

Hydride formation on the Si(100):H₂O surface

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(Received 31 October 1983)

H₂O chemisorption on Si(100) is studied with high-resolution infrared spectroscopy. Water molecules are found to dissociate upon room-temperature exposure forming Si-H and Si-OH. Mild annealing breaks up the O-H molecule resulting in oxide, monohydride, and dihydride species. The angle made by the effective dynamic dipole moment associated with the Si-H bond, with respect to the surface normal, is measured for the different hydrides formed.

The interaction of H₂O with silicon surfaces is important for understanding the kinetics of wet oxide formation and, more generally, for isolating the mechanism of molecular dissociation or molecular chemisorption on semiconductor surfaces. The present understanding is sketchy and somewhat inconsistent as opposite views are held. Ten years after the ellipsometric work of Meyer,¹ who proposed dissociation into 2H and O, Fujiwara² interpreted ultraviolet photoemission spectroscopy (UPS) data in terms of nondissociative adsorption. Electron-energy-loss spectroscopy (EELS) results^{3,4} later indicated that water dissociates upon room-temperature exposure on the Si(100) surface to form Si-H and Si-OH units. In contrast, very recent UPS work⁵ concluded that only molecular adsorption takes place under similar conditions.

High-resolution infrared spectroscopy is ideally suited to identify molecular from dissociated water with no possibility of probe-induced dissociation. More importantly, polarization information allows the identification of the specific hydrides formed (e.g., monohydride or dihydride) and the orientation of the modes under consideration. Using a newly developed surface infrared spectrometer, we observe that water dissociates⁶ to form Si-H and Si-OH in agreement with the EELS results. We focus on the dissociated water and show that upon annealing the OH radicals break up without desorbing resulting in the formation of an oxide and of both monohydrides and dihydrides on the remaining oxygen-free silicon surface atoms.

The surface infrared spectrometer has been described previously.⁷⁻¹⁰ A broad frequency region (1000-4000 cm⁻¹) can be covered with typical resolution of 1 cm⁻¹ and high sensitivity ($\frac{1}{100}$ monolayer of the weakest dipoles).⁸ The Si(100) (*n* type, $\rho > 500 \Omega \text{ cm}$) is cleaned by a mild sputtering (60° incidence, 0.5 kV @ 10 $\mu\text{A}/\text{cm}^2$) at room temperature for a few minutes to remove the oxide layer followed by an extended anneal at 850°C (~1 h). The resulting surface exhibits less than 0.3% monolayer of carbon and no detectable amount of oxygen. However, the clean surface is very reactive and small amounts of oxygen (water) can be detected in a period of $\frac{1}{2}$ hour in a vacuum of 2×10^{-10} Torr. The low-energy-electron diffraction (LEED) pattern of the clean surface is a 2×1 with very faint streaks where the $\frac{1}{4}$ -order spots of the $c(2 \times 4)$ are expected.¹¹ The long-range order is, however, dominated by a 2×1 reconstruction. Water exposure was achieved by opening a leak valve separating a distilled water reservoir from the vacuum chamber. The sample was positioned 15 cm in front of the valve while the ion gauge was over 75 cm away

from the valve and located behind the sublimator cryoshroud. As a result, the absolute effective water pressure at the sample (and the overall exposure) could not be determined accurately. According to the gauge reading, exposures ranging from 0.5 to 2 L [1 langmuir (L) = 10^{-6} Torr sec] were typically performed, yielding saturation coverage. The actual exposures are larger.

The absorption of the Si-H mode measured by internal reflection can be described by a three-layer model^{7,12} where the second layer corresponds to the Si-H layer characterized by complex dielectric constant $\hat{\epsilon}_2$ which, in general, has two different components, $\hat{\epsilon}_{\parallel}$ and $\hat{\epsilon}_{\perp}$, for a given orientation of the dipole. For example, within the Lorentz oscillator picture, the components can be written

$$\hat{\epsilon}_{\parallel} = \epsilon'_{\parallel} + i\epsilon''_{\parallel} = \epsilon_{\infty\parallel} + \frac{\nu_p^2_{\parallel}(\nu_T^2 - \nu^2)}{(\nu_T^2 - \nu^2)^2 + \Gamma^2\nu^2} + i\frac{\nu_p^2_{\parallel}\Gamma\nu}{(\nu_T^2 - \nu^2)^2 + \Gamma^2\nu^2}$$

and

$$\hat{\epsilon}_{\perp} = \epsilon'_{\perp} + i\epsilon''_{\perp} = \epsilon_{\infty\perp} + \frac{\nu_p^2_{\perp}(\nu_T^2 - \nu^2)}{(\nu_T^2 - \nu^2)^2 + \Gamma^2\nu^2} + i\frac{\nu_p^2_{\perp}\Gamma\nu}{(\nu_T^2 - \nu^2)^2 + \Gamma^2\nu^2},$$

where

$$\nu_{p\parallel} = \left(\frac{4\pi n_{\parallel}^*}{m^*c^2} \right)^{1/2} e^* \sin\alpha,$$

$$\nu_{p\perp} = \left(\frac{4\pi n_{\perp}^*}{m^*c^2} \right)^{1/2} e^* \cos\alpha.$$

