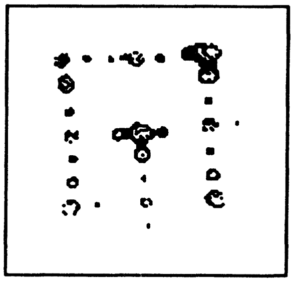
II. EXPERIMENT

The UHV system[12] and crystal preparation[13] involving chemical cleaning, Ar^+ bombardment, and annealing to 1200 K followed by cooling at ~3 K s^{-1} have been described previously. The Si(100) crystal was Czochralski grown, 10 Ω cm, p-type (B-doped), and cut into squares of dimension $15\times15\times1.7$ mm^3 from an oriented ($\pm1°$) wafer. Surface cleanliness was checked by Auger-electron spectroscopy (AES), and impurities after preparation were below the detectable limits of AES (<0.01 atomic fraction within the sampling depth).[14] For hydrogen-dosing experiments, a W spiral filament (diam = 1 cm) at 1800 K was used to produce atomic hydrogen during H_2 exposure. Because of the difficulties in determining the *accurate atomic* hydrogen exposures, all exposures are given in terms of *molecular* hydrogen exposures (not corrected for ion gauge sensitivity) and reported as langmuirs [1 langmuir (L) $\equiv 1\times10^{-6}$ Torr s]. A 45 L H_2 exposure was used to saturate the substrate with atomic hydrogen at different adsorption temperatures, according to our coverage calibration using TPD mass spectroscopy. TPD measurements were made with a shielded, differentially pumped quadrupole mass spectrometer (QMS). To ensure that only species desorbing from the central area of the prepared surface were detected, the shielded QMS was equipped with a small conical axially oriented aperture (diam = 5 mm), and during TPD experiments the crystal was accurately and reproducibly placed 2 mm away from the aperture.[12] Relative surface H coverages were determined by measuring the time integral of the H_2 desorption rate above the background level throughout the desorption process. LEED patterns of the clean and H-exposed surface were measured, using a LEED apparatus equipped with digital data acquisition facilities, at a crystal temperature of 130 K. The electron beam ($<1\times10^{-9}$ A, 100 V) used for LEED measurements was 1 mm in diameter. A (2×1) LEED pattern obtained from a clean Si(100) surface is shown in Fig. 1(a).

(a) clean Si(100)(2x1)



(b) H-saturated (3x1) phase



(c) H-saturated (1x1) phase

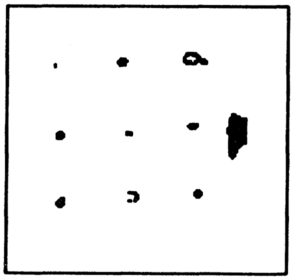


FIG. 1. (a) LEED pattern showing two domains of (2×1) reconstruction of a clean Si(100)-(2×1) surface. (b) LEED pattern showing two domains of a (3×1) superlattice resulting from H saturation of Si(100) at 400 K. (c) A (1×1) pattern obtained by H saturation at 210 K. All data were taken at 130 K with an electron beam energy of 100 eV and with the crystal biased +90 V.

III. RESULTS AND DISCUSSION

In agreement with previous observations, different hydride phases are formed on the Si(100) surface by H adsorption at different temperatures.[1–10,15,16] Chemisorption of atomic hydrogen at $T=630$ K produces only the monohydride phase which exhibits a sharp (2×1) LEED pattern.[1,4,7,15] Temperature-programmed desorption from this phase yields a single β_1-H_2 desorption state [see Fig. 2(a)]. In contrast to adsorption experiments at 630 K which culminate in producing the saturated β_1-H_2 desorption state, H chemisorption at $T=300-350$ K initially produces a (2×1) pattern, and according to the literature this (2×1) pattern gradually transforms into a (1×1) pattern as the coverage approaches ~1.5 ML.[9,16] Major desorption features from the (1×1) phase are β_1-H_2, β_2-H_2, and SiH_4 desorption which are believed to correspond to the monohydride, dihydride, and trihydride phases, respectively.[16]

An intermediate surface condition between the (2×1) monohydride and the (1×1) saturated surface may be achieved by adsorption of H at 400±10 K. This is shown by the production of a (3×1) LEED pattern in Fig. 1(b). Annealing of both (1×1) and (3×1) phases to ~600 K desorbs H_2 from higher hydrides and restores a sharp (2×1) LEED pattern with all hydrogen bonded in the monohydride configuration.[7,8,15]

We shall show next that a distinct difference between the (1×1) and (3×1) phases is the involvement of surface trihydride in the (1×1) phase; the formation of $SiH_3(a)$ is associated with the conversion of the (3×1) long-range ordering to produce the (1×1) phase.

