New Ordered Structure for the H-Saturated Si(100) Surface: The (3×1) Phase

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High-resolution infrared data of Si(100) surfaces saturated with H at room temperature show that the so-called 1×1 surface is in fact a disordered phase with roughly half the H bonded in monohydride (H-Si-Si-H) and half in dihydride (SiH_2) configurations. Upon saturation exposure at 380 K, the surface is ordered into a newly identified 3×1 phase, as evidenced by LEED, involving repeated alternating monohydride and dihydride units.

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In this Letter, we report the first observation of an ordered phase for the H-saturated Si(100) surface with 3×1 periodicity. With this observation we are able to resolve the controversy regarding the nature of the previously studied H-saturated phase, which is characterized by a 1×1 LEED pattern. Traditionally, this phase has been considered to have a bulklike arrangement of the Si surface atoms with the H in a uniform "dihydride" configuration, i.e., two H per surface atom.[1] The observation of the dihydride scissor mode by electron energy-loss spectroscopy (EELS) is consistent with this interpretation.[2] However, nuclear microanalysis (NMA) shows that the saturation coverage has only 1.5 H per Si surface atom and high-energy ion scattering (HEIS) data indicate that the saturated phase has a substantial number of surface atoms displaced from a bulklike position.[3] Despite the fact that simply observing a 1×1 LEED pattern[4] does not distinguish between a uniform dihydride phase and a disordered phase, a number of recent studies have assumed the formation of a uniform dihydride phase at saturation.[5–8]

In this work, high-resolution infrared (ir) data and *ab initio* cluster calculations have been used to clearly identify the presence of *both* monohydride—involving a silicon dimer with only one H per Si—and dihydride structures in the saturated 3×1 phase. Thus, the 3×1 unit cell consists of alternating monohydride and dihydride units. Comparison of the 1×1 and 3×1 H-saturated phases shows that their ir spectra are essentially identical. Thus the 1×1 phase is made up of disordered 3×1 units. These results give a natural explanation for the NMA and HEIS data[3] as well as for the discrepancies in the relative intensities of EELS spectra[2] and suggest caution in the interpretation of experiments which have assumed a pure dihydride phase.[5–8]

High-resolution ($\leqslant 1\ \mathrm{cm}^{-1}$) infrared experiments were performed on flat and vicinal Si(100) surfaces as previously described.[9] Surfaces vicinal to the (100) plane have been shown[10] to consist of a uniform array of double-layer steps with *single-domain* 2×1 reconstruction on each terrace. Thus, the use of polarized radiation makes it possible to identify all the vibrational modes associated with H adsorbed on the (100) terraces ("terrace modes") which are all polarized within the same plane.[9] Modes associated with H adsorbed at step edges ("step modes") will have components perpendicular to that plane.

The sample preparation and resulting cleanness have been described previously.[9,11,12] In agreement with previous observations,[1–8] we find that H chemisorption at room temperature initially produces a sharp 2×1 pattern followed by a 1×1 pattern with low background at saturation. Annealing to 600 K yields a very sharp 2×1 pattern[1,5] with all the hydrogen bonded in a monohydride configuration.[9] We find here that *saturation* coverage on a substrate at 380 ± 20 K produces a 3×1 LEED pattern as shown in Figs. 1(a) and 1(b). Rutherford-backscattering analysis of the samples after the runs has shown that no heavy-metal impurities ($\leqslant 10^{11}/\mathrm{cm}^2$) were present in the surface region. Further, a mild anneal to 575 K restores a sharp 2×1 pattern with an ir spectrum characteristic of a pure monohydride, and further exposure at room temperature produces a 1×1 pattern with an ir spectrum similar to that of the 3×1. Hence, the 3×1 is a H-induced reconstruction. We show next that both the 1×1 and 3×1 phases involve the formation of monohydride and dihydride arranged as depicted in Fig. 1(c).