Here α is the angle made by the effective dynamic dipole moment with respect to the surface normal and $n_{\parallel}^* = \frac{1}{2}n_T^*$.¹³ ν_{\perp} is the natural oscillator frequency and Γ , its width. $\epsilon_{\infty\parallel, \perp}$ is the electronic screening for the \parallel or \perp modes. The oscillator *per se* is described by an effective charge e^* and mass m^* . From studies of H chemisorption on Si(100), assuming $m^* \approx 1$ amu, we have established that $e^*/e \approx 0.04$, $\epsilon_{\infty\parallel} = 1.0$, and $\epsilon_{\infty\perp} = 1.3$.¹⁴

Figure 1 shows the adsorption spectrum induced by saturation coverage on a clean Si(100) held at 302 K, normalized in the 2100- and 3650-cm⁻¹ regions.¹⁵ We focus on the Si-H stretching mode at 2080 cm⁻¹ and the OH stretching mode at 3650 cm⁻¹, which have also been observed with low resolution by EELS.² With the three-layer model analysis, the mode at 2080 cm⁻¹ at the top left of Fig. 1, the shift of 2 cm⁻¹ for *p*-polarized radiation, and the

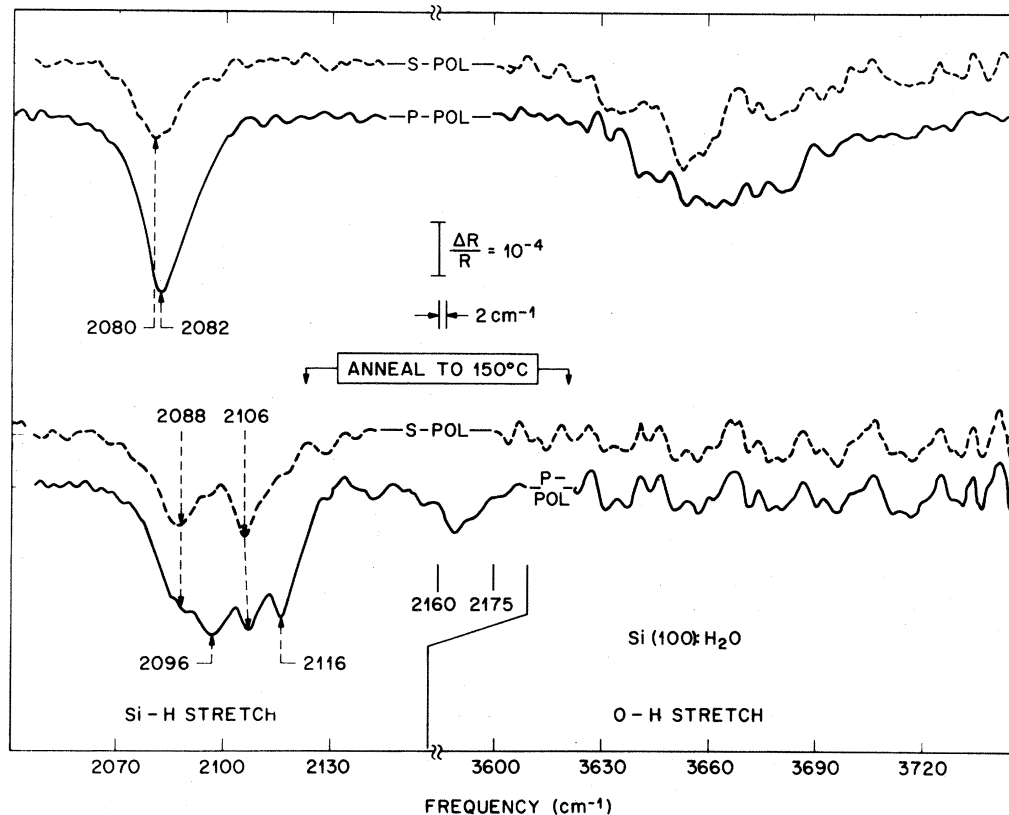


FIG. 1. *Top*: Normalized reflectivity change induced by water adsorption after a nominal 1-L exposure at room temperature. *Bottom*: Spectrum after a 150°C anneal. Water-induced spectra are referenced to those of the clean Si(100) surface. The dashed curves are obtained with *s*-polarized light while the solid curves are obtained with *p*-polarized light.