The H_2 TPD spectra of the (3×1) and (1×1) H-saturated phases are shown in Figs. 2(b) and 2(c), respec-

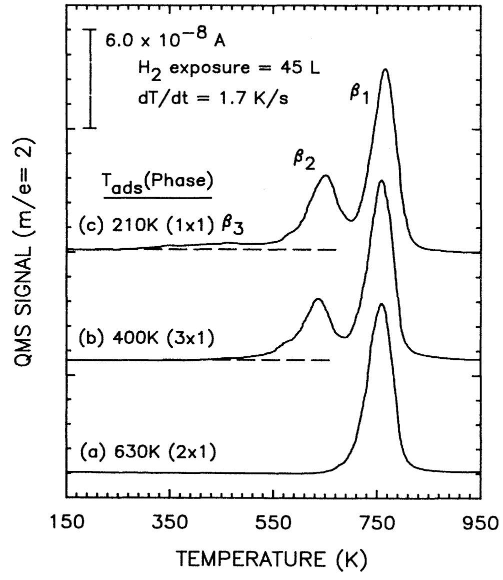


FIG. 2. TPD spectra of H_2 desorption obtained from H-saturated Si(100) at different adsorption temperatures: (a) 630 K, (b) 400 K, (c) 210 K. TPD spectra were taken with a heating rate of 1.7 K/s after the crystal was cooled down to 130 K.

tively. The observation of only the β_1- and β_2-H_2 desorption states from the saturated (3×1) phase [Fig. 2(b)] clearly indicates that this H-induced surface reconstruction includes the formation of both monohydride and dihydride phases. Experiments with the same H exposures but lower adsorption temperatures ($T<400$ K) show a distinct decrease of the intensity of the $\frac{1}{3}$-order LEED beams, and in the limit, a (1×1) LEED pattern is produced. Furthermore, a broad low-temperature H_2 desorption feature, in addition to the β_1 and β_2 states, is observed from the (1×1) phase, as shown in Fig. 2(c). This feature, designated as the β_3-H_2 state in this work, is produced on lowering the adsorption temperature and increasing the H coverage. The presence of the β_3 state is indicative of the formation of the (1×1) phase.[17]

The existence of the β_3-H_2 desorption state during low-temperature adsorption is indicative of the formation of $SiH_3(a)$ which also produces $SiH_4(g)$ upon thermal desorption. Figures 3(b) and 3(c) show the TPD spectra of silane desorption from the (3×1) and (1×1) H-saturated phases, respectively. Almost no silane desorbs from the (3×1) phase. The silane-desorption feature, used as an indicator of the presence of $SiH_3(a)$ on the Si(100) surface,[16] is confirmed by comparing the mass spectrometer fragments of $m/e=28-32$, and only the major fragment at $m/e=30$ (SiH_2^+) is shown. While the (3×1) phase is nearly free of the additional adsorption states as shown in Figs. 2(b) and 3(b), the (1×1) phase clearly liberates SiH_4 and β_3-H_2 by thermal desorption as a result of the presence of surface trihydride species.[18] The behavior of the SiH_4 and β_3-H_2 normalized desorption yields as a function of H adsorption temperature are shown in Fig. 4. The similar temperature dependence of the yield of the SiH_4 and β_3-H_2 desorption states suggests that the same surface species is responsible for these two desorption processes. In fact, a similar trend for the formation of $SiH_3(a)$ has been observed on the Si(111)-(7×7) surface by H adsorption over the temperature range of 100–400 K, using multiple internal reflection (MIR) infrared spectroscopy.[19] Therefore, it is concluded that on Si(100) the inhibition of $SiH_3(a)$ formation during H adsorption at 400±10 K maintains the (3×1) periodicity. Lowering the adsorption temperature causes the formation of $SiH_3(a)$. This is associated with the conversion of the (3×1) phase into the (1×1) phase. $SiH_3(a)$ reacts with additional $SiH_x(a)$ ($x=1-3$) species to produce $SiH_4(g)$ above ~200 K.