Figure 2 shows the spectra associated with the 1×1 and 3×1 phases obtained by saturation exposure at 300 and 375 K, respectively. Both sets of spectra display similar features (broader for the 1×1) involving monohydride, step modes, and, as will be shown shortly, dihydride. The total integrated areas are the same within 1% indicating that the coverages for the two phases are within a few percent.[13] Both spectra are dominated by the peaks labeled $M_{\parallel}$ (*s* polarization) and $M_{\perp}$ (*p* polarization) of the monohydride. Weaker modes on the low-frequency side ($\leqslant 2080\ \mathrm{cm}^{-1}$) and high-frequency side ($\geqslant 2110\ \mathrm{cm}^{-1}$) have polarization and desorption properties of H adsorbed at steps and defects.[9] In addition, there is a relatively strong peak at 2103.8 cm^{-1} labeled $DI_{\parallel}$ (*s*-pol.), polarized along

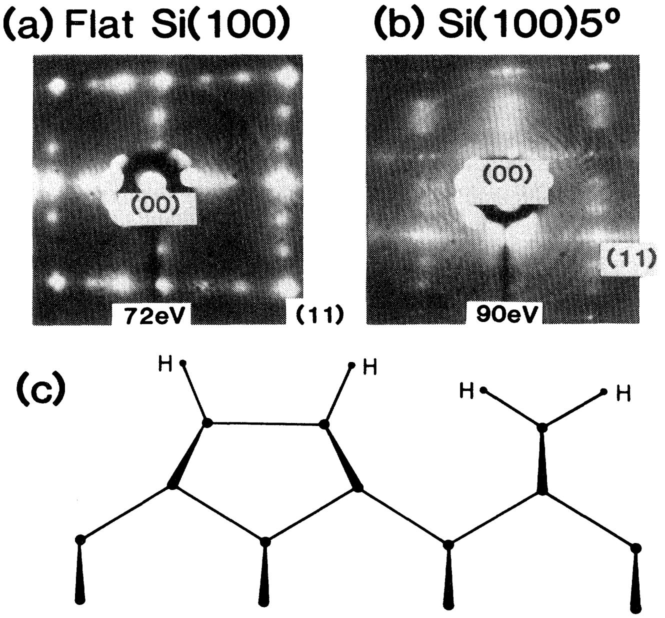

FIG. 1. (a) LEED pattern (taken at 80 K, 72 eV) showing two domains of 3×1 resulting from H saturation of flat Si(100) at 400 K. The integral-order spots are overexposed to bring out the 3×1 superlattice spots and to show the low background of this well-ordered phase. (b) LEED pattern (taken at 300 K, 90 eV) showing only one domain of 3×1 resulting from H saturation of vicinal Si(100)5° at 375 K. The picture is not overexposed to show the splitting of integral order spots due to the step array in a direction orthogonal to the 3×1 reconstruction. (c) Model (drawn to scale) of the 3×1 unit cell. The top layer Si and H atoms are all along the $\langle 0\bar{1}1\rangle$ axis, i.e., parallel to the step edge.

the $\langle 0\bar{1}1\rangle$ direction.[14] Similar observations are made for the D-covered surface for which a strong peak with identical polarization is seen at 1537 cm^{-1}. The unambiguous assignment of $\mathrm{DI}_{\parallel}$ to the antisymmetric stretch of the dihydride requires the detection of the weak symmetric stretch, $\mathrm{DI}_{\perp}$, which has been predicted to be further removed from $\mathrm{DI}_{\parallel}$ for the dideuteride than for the dihydride.[9]

To clearly isolate $\mathrm{DI}_{\perp}$ from the interfering step modes, we use the observation that annealing to 475 K results in the disappearance of $\mathrm{DI}_{\parallel}$ *only*, while annealing to 625 K produces the desorption of all step atoms. Further, since modes have been found to narrow at low temperatures,[15] we perform higher-resolution (0.5 cm^{-1}) runs at 80 K. A separate contribution, labeled $\mathrm{DI}_{\perp}$ in Fig. 3 (*p*-pol.), can now be identified at 1516 cm^{-1} for D and 2091.3 cm^{-1} for H and is seen to scale as $\mathrm{DI}_{\parallel}$ upon thermal treatment. Further confirmation is obtained by isotopic-mixture experiments since the "isolated" frequency, i.e., the mean frequency between $\mathrm{DI}_{\parallel}$ and $\mathrm{DI}_{\perp}$, will appear in the spectrum of the minority species. Figure 4 shows that, for $\mathrm{H/D}=0.08$, e.g., the 3×1 phase is characterized by an isolated mode at 2097.3 cm^{-1} with a strong component parallel to the surface (*s*-pol.) which falls at the mean of $\nu(\mathrm{DI}_{\perp})=2091.3\ \mathrm{cm}^{-1}$ and $\nu(\mathrm{DI}_{\parallel}=2103.8$ cm^{-1}. Similar data for $\mathrm{D/H} << 1$ (not shown) give a peak at 1526 cm^{-1} for the 3×1 phase, again at the mean of $\nu(\mathrm{DI}_{\perp})=1516\ \mathrm{cm}^{-1}$ and $\nu(\mathrm{DI}_{\parallel})=1537$