respective areas of the modes are well accounted for with $n_s = 3.4 \times 10^{14} \text{ cm}^{-2}$ and $\alpha = 40^\circ$. The determination of the angle α does not depend on the accurate knowledge of n_s or e^* but does depend on the value of $\epsilon_{\infty \perp}$, the electronic screening of the perpendicular mode. For that reason we do not give a value for the angle made by the OH oscillator which, as can be seen in Fig. 1 (top two curves), has a substantial contribution parallel to the surface (*s* polarized), indicating a large tilt from the surface normal. Because the LEED pattern remains a sharp 2×1 , it is probable that the H and OH entities are chemisorbed on the two adjacent silicon atoms belonging to the same dimer as suggested earlier.^{3,4} This is consistent with the fact that only one Si-H mode with no chemical splitting is observed. Monohydride formation with one H on each silicon atom of the same dimer or dihydride formation with two hydrogen atoms on the same silicon atom would result in some chemical interaction in addition to the 2-cm^{-1} dipole-dipole interaction. Such monohydride and dihydride formations do, however, take place upon annealing to 150°C, as can be seen in the bottom two curves of Fig. 1. Instead of one mode at 2080 cm^{-1} , four modes can now be identified, two polarized parallel to the surface at 2088 and 2106 cm^{-1} , as shown by the *s*-polarized data, and two polarized perpendicular to the surface at 2096 and 2116 cm^{-1} , as revealed by the *p*-polarized data, where both parallel and perpendicular modes are probed. The key observation is that, while the O-H stretching mode disappears, the overall integrated area

under the Si-H modes *doubles*. Hence the hydrogen atom belonging to the OH group dissociates and combines to an adjacent Si atom, resulting alternatively in a monohydride configuration characterized by modes at 2088 and 2096 cm^{-1} ,¹⁶ or in a dihydride configuration characterized by modes at 2106 and 2116 cm^{-1} .¹⁷ In both configurations the modes parallel to the surface are lower in frequency than the corresponding modes perpendicular to the surface. However, the relative amplitude between parallel and perpendicular modes varies. While the perpendicular mode dominates in the case of the monohydride, the dihydride displays a stronger component parallel to the surface, consistent with the fact that the Si-H oscillator is more tilted with respect to the surface normal ($\alpha \approx 55^\circ$).

This assignment can be tested experimentally as follows. First, a Si(100) surface held at 242°C is exposed to a few langmuirs of water. The resulting spectra are shown at the top of Fig. 2 and are characteristic of a mixture of monohydride and isolated Si-H units throughout the surface. No OH stretch can be seen confirming that the OH is dissociated at that temperature. We note that the relative intensity of the mode in the *p*- and *s*-polarized spectra indicates that the angle is $\alpha \approx 33^\circ$, i.e., smaller than that formed when the OH was undissociated. Next, a small amount of *atomic* hydrogen is added¹⁸ resulting in the two intermediate spectra. Although the lines are rather broad, four peaks can be identified at 2088, 2097, 2106, and 2116 cm^{-1} . These peaks can be seen better by annealing the surface slightly, which has

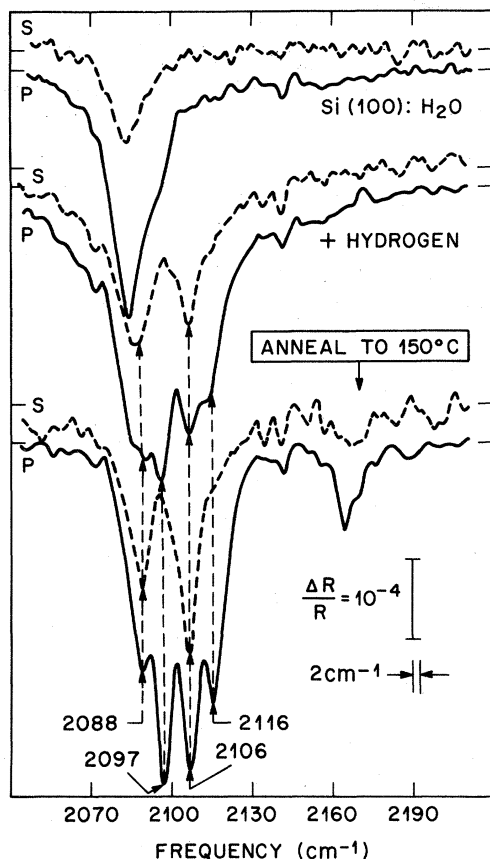


FIG. 2. *Top*: Normalized reflectivity change induced by water adsorption on a sample held at 242°C during a nominal 1-L exposure. *Middle*: Spectrum after exposing to a small amount of atomic hydrogen (~ 35 -L H_2). *Bottom*: Spectrum after annealing the surface to 150°C with no further exposure.