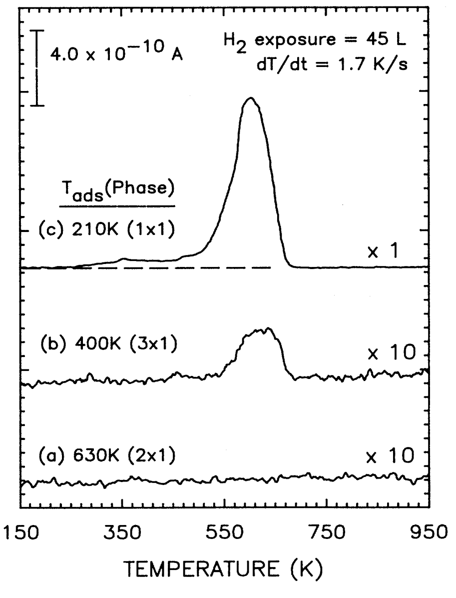


FIG. 3. TPD spectra of SiH_4 desorption corresponding to the experimental conditions described in Fig. 2.

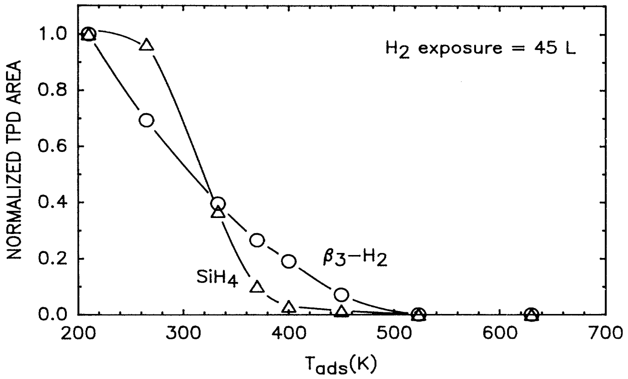


FIG. 4. Behavior of SiH_4 and β_3-H_2 desorption yields as a function of substrate temperature during H adsorption. All yields are normalized to that obtained at $T_{ads}=210$ K.

The effect of temperature on the surface phases is also studied by annealing a hydrogenated Si(100) surface. Reversible phase changes from both (1×1) and (3×1) phases to the (2×1) have has been confirmed by annealing to ~600 K.[8] However, no change from the (1×1) phase to the (3×1) phase is observable by annealing a (1×1) phase to $T<600$ K. This observation indicates that the phase change from the (3×1) phase to the (1×1) phase as additional hydrogen is adsorbed is an irreversible process; this observation is consistent with the view that the (1×1) phase is related to a disordered surface.[8]

The presence of $SiH_3(a)$ on the hydrogenated Si(100)-(1×1) surface leads to both SiH_4 and β_3-H_2 desorbing species. Fortunately, most of the surface hydrogen desorbs as $H_2(g)$, and we can estimate that less than 1% of the hydrogen desorption occurs as SiH_4 in the experiments performed here by quantitatively comparing the yields of H_2 and SiH_4 in Figs. 2 and 3. Hence, the silane-desorption channel is not included in our estimation of total hydrogen coverage here. The saturation coverages of hydrogen at various adsorption temperatures were determined by comparing the H_2 desorption yields to that of 1 ML hydrogen coverage which is obtained by saturating the Si(100)-(2×1) surface at 630 K.[4,7,15] Saturation coverage of a (1×1) phase formed by H adsorption at 210±10 K is 1.9 ML hydrogen, while the saturation coverage of a (3×1) phase formed at 400±10 K is ~1.4 ML hydrogen (expected coverage = 1.33 ML). In addition, the ratio between the β_2-H_2 and β_1-H_2 desorption yields from a saturated (3×1) phase is approximately 1:3.

TABLE I. comparison of H-saturation coverages measured at different adsorption temperatures and for different surface phases of Si(100).

H-saturation coverage (ML) (2×1)	(3×1)	(1×1)	Experimental method used	References
1.0 (630 K)	1.4 (400 K)	1.9 (210 K)	Line-of-sight TPD	This work
1.0 (670 K)	1.7 (373 K)	1.85 (300 K)	Elastic recoil detection analysis	a
		1.5 and 1.7 (< 400 K)[b]	Nuclear reaction analysis	c and d

[a] Reference 7.

