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Evidence of dissociation of water on the Si(100)2×1 surface

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High-resolution infrared spectroscopy of the Si(100)2×1 surface upon water exposure shows that, in the temperature range investigated (80 to 500 K), the adsorption is dissociative. Molecular water can only be adsorbed at low temperatures on a surface with saturated dangling bonds.

The mechanism of wet oxidation has important technological applications which have warranted a number of studies on well-characterized surfaces[1-10] to assess the conditions under which water dissociates and to isolate the mechanisms leading to the substrate oxidation. For the Si(100) surface, which is the most common device substrate, the original picture of Meyer[1] involving dissociative adsorption has been alternatively disproved[2-5] and supported.[6-10]. In 1971 Fujiwara[2] interpreted his ultraviolet photoemission spectra (UPS) in terms of nondissociative adsorption after correlating the three prominent features observed in the water-induced spectrum to the $1b_1$, $2a_1$, and $1b_2$ orbitals of the free H_2O molecule. This conclusion was challenged by the vibrational study of Ibach and co-workers[6,7] who identified in their electron-energy-loss spectra (EELS) only the stretching modes associated with Si–H and Si–OH and found no evidence for molecular H_2O modes. Shortly afterward, Ciraci and Wagner[8] used a semiempirical approach to show that molecularly adsorbed water would exhibit an unstable electronic configuration. They found that, in contrast, dissociated water was quite stable, and reinterpreted Fujiwara's data in terms of dissociative adsorption. However, in 1983 Schmeisser, Himpsel, and Hollinger[4] reported that new UPS data and photostimulated desorption (PDS) results could not be reconciled with dissociative adsorption. From their UPS data, which were distinctly different from Fujiwara's data, they suggested that H_2O was chemisorbed with its oxygen end toward the surface and argued that, since these conclusions were inconsistent with the observation of the Si–H stretching mode, dissociation induced by low-energy electrons or by rough surfaces (with steps and defects) might account for the EELS results of Ref. 6. They also pointed out that the coexistence of molecular and dissociated water could not be ruled out for certain temperature and surface conditions. Finally, very recent UPS work[5] indicates that water is molecularly physisorbed at 100 K and remains undissociated up to 600 K.

In view of these conflicting results and of the importance of a reliable theoretical treatment of H_2O adsorption on Si(100), it is critical to establish unambiguously whether and under which conditions water dissociates on Si(100). The use of high-resolution infrared spectroscopy is best suited for this investigation since it is sensitive enough to detect weak vibrations such as SiH (Ref. 11) without the possibility of probe-induced dissociation; further, the symmetry of the modes can be measured from polarization studies.[12] We have therefore used this technique to investigate H_2O adsorption in the temperature range 80 to 500 K on flat and vicinal Si(100)2×1 surfaces. We find that water does chemisorb dissociatively in this range with a unity sticking coefficient, and that surface roughness is not instrumental in this dissociation. Further, no molecular water can be physisorbed at low temperature until the surface dangling bonds are saturated. This is in contrast to H_2O adsorption on Si(111) and Ge(100) where dissociation does not readily take place.

