

Chemisorption of H<sub>2</sub>O on Si(100)

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The chemisorption of H<sub>2</sub>O on Si(100)-(2×1) has been studied at room temperature using photoelectron spectroscopy and photon-stimulated desorption. Three H<sub>2</sub>O-induced valence orbitals are found at 6.2, 7.2, and 11.5 eV below the valence-band maximum (which is 0.4 eV below  $E_F$ ). They can be assigned to chemisorbed molecular H<sub>2</sub>O. The Si 2*p* level is chemically shifted by -0.9 eV corresponding to a single silicon-oxygen bond. Together with the observed work-function decrease, we suggest that H<sub>2</sub>O is adsorbed oxygen end down (possibly tilted).

The interaction of H<sub>2</sub>O with silicon surfaces has been studied very little despite the widespread usage of the fast steam oxidation process in device technology. Present photoemission<sup>1</sup> and electron-energy-loss experiments<sup>2</sup> have come to opposite conclusions concerning the question whether the H<sub>2</sub>O molecule stays intact or dissociates into OH and H on a Si surface. The Si(100) surface is not only the most common device substrate but has also a sticking coefficient near unity for H<sub>2</sub>O which is several orders of magnitude higher than for the Si(111)-(7×7) surface.<sup>2</sup>

For our study we have used a photoemission system at the synchrotron radiation source Tantalus I which has been described earlier.<sup>3</sup> By reversing the polarity of the electron spectrometer<sup>4</sup> we have also observed electron- and photon-stimulated desorption of positive ions. We found this process so efficient for H<sub>2</sub>O on Si(100) that a substantial portion of the adsorbate is decomposed within seconds under current densities as used for low-energy-electron diffraction and Auger spectroscopy studies. Si(100) wafers (nearly intrinsic *n*-type 10 Ω cm) were cleaned with buffered HF before introducing them into the preparation chamber through a vacuum lock. Heating to about 1000 °C sublimed the remaining oxide layer leaving a clean surface which exhibited surface states and shifted surface core levels almost as intense as published previously.<sup>5,6</sup>

The photoelectron spectra of a Si(100) surface after saturation exposure with H<sub>2</sub>O are shown in Fig. 1 for various photon energies. The broad emission centered around -3 eV is due to emission from the Si valence band which dominates in the spectra of the clean surface. The spectrum of a clean Si(100) surface (at  $h\nu = 51$  eV) is indicated by the dashed line in Fig. 1. The structure at -0.5 eV represents surface states<sup>5</sup> and disappears upon exposure to H<sub>2</sub>O. The Fermi level lies 0.4 eV above the top of the valence band<sup>7</sup> for clean Si(100). The water-induced emission shows three bands peaking at -6.2, -7.2, and -11.5 eV. There are only weak changes when the incident photon energy is varied. At 21 eV the H<sub>2</sub>O orbital

emission rides on a sloping background of secondary electrons. At 51 eV the Si substrate emission is minimized due to a Cooper minimum of the Si 3*p* states. We derive a decrease in the work function by at least 0.4 eV after H<sub>2</sub>O adsorption using the width of the spectra taken at 21-eV photon energy.<sup>8</sup> This indicates that OH or H<sub>2</sub>O dipoles point with their oxygen end towards the surface.

If one assumes undissociated H<sub>2</sub>O, the three adsor-

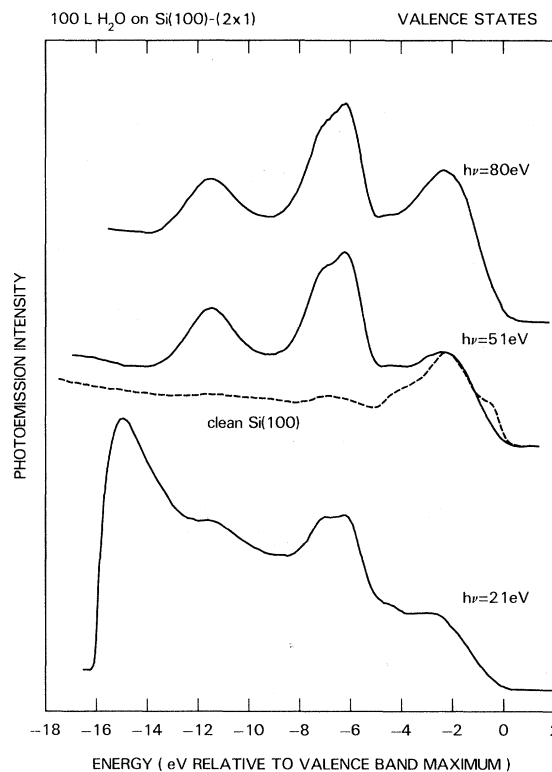


FIG. 1. Angle-integrated photoelectron spectra for saturation coverage of H<sub>2</sub>O on Si(100)-(2×1) taken at room temperature with different photon energies. The Fermi level is 0.4 eV above the valence-band maximum.