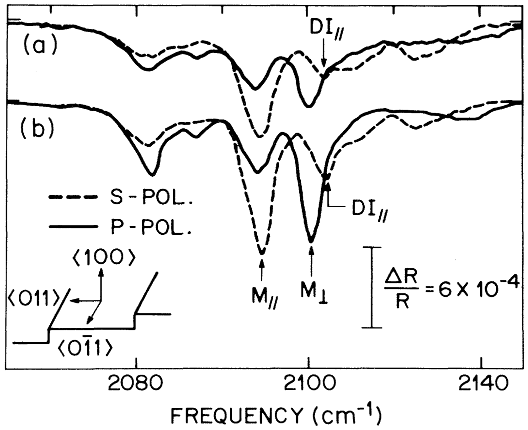

FIG. 2. Raw spectra associated with (a) the 1×1 and (b) the 3×1 H-induced phases on a Si(100)5° at 300 K. Dashed curves are for the electric field purely along the $\langle 0\bar{1}1\rangle$ direction while solid curves are for the electric field with components along the $\langle 100\rangle$ and $\langle 011\rangle$ directions. The resolution is 1 cm^{-1}.

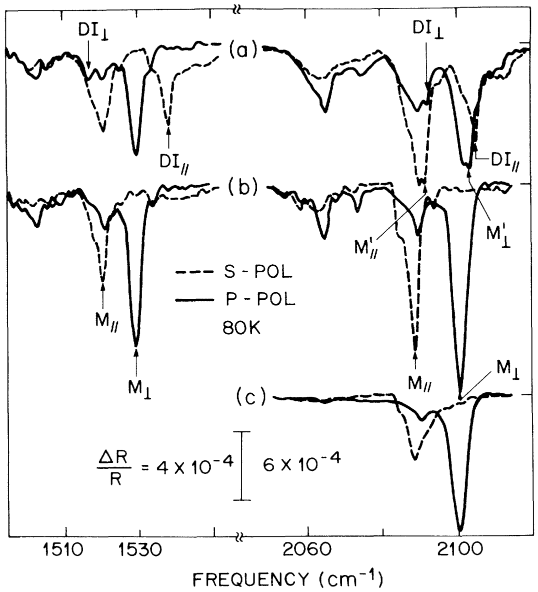

FIG. 3. Raw spectra associated with (a) the 3×1, (b) the 2×1 (475 K anneal), and (c) the 2×1 (625 K anneal) D- and H-induced phases on a Si(100)5° at 80 K. The resolution is 0.5 cm^{-1} for the SiH region (1 cm^{-1} for SiD) and the polarizations are as in Fig. 2 (*s* polarization ∥ $\langle 0\bar{1}1\rangle$).

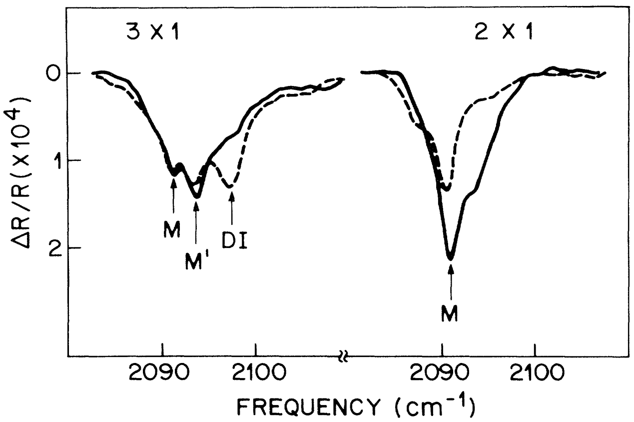

FIG. 4. Raw spectra of the SiH stretch region induced by 7.5% H, 92.5% D for saturation exposure at 375 K (3×1), and after a 475 K anneal (2×1). Data taken for a Si(100)5° substrate at 300 K with 1 cm^{-1} resolution. M, M′, and DI correspond to the isolated frequencies of pure monohydride, monohydride with a neighboring dihydride, and dihydride, respectively.