The surface infrared spectrometer has been described previously.[13,14] The samples were cut from Si(100) wafers (n type, $\rho > 500\ \Omega\,\mathrm{cm}$) and cleaned by a mild sputtering (60° incidence, 0.5 kV, 10 $\mu\mathrm{A/cm^2}$) at room temperature for 2–5 min to remove the native oxide layer of the front face only, followed by an extended anneal (800 °C, 1 h). The resulting surface exhibits less than 0.3% monolayer of carbon and no detectable amount of oxygen ($\leq 0.1\%$ monolayer). The low-energy-electron diffraction (LEED) patterns of the flat samples show a sharp 2×1 reconstruction with very faint streaks at the $\frac{1}{4}$-order of the $c(2\times4)$ reconstruction.[15] The stepped samples, cut at 9° from the {100} plane, exhibit sharp $\frac{1}{4}$-order spots along the terrace normal and a strongly anisotropic $\frac{1}{2}$-order spot parallel to the terrace edge indicating that the dimers are aligned parallel to the terrace edge. Once the surface was characterized, *all filaments* were turned off in the vacuum chamber (ion gauge, mass spectrometer, LEED, and Auger spectrometers). Water exposure was achieved by opening a leak valve separating a distilled water (or D_2O) reservoir from the vacuum chamber and located 15 cm from the sample front surface. During the exposure, the ion pumps were valved off, the titanium sublimator turned off, and the chamber dynamically pumped by a turbomolecular pump located 1.5 m away from the sample, thus establishing a positive flow from the leak valve and sample area to the pump. An ion gauge, located at the mouth of the turbomolecular gauge and separated from the sample by three right-angle elbows and one *cold* shield was used to monitor the pressure. Thus the probability for a water molecule dissociated at the gauge to reach the sample was negligible. However, this arrangement prevented the accurate measure of the absolute water exposure at the sample. All the exposures quoted in this paper are deduced from the gauge reading and are, therefore, lower than the actual exposures. The relative exposures can be known within 5%.

The water-induced infrared spectra, $\Delta R/R$, were obtained as follows: First, spectra of the clean Si(100)2×1 were taken within 15 min of the end of the cleaning procedure in a background pressure of 7×10^{-11} Torr. Then, water was introduced and the resulting spectra recorded. Finally, the sample was flashed to 800 °C, leaving on the surface only the oxygen, and background spectra were recorded. The broad surface-state-induced absorption which is present on the clean Si(100)2×1 surface but absent on the oxygen-covered surface[16] could be removed from the clean surface spectra which could then be averaged with the background spectra.[17] This procedure eliminated any time-dependent effects, such as occasional water condensation on the cold infrared detector,[18] and consistently gave a very flat base line. The data were recorded for both *s* and *p* polarizations[19] but, for clarity, only *p*-polarized data are plotted in this paper.

In Fig. 1 spectra obtained upon various exposures on the clean Si(100)2×1 surface at room temperature (curves a and b) are compared with a spectrum obtained by physisorption of water on the Si(100) surface at 80 K still covered with its native oxide (before sputtering and annealing) (curve c). The latter spectrum is characterized by a mode at 1670 cm^{-1}, the water scissor mode, and a broad and strong mode centered around 3300 cm^{-1} characteristic of H-bonded H_2O stretching mode. Since the exposure resulting in curve b is 20 times larger than that yielding curve a, and yet the line intensities are equal in both curves, it can be concluded that saturation coverage can be obtained with 0.5-L (1 L$=10^{-6}$ Torr sec) exposure, as measured with the remote gauge, and that *no other form* of water adsorption takes place at room temperature but that giving rise to the modes at 2082 and 3600 cm^{-1}. These modes have been identified both with EELS[6] and infrared[12] as the stretching mode of the Si–H (monohydride) and of the –O–H (hydroxyl) molecules.[20] The absence of the H_2O scissor mode at 1670 cm^{-1} *and* the lack of softening and broadening of the OH mode in the spectra a and b rule out the presence of molecular water adsorbed at room temperature.

To test whether water dissociation into H and OH is activated by steps or defects, the following experiments were performed. First, a number of flat Si(100) samples cut with a precision of ±0.5° were used with a variety of sputtering annealing conditions[21] without any measurable change in the line intensities or sticking coefficient. The integrated absorption of the SiH mode at saturation corresponds to $\frac{1}{2}$ monolayer, i.e., one hydrogen per two silicon atoms. Next, vicinal surfaces were prepared (9° from {100} plane) and water exposures carried out. For these samples no new modes were observed, and the integrated area of the SiH mode at saturation was about $\frac{4}{5}$ of that of the flat sample. Further, no absorption was detected along the direction of the dangling bonds associated with the step atoms. These observations indicate that water dissociation takes place on the terrace and *not at the steps.* In fact, the step edges were found *less* reactive to atomic hydrogen than the terraces.[22] The participation of steps to water dissociation can therefore be ruled out.