bate orbitals can be identified by comparison with the free H<sub>2</sub>O molecule<sup>9</sup> (see Fig. 2) or with H<sub>2</sub>O physisorbed on metal surfaces at low temperatures.<sup>10</sup> The lower two states correspond to bonding and antibonding OH orbitals ( $b_2$  and  $a_1$ , respectively). The uppermost state is assigned to the oxygen lone pair orbital ( $b_1$ ). It is shifted downwards relative to the OH orbitals for H<sub>2</sub>O on Si(100). This indicates bonding of the oxygen end to the surface in agreement with the observed core-level shift (see below). A chemical shift of the uppermost orbital has been observed for other chemisorbed molecules as well, e.g., for CO on Ni, where the  $5\sigma$  orbital shifts down relative to the other orbitals because it is associated with the carbon atom which bonds to the Ni surface. The extra Si-O bond seems to weaken the O-H bonds for H<sub>2</sub>O on Si(100). This shows up as an upwards shift of the antibonding OH orbital ( $a_1$ ) which almost compensates the downshift of the  $b_1$  orbital. The average shift of 3 eV for all H<sub>2</sub>O orbitals relative to the gas phase is due to screening by the substrate similar to other chemisorption systems (e.g., CO on transition metals). Chemical shifts are not observed for H<sub>2</sub>O adsorbed on metal surfaces where H<sub>2</sub>O is bound weakly and desorbs well below room temperature [at

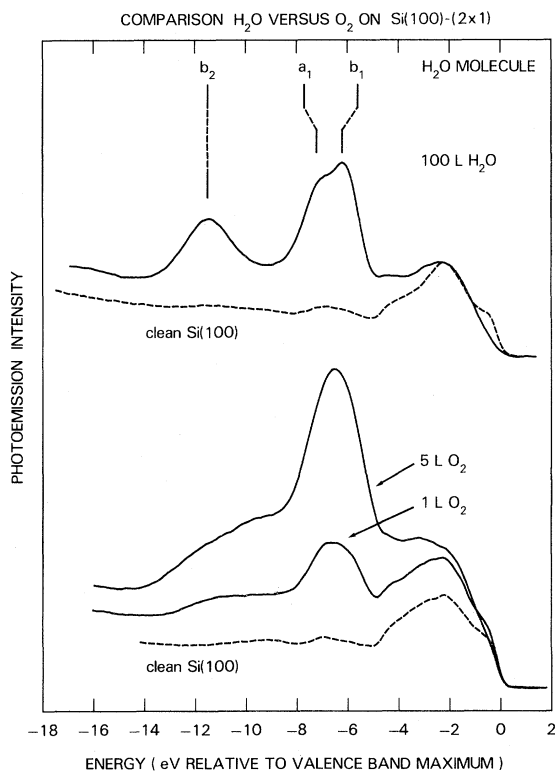


FIG. 2. Comparison of H<sub>2</sub>O and O valence states on Si(100)-(2 × 1). A possible assignment in terms of H<sub>2</sub>O molecular orbitals (shifted up from the gas phase by 3 eV) is given.

about 150 K (Ref. 10)]. The strong H<sub>2</sub>O-Si interaction prevents the formation of hydrogen bonds between H<sub>2</sub>O molecules which is typical for H<sub>2</sub>O on metals.<sup>10</sup> In contrast to the broad oxygen-induced features one can see relative sharp H<sub>2</sub>O states. This is indicative of a well-defined bonding geometry for H<sub>2</sub>O on Si(100) compared to oxygen on Si(100).

Our core-level results (see Fig. 3 for H<sub>2</sub>O on Si and Ref. 11 for oxygen/Si) exhibit a single chemical shift of -0.9 eV for H<sub>2</sub>O on Si and multiple chemical shifts for oxygen/Si at saturation. A core-level shift of -0.9 eV occurs for 1-L (1 L = 10<sup>-6</sup> Torr sec) oxygen on Si(100) as well and has been assigned to a *single* oxygen bonding to Si. The additional shifts seen for oxygen on Si at higher exposures<sup>12</sup> are multiples of -0.9 eV and correspond to several (up to four) oxygen atoms bonding to a Si atom.