the effect of ordering the surface, i.e., of sharpening the modes. This is shown in the set of lower curves where the four peaks can now easily be resolved. Qualitatively, it is clear that the Si-H mode of the monohydride species lies closer to the surface normal than that of the dihydride species. More quantitatively, using the relative strengths of the modes at 2088 and 2097 cm^{-1} in the *s*- and *p*-polarized data (lower two curves of Fig. 2), we calculate $\alpha \approx 45^\circ$ for the monohydride. Similarly, the relative strengths of the modes at 2106 and 2116 cm^{-1} give $\alpha \approx 55^\circ$ for the dihydride. Assuming a similar dynamic dipole moment, the concentration of monohydride and dihydride is about equal. Finally, we note that the mode appearing at 2165 cm^{-1} is

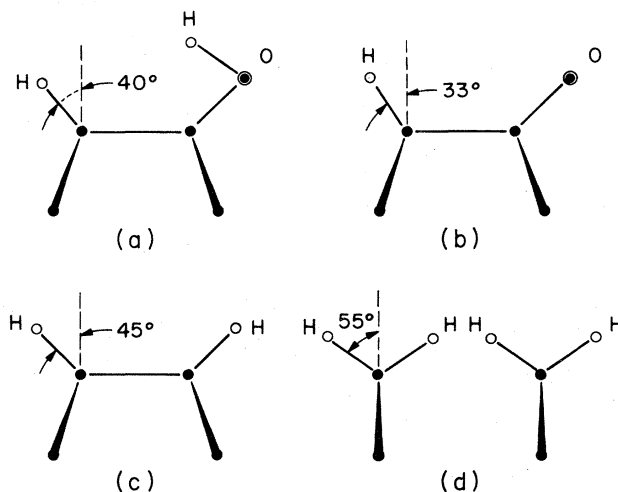


FIG. 3. Suggested arrangements: (a) monohydride with OH nearest neighbor; (b) monohydride with O nearest neighbor; (c) pure monohydride; (d) dihydride. Note that the angles are associated with the effective dynamic dipole moment rather than the geometric bond.

polarized perpendicular to the surface and is probably the result of Si-H where the Si atom is bonded to an oxygen atom.⁴

The picture which emerges is summarized in Fig. 3. Upon room-temperature water adsorption, a monohydride species is formed with an OH molecule adsorbed on the other silicon atom of the same dimer. The angle with respect to the normal is 40° [Fig. 3(a)]. This angle is reduced to 33° after the H from the OH is removed [Fig. 3(b)]. When pure monohydride is formed, the angle is 45° [Fig. 3(c)] while it is increased to 55° for the dihydride geometry [Fig. 3(d)]. It should be stressed that α is the angle made by the effective dynamic dipole moment with respect to the surface normal and not the normal to the dimer axis. Part of the variations measured for the various monohydride configurations [Figs. 3(a), 3(b), and 3(c)] can result from some asymmetry in the dimer, and in the charge-density distribution, particularly when oxygen is chemisorbed on one end.

ACKNOWLEDGMENTS

The author is grateful to H. H. Farrell, F. Stucki, and D. Schmeisser for discussing their EELS and UPS results prior to publication. This work was performed with the invaluable technical assistance of S.B. Christman.

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¹³Note that α does not necessarily correspond to the angle made by

the geometric Si-H bond. Also, because of the presence of two domains orthogonal to each other on the Si(100) surface, the \parallel component of the electric field can only interact on average with half of the oscillators. This factor must also be taken into account in the evaluation of the effective thickness d^* where $d_{\parallel}^* = n_s/n_{\parallel}^*$ and $d_{\perp}^* = n_s/n_{\perp}^*$, where n_s is the coverage as described in Ref. 7.

¹⁴These values differ from those reported in Ref. 7 because (a) the number of relevant reflections was off by a factor of 2 since the back face was later shown not to contribute, (b) the coverage was poorly known, and (c) the correction for anisotropy in the dielectric constant was not made.

¹⁵Normalization is performed as described in Ref. 10 in order to subtract the contributions of the electronic surface states present on the clean Si(100) surface. See Y. J. Chabal, S. B. Christman, E. E. Chaban, and M. T. Yin, *J. Vac. Sci. Technol. A* **1**, 1241

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¹⁶We now believe that the modes observed at 2087 and 2099 cm^{-1} in Ref. 7 are due to monohydride rather than dihydride. Indeed, these modes persist upon annealing to 250°C after which a sharp 2×1 LEED pattern is observed. See S. Maruno, H. Iwasaki, K. Horioka, S-T. Li, and S. Nakamura, *Phys. Rev. B* **27**, 4110 (1983). EELS work on a similarly prepared surface shows the absence of any scissor mode characteristics of SiH_2 , as described in Ref. 17.

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¹⁸It was found that molecular hydrogen does not chemisorb even on this surface preexposed with H_2O . Note that the exposure of atomic hydrogen cannot be measured precisely.