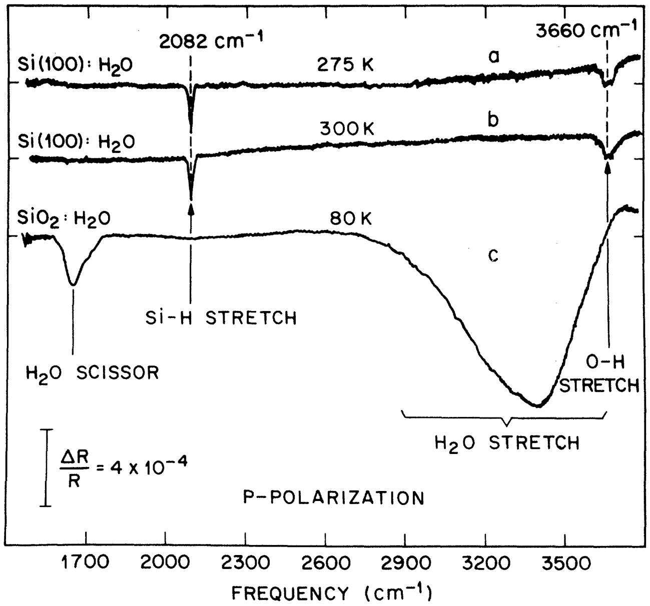

FIG. 1. Water-induced spectra, $\Delta R/R$, on clean Si(100)2×1 at room temperature (curves a and b) and on oxidized silicon at 80 K (curve c). The minimal exposures are a, 0.5 L with sample held at $T_s=275$ K; b, 10 L with $T_s=300$ K; and c, 10 L with $T_s=80$ K. Data were taken at the temperatures indicated on each spectrum.

We address next the problem of water adsorption at low temperatures by extending the range covered by Ibach, Wagner, and Bruchmann[6] to 80 K. The first observation is that the mode at 2082 cm^{-1} appears after $\frac{1}{2}$ h in the vacuum chamber (with a residual H_2O pressure of 1×10^{-10} Torr) just as it did with the sample at room temperature, indicating that dissociation takes place. This is confirmed by exposing the surface with 0.5 L at 80 K resulting in the spectrum of Fig. 2, curve a. Only the modes at 2082 and 3660 cm^{-1} are observed with equal intensity as those observed in Fig. 1, curve a, but with broadening of the SiH mode [$\Delta=20$ cm^{-1} instead of 15 cm^{-1} observed upon room-temperature (RT) exposure]. Annealing to 285 K results in a sharpening of the modes to a width comparable with that measured for exposures at RT and with no loss of intensity (Fig. 2, curve b). The shoulder on the high-frequency side of the SiH mode is due to a small fraction of symmetric monohydride formation with two hydrogens per dimer[12] as the center of the sample was hotter than 285 K.

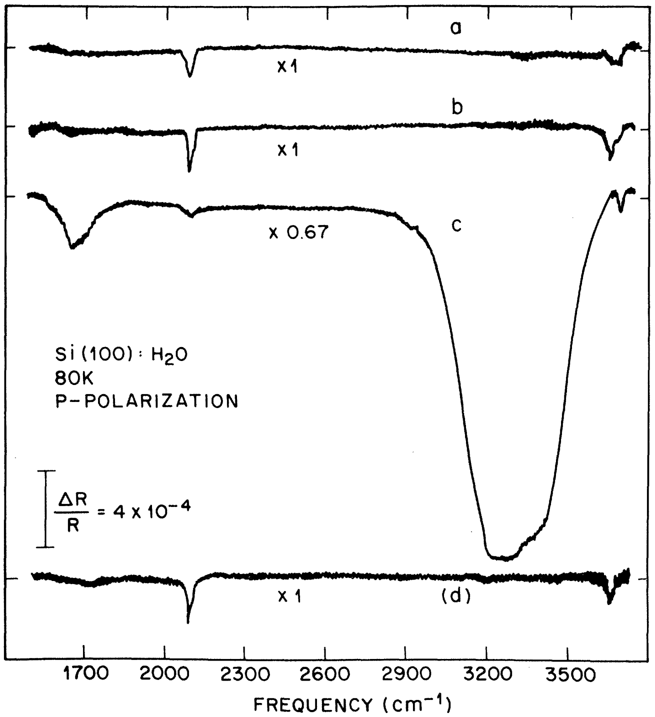

FIG. 2. Water-induced spectra, $\Delta R/R$, upon water exposure on clean Si(100)2×1 at 80 K: a, 0.5 L with $T_s=80$ K; b, 0.5 L with $T_s=80$ K and after annealing to 285 K for 1 min with no additional water exposure; c, 10 L with $T_s=80$ K; and d, 10 L with $T_s=80$ K and after annealing to 280 K for 1 min.