cm^{-1}. Thus, the dihydride (dideuteride) is experimentally characterized by two modes, $\mathrm{DI}_\perp$ and $\mathrm{DI}_\parallel$ polarized along the $\langle 100\rangle$ and $\langle 0\bar{1}1\rangle$ directions, respectively, and split by $\nu(\mathrm{DI}_\perp) - \nu(\mathrm{DI}_\parallel) = -12.5$ cm^{-1} (-21 cm^{-1}). The isolated frequency of the dihydride (dideuteride), $\nu(\mathrm{DI})$, is 6.5 cm^{-1} (5 cm^{-1}) higher than that of the pure monohydride (monodeuteride), $\nu(\mathrm{M})$.[16]

Theoretically, *ab initio* calculations, previously shown to yield accurate geometries and vibrational parameters,[9,17] were performed to characterize the dihydride structure with a Si_3H_8 cluster used to represent its local environment. Geometry optimization yielded $d_{\mathrm{Si-H}} = 1.48$Å and $\theta(\mathrm{HSiH}) = 110°$, both parameters being relatively insensitive to the basis set and the level of electron correlation employed in the calculations. The splittings of the dihydride (dideuteride) were evaluated with $Si_3H_2D_6$ ($Si_3D_2H_6$) isotopic species. Our best computed results[18,19] are $\nu(\mathrm{DI}_\perp) - \nu(\mathrm{DI}_\parallel) = -9$ cm^{-1} for H (-22 cm^{-1} for D), in good agreement with the experimental data. The larger splitting in the dideuteride compared to the dihydride has been pointed out before[9] and is now confirmed in this work. It is due to the increased dynamic coupling of the silicon atom motion with the vibrations involving the heavier deuterium atoms. The dynamic dipole moments were then evaluated[9] for the two vibrational modes yielding the intensity ratio $\mathrm{DI}_\parallel/\mathrm{DI}_\perp \approx 3$ in agreement with the observed weak intensity of the perpendicular mode.[20]

The isolated frequency of the dihydride relative to the position of the corresponding monohydride frequency was also evaluated. The use of the proper monohydride geometry was found to be important since the strain present in the monohydride ($d_{\mathrm{Si-Si}} = 2.51$ Å compared to a distance of 2.35 Å in bulk silicon) decreases the Si-H distances slightly and hence shifts up the isolated frequency. The calculated separations, $\nu(\mathrm{DI}) - \nu(\mathrm{M}) = +7$ cm^{-1} for H and $+5$ cm^{-1} for D, are both in excellent agreement with experiment, providing additional confirmation of the assignments.

The observation of the 3×1 unit cell involving three Si surface atoms coupled with the presence of roughly equal amounts of hydrogen in monohydride and dihydride configurations[13] confirms the arrangement of Fig. 1(c). The formation of a uniform dihydride phase is inhibited by the repulsive interaction between H atoms on adjacent units, which would be separated by approximately 1.4 Å. The recently proposed uniform phase with the dihydride units rotated from the (011) plane to reduce this repulsion[8] apparently does not occur. The 3×1 arrangement does not have such unfavorable interactions since the closest H-H distance is 2.8 Å.

Finally, the monohydride frequencies in the 3×1 structure ($\mathrm{M}'_{\parallel,\perp}$ in Figs. 3 and 4) and in the 1×1 ($\mathrm{M}_{\parallel,\perp}$ in Fig. 2) are seen to be shifted up by ≈ 2 cm^{-1} from the pure monohydride frequencies. This is consistent with the back-bond relaxation caused by neighboring dihydrides.[21]

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[13] Because the spectral features are similar, we assume that

the average dynamic dipole moment is the same for the 1×1 and 3×1 phases. Accounting for the fact that the edges of the long sample (3.8 cm) are not 3×1 upon saturation exposure at 375 K, the area of the monohydride peaks ($M_{\parallel}$ and $M_{\perp}$) in the 1×1 and 3×1 phases is roughly 0.7 that observed in the pure monohydride phase (Ref. 9) obtained by saturation at 575 K.