[b] The measurement made in this work involves D/Si(100) due to the nature of the method used. Substrate temperatures during H adsorption were not emphasized in these two works, but based on the observed (1×1) LEED pattern, a substrate temperature of less than ~400 K is assumed.

[c] Reference 9.

[d] Reference 10.

These results support the configuration of a (3×1) phase proposed by Chabal and Raghavachari,[8] assuming that one hydrogen atom from each surface dihydride species becomes engaged in the β_2 desorption process: $2SiH_2(a) \rightarrow H_2(g) + 2SiH(a)$.[20] The overall error including systematic errors of our present measurement of H coverage is ±4.5%, based on three to four duplicate measurements at each coverage. This work, in comparison with other work concerned with hydrogen coverages on Si(100), is summarized in Table I.

A structural assignment of the (1×1) phase produced at the highest coverages at a substrate temperature of 210 K is not possible at this time. The (1×1) phase was interpreted as being a disordered phase made up of (3×1) units,[8] and the (3×1) phase consisting of alternating HSi-SiH(a) and $SiH_2(a)$ species would have a coverage of 1.33 ML H (1.5 ML H measured by Feldman, Silverman, and Stensgaard[9]). This interpretation is inconsistent with the higher (up to 1.9 ML H) saturation-coverage measurement for the (1×1) phase shown in Table I. The involvement of $SiH_3(a)$ in disordering the (3×1) phase to produce the (1×1) phase accounts for this higher saturation coverage. Production of $SiH_3(a)$ species is indicative of Si—Si bond breaking in the Si(100) surface, and subsequent $SiH_4(g)$ production from $SiH_3(a)$ species is consistent with Si—Si bond breaking. Our inability to determine the coverage of $SiH_3(a)$ with certainty[18] prevents the development of structural models for the (1×1) phase based on the population of various surface species.

IV. CONCLUSIONS

The following features of hydrogen adsorption on and desorption from Si(100) have been found.

(1) The sequential development of the (2×1) monohydride, the (3×1) monohydride+dihydride, and the (1×1) surface phase containing some trihydride species has been observed, through correlation of LEED and line-of-sight thermal-desorption measurements.

(2) The observation of the liberation of the β_3-H_2 from the adsorbed trihydride species is found to be closely correlated with SiH_4 liberation, and with the (1×1) phase seen by LEED.

(3) It has been found that the discrepancies in measured saturation H coverages reported by others are related to differences in the Si(100) adsorption temperatures employed, since β_3-H_2 begins to desorb near 200 K from the (1×1) phase, and variation in the adsorption temperature in the range 200–400 K will therefore cause its saturation coverage to vary. At 210±10 K a final saturation coverage of 1.9 ML H is found.

(4) A structural assignment of the (1×1) surface phase, containing 1.9 ML of adsorbed H is not possible based on these studies because of uncertainties in determining the coverage of $SiH_3(a)$ which is associated with β_3-H_2 desorption. It may be postulated that the (1×1) LEED pattern seen at high-H coverages is due to the underlying Si(100) subsurface structure, as observed through a highly disordered surface.

(5) Since the production of $SiH_3(a)$ requires Si—Si bond breaking, significant surface reconstruction and disordering is likely to be involved in producing surface conditions allowing the observation of the (1×1) surface phase. This implies that the saturation coverage of 1.9 ML should not be rationalized on the basis of a complete and uniform layer of $SiH_2(a)$ species.

ACKNOWLEDGMENTS

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[14] Care has been taken to ensure that no carbon and metal contamination is present on the surface. The presence of a small amount of metal such as Ni on Si surfaces has been known to affect the ordering and chemistry on these surfaces. [See, for example, R. W. Wallace, C. C. Cheng, P. A. Taylor, W. J. Choyke, and J. T. Yates, Jr., Appl. Surf. Sci. **45**, 201 (1990).] Also, it has been reported that the (3×1) LEED pattern cannot be obtained from H adsorption if $C>0.5\%$ monolayer (Ref. 8).

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[18] The concentration of surface trihydride species cannot be determined using TPD mass spectrometry only, because thermal decomposition of $SiH_3(a)$ into lower hydride species seems to occur during the thermal-desorption process, as suggested by the β_3-H_2 desorption (see also Ref. 17).

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