From Fig. 2, curves a and b we conclude that water does adsorb dissociatively at 80 K up to one monolayer coverage (one H_2O per dimer).

For a 10-L exposure on a clean Si(100) surface, Fig. 2, curve c clearly shows the adsorption of *molecular* water on the front face of the sample. We note, however, that the SiH and SiOH modes are still present, but the SiH mode is now dramatically broadened ($\Delta = 80$ cm^{-1}) while the OH mode is narrower ($\Delta = 10$ cm^{-1}) and shifted to a higher frequency, $\nu_0 = 3695$ cm^{-1}. Both modes are reduced in intensity from that of Fig. 2, curves a or b. This reduction is attributed to a screening due to the overlayers of physisorbed water rather than a lower coverage of chemisorbed H and OH since the same intensity is obtained either by stopping the exposure at 0.5 L or by subsequently warming up the sample to room temperature (Fig. 2, curve d). Hence molecular water can only by physisorbed at low temperatures on Si(100) after saturation (one dissociated H_2O molecular per dimer) of the surface with dissociated water or with oxygen, i.e., after the dimer dangling bonds have been occupied. Finally, above room temperature (up to 500 K) the adsorption is also dissociative.[12]

In contrast, we find that no Si–H or Ge–H modes can be observed on the Si(111)7×7 or Ge(100)2×1 surface, respectively, for equivalent room-temperature exposures (10 L). In both cases molecular adsorption takes place at 80 K, and dissociation occurs upon warming to room temperature, as previously noted by Ibach *et al.*[6] in the case of Si(111)7×7. This observation is more surprising in the case of Ge(100)2×1 surface, the reconstruction of which is also believed to involve dimers,[23] and indicates that differences in the density of surface states[24] may play a crucial role in the dissociation mechanism as suggested by Ciraci *et al.*[8]

In summary, we find that, in agreement with EELS work,[6] chemisorption of water on the clean Si(100)2×1 is dissociative over the range of temperatures investigated (80 K $\leq T \leq$ 500 K). We have shown that this dissociation was not initiated at steps or defects and did not result from gas phase dissociation due to filaments in the chamber. Molecular adsorption could only be observed at low T for a sample oxidized or saturated with dissociated water. Since these results are in contradiction with the conclusions of Schmeisser *et al.*,[4,5] we must consider the evidence which they put forth to establish the presence of molecular adsorption: (i) the presence of three features in the UPS spectrum instead of two expected for H and OH,[25-27] and (ii) the fact that hydrogen bonding to Si(100) is known to give a peak at −5.2 eV below the top of the valence band and thus cannot account for the −6.2-eV peak observed.[28] The first point (i) is not a strong one since the semiempirical calculations of Ciraci *et al.*[8] yield three strong features in the density of state with binding energies less than 15 eV. The second point (ii) cannot be stressed since the UPS data of Sakurai and Hagstrum[29] and the ELS (electron-loss spectroscopy) work of Maruno *et al.*[30] show that there is a shift of 1 to 2 eV towards higher binding energy in going from dihydride to monohydride. For the dissociated water on Si(100) the single hydrogen is believed to bond in a monohydride geometry[6,12] and the presence of the oxygen should affect the orbital associated with the Si–H bond. It is therefore just as conceivable that the features observed at −6.1 eV by Schmeisser *et al.* could be attributed to the Si–H rather than to the oxygen lone-pair orbital b_1. This can only be answered by a realistic treatment of the surface electronic structure using the proper geometry for the adsorbate.[12]

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