Although we come to similar conclusions as Fujiwara's previous photoemission experiment,<sup>1</sup> our data bear little resemblance with the previously published results. The positions of the H<sub>2</sub>O-induced features at 6.1, 8.0, and 10.6 eV below  $E_F$  in Ref. 1 differ significantly from our measurement (6.6, 7.6, and 11.9 eV below  $E_F$ , respectively). Also, the intensity ratio between the upper two peaks is reversed, i.e., the shoulder at  $E_F - 6.1$  eV in Ref. 1 is weaker than the peak at  $E_F - 8.0$  eV, whereas the peak at -6.6 eV is stronger than the shoulder at -7.6 eV in our data. In physisorbed molecular H<sub>2</sub>O the uppermost orbital gives a larger peak than the middle orbital.<sup>10</sup> Therefore we believe that the H<sub>2</sub>O-induced features in Ref. 1 are not due to molecular H<sub>2</sub>O as proposed there. An upward shift of the lowest orbital

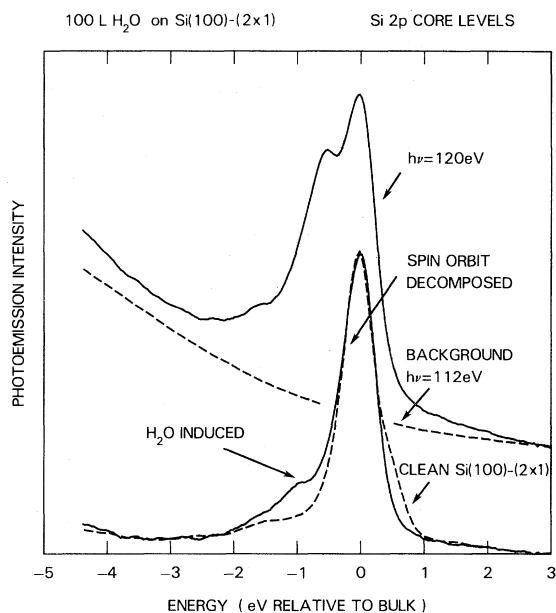


FIG. 3. Si 2p core-level spectra for H<sub>2</sub>O on Si(100) showing a chemically shifted core level centered at -0.9 eV.

and an intensity reversal of the upper two structures similar to Ref. 1 is observed upon warming our H<sub>2</sub>O-exposed surface just above room temperature.<sup>13</sup> These spectra are interpreted in terms of a mixture of OH (lowest two orbitals) and H. After further annealing (> 600 K), we find a decomposition into chemisorbed oxygen<sup>13</sup> in agreement with Fujiwara's results. The different results at room temperature are probably caused by different surface order of the clean Si(100) starting surfaces. H<sub>2</sub>O seems to dissociate on a disordered Si(100) surface. This is consistent with the lower surface state intensity in Ref. 1 (compare Ref. 5 for spectra at  $h\nu = 21$  eV) and with the small differences observed for H<sub>2</sub>O adsorption on disordered Si surfaces in Ref. 1. Thus we do not agree with Fujiwara's conclusion that H<sub>2</sub>O adsorption is independent of the detailed structures of the surface silicon atoms. Actually, electron-energy-loss spectroscopy has found strong crystallographic influence on H<sub>2</sub>O chemisorption. The discrepancy between Fujiwara's photoemission results<sup>1</sup> and electron-energy-loss spectroscopy data<sup>2</sup> can be resolved by assuming that both data sets are characteristic of dissociated H<sub>2</sub>O which we observe on disordered Si(100) surfaces or just above room temperature. A recent calculation<sup>14</sup> finds good agreement with Fujiwara's spectra for dissociated H<sub>2</sub>O but not for molecular H<sub>2</sub>O in agreement with our conclusion.

It is very difficult to explain our data by assuming dissociated H<sub>2</sub>O. If all H<sub>2</sub>O molecules were to break up into OH and H one would expect to see only two OH orbitals<sup>15-17</sup> instead of three H<sub>2</sub>O orbitals. Hydrogen bonding to Si(100) is known to give rise to a peak at about -5.2 eV (Ref. 5) which is too weak to explain any of the three major structures in Fig. 1. In addition, the H cross section decreases strongly relative to the Si 3*p* cross section at photon energies above 30 eV which is not seen for any of the H<sub>2</sub>O-induced states. At best, the bonding Si2*s* + O2*p<sub>z</sub>* state (labeled Oσ in Ref. 14) could explain our third orbital. For the geometries considered in the calculation of Ref. 14 this Oσ state comes out more than 2

eV lower than the lowest orbital in our spectra. The calculation for molecularly adsorbed water in the on-top geometry does not agree with our data either.<sup>14</sup> Therefore H<sub>2</sub>O seems to adsorb in a geometry of lower symmetry (e.g., tilted) which has yet to be determined.