[14] Accuracy in peak position is $\pm 0.3\ \mathrm{cm}^{-1}$ for SiH modes and $\pm 0.5\ \mathrm{cm}^{-1}$ for SiD modes.

[15] There is a narrowing and a 1.3-cm^{-1} blue shift of all modes upon cooling to 80 K: J. C. Tully, Y. J. Chabal, K. Raghavachari, J. M. Bowman, and R. R. Lucchese, Phys. Rev. B **31**, 1184 (1985).

[16] These results show that the 2116-cm^{-1} mode observed upon H_2O dissociation (Ref. 12) cannot be due to the $DI_{\perp}$ vibration of unperturbed dihydride.

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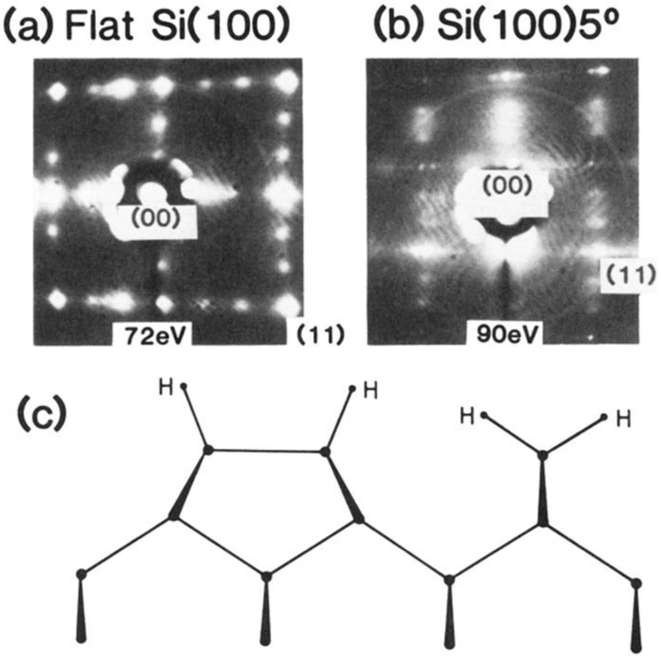
[18] The computed splittings at the Hartree-Fock (HF) level using the large 6-31G** basis (including *d* functions on Si and *p* functions on H) (Ref. 31 of Ref. 10) are $\nu(DI_{\perp}) - \nu(DI_{\parallel}) = -1\ \mathrm{cm}^{-1}$ for H and $-16\ \mathrm{cm}^{-1}$ for D. Electron correlation effects, evaluated using second-order Moller-Plesset perturbation theory [J. S. Binkley and J. A. Pople, Int. J. Quantum Chem. **9**, 229 (1975)] with the double-zeta 3-21G basis (Ref. 29 of Ref. 9) increased the magnitude of the splitting by $8\ \mathrm{cm}^{-1}$ for H and $6\ \mathrm{cm}^{-1}$ for D. Hence the best projected values for the splitting are $-9\ \mathrm{cm}^{-1}$ for H and $-22\ \mathrm{cm}^{-1}$ for D. Note that previous estimates (Ref. 9) of the dihydride splittings were calculated only at the HF level with the smaller SiH_2D_2 cluster.

[19] Binkley and Pople, Ref. 18.

[20] This value takes into account the screening discussed in Ref. 9.

[21] This shift does not arise from dipole interactions since $M_{\parallel}$ is also shifted. The relatively large unshifted monohydride intensity ($M_{\parallel,\perp}$ in Figs. 3 and 4) is partly explained by LEED observations which show some 2×1 at the edges of our very long (3.8 cm) sample due to higher C contamination (the 3×1 cannot be obtained if C > 0.5% monolayer). It is also partly due to the presence of steps and defects next to which the more stable monohydride is formed.



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