

# ESDIAD of First-Row Protic Hydrides Adsorbed on Si(100): Structure and Reactivity<sup>†</sup>

A. L. Johnson,\*<sup>‡</sup> M. M. Walczak,<sup>§</sup> and T. E. Madey

Surface Science Division, National Bureau of Standards, Gaithersburg, Maryland 20899

Received July 17, 1987. In Final Form: August 21, 1987

The interaction of the first-row protic hydrides ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{HF}$ ) with silicon is of scientific interest in the investigation of bonding of small molecules to semiconductor surfaces and of technological interest due to their importance in device processing. These chemisorption systems on stepped Si(100) have been investigated by using ESDIAD (electron-stimulated desorption ion angular distributions) and other surface-sensitive techniques. We relate the results to the chemisorption geometry and the state of hydrogen in these adsorbates and suggest trends in the modes of chemisorption. Reversible temperature-dependent azimuthal ordering of the ESDIAD patterns has been found in some cases; implications in terms of lateral surface interactions and the mode of chemisorption of these molecules are discussed.

## Introduction

There has been much interest in the chemisorption of the first-row protic hydrides ( $\text{HF}$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ ) on Si(100) due to their importance in the manufacture of semiconductor devices.  $\text{HF}$  is used in the reactive etching of silicon, while the use of  $\text{H}_2\text{O}$  in the production of  $\text{SiO}_2$  and of  $\text{NH}_3$  in the production of  $\text{Si}_3\text{N}_4$  is important because of the structural and insulation properties of the reaction products. An investigation of these molecules adsorbed on Si(100) should yield trends in the chemistry of these compounds and of the surface chemistry of silicon in general.

The structure of planar and stepped clean Si(100) has been the subject of many investigations. Si(100) is used in the majority of semiconductor devices due to its anisotropic etch behavior. The clean, planar Si(100) surface reconstructs to form a two-domain  $2\times 1$  LEED pattern. Many approaches have been used to study Si(100), including LEED,<sup>1-5</sup> UPS,<sup>6,7</sup> STM,<sup>8,9</sup> and theoretical treatments.<sup>10-18</sup> These studies indicate that, while the details of the  $2\times 1$  reconstruction are still unresolved, Si(100) reconstructs to form surface silicon dimers, with a bond length often assumed to be only slightly perturbed from the bulk silicon bond length, arrayed in rows along the surface (Figure 1). The dimers have dangling bonds at their ends that are thought to be the reactive sites. The planar surface has two domains of the  $2\times 1$  dimer rows that give the surface LEED pattern overall fourfold symmetry. We have found it useful to study the vicinal Si(100) surface where steps induced by cutting the surface  $5^\circ$  toward the (011) direction create domains having predominantly a single dimer orientation. The  $5^\circ$  stepped surface is composed of terraces  $22$  dimers wide (with the dimers and dangling bonds *parallel* to the step edges) and step edge faces  $2$  atoms high (Figure 1d). The dominance of the Si(100) surface chemistry by the dangling bonds is illustrated by work of Chabal,<sup>19,20</sup> who used IRAS to provide evidence that  $\text{H}_2\text{O}$  dissociates across the dimer, saturating the dangling bonds.

There is ongoing controversy as to the mode of chemisorption of these molecules at room temperature; for example, in the case of water, the majority of investiga-

tors<sup>19-23</sup> have presented strong evidence to indicate dissociative chemisorption, while some authors<sup>24,25</sup> interpret their results in terms of a chemisorption state similar to molecular water. There has been discussion in the literature of  $\text{NH}_3$  adsorption on Si(100) indicating varying degrees of dissociation of the adsorbate.<sup>26,27</sup> The ESDIAD of  $\text{F}^+$  ion emission from Si(100) has been reported recently,<sup>28</sup> but the source of the  $\text{F}^+$  and the coverage of fluorine-