Two additional adsorption models have been proposed for H<sub>2</sub>O on metals. For H<sub>2</sub>O on Ti(0001) adsorbate orbitals at 11.4, 7.4, and 6.1 eV below  $E_F$  have been observed.<sup>15</sup> This has been interpreted in terms of a mixture of OH, O, and H where the lowest two states belong to OH and the third to atomic O. For H<sub>2</sub>O on Si(100) we can rule out the existence of O on the surface at room temperature for several reasons. Oxygen adsorption produces very broad valence features (see Fig. 2) and multiple core-level shifts<sup>11</sup> in distinct contrast to the well-defined valence and core-level features of H<sub>2</sub>O on Si(100). The saturation coverage of oxygen on Si(100) is much larger<sup>11,12</sup> than for H<sub>2</sub>O. H<sub>2</sub>O seems to bond only to the  $\frac{1}{2}$  monolayer of surface atoms which exhibit intrinsic surface core-level shifts,<sup>6</sup> but oxygen attacks the whole surface and even penetrates below the surface.

The possibility of undissociated H<sub>2</sub>O molecules coexisting with OH and H species has been proposed in Ref. 18 for H<sub>2</sub>O on Cu(110). This cannot be ruled out from the room-temperature data. Temperature-dependent photoemission data<sup>13</sup> should be able to resolve this question. For H<sub>2</sub>O on GaAs(110) a physisorbed low-temperature phase and a chemisorbed phase at room temperature have been inferred from photoemission data.<sup>19</sup>

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<sup>1</sup>K. Fujiwara, Surf. Sci. **108**, 124 (1981).

<sup>2</sup>H. Ibach, H. Wagner, and D. Bruchmann, Solid State Commun. **42**, 457 (1982).

<sup>3</sup>D. E. Eastman, J. J. Donelon, N. C. Hien, and F. J. Himpsel, Nucl. Instrum. Methods **172**, 327 (1980).

<sup>4</sup>J. F. van der Veen, F. J. Himpsel, D. E. Eastman, and P. Heimann, Solid State Commun. **36**, 99 (1980).

<sup>5</sup>F. J. Himpsel and D. E. Eastman, J. Vac. Sci. Technol. **16**, 1297 (1979).

<sup>6</sup>F. J. Himpsel, P. Heimann, T.-C. Chiang, and D. E. Eastman, Phys. Rev. Lett. **45**, 1112 (1980).

<sup>7</sup>F. J. Himpsel, G. Hollinger, and R. A. Pollak (unpublished). This value differs slightly from the value of 0.34 eV given in Ref. 6 which was based on measurements by F. G. Allen and G. W. Gobeli, Phys. Rev. **127**, 150 (1962) for Si(111).

<sup>8</sup>A lower bound for the work function cannot be given since the sample was not biased. The clean Si(100)-(2 × 1) surface has  $\phi = 4.85$  eV (Ref. 5). For relating the spectra to the gas-phase molecular orbitals  $\phi = 4.1$  eV has been assumed for Si(100) + H<sub>2</sub>O (see Ref. 15).

<sup>9</sup>J. W. Rabalais, T. P. Debies, J. L. Berkosky, J.-T.J. Huang and F. O. Ellison, J. Chem. Phys. **61**, 516 (1974).

<sup>10</sup>D. Schmeisser, F. J. Himpsel, G. Hollinger, B. Reihl, and K. Jacobi, Phys. Rev. B **27**, 3279 (1983).

- <sup>11</sup>G. Hollinger and F. J. Himpsel, *J. Vac. Sci. Technol.* (unpublished).
- <sup>12</sup>The number of Si atoms bonding to H<sub>2</sub>O and O has been estimated (see Ref. 6) from the intensity of chemically shifted core levels. We find about 0.5 layer of Si atoms chemically shifted by H<sub>2</sub>O at saturation versus 0.2 (0.8) layer for 1-L (5-L) oxygen exposure and 1.5 layers for oxygen saturation (1000 L).
- <sup>13</sup>D. Schmeisser (unpublished).
- <sup>14</sup>S. Ciraci, S. Erkok, and S. Ellialioğlu, *Solid State Commun.* 45, 35 (1983); S. Ciraci and H. Wagner, *Phys. Rev. B* 27, 5180 (1983).
- <sup>15</sup>R. L. Stockbauer, D. M. Hanson, S. A. Flodström, and T. E. Madey, *J. Vac. Sci. Technol.* 20, 562 (1982).
- <sup>16</sup>G. B. Fisher and B. A. Sexton, *Phys. Rev. Lett.* 44, 683 (1980).
- <sup>17</sup>S. Katsumata and D. R. Lloyd, *Chem. Phys. Lett.* 45, 519 (1977).
- <sup>18</sup>A. Spitzer and H. Lüth, *Surf. Sci.* 120, 376 (1982).
- <sup>19</sup>M. Büchel and H. Lüth, *Surf. Sci.* 87, 285 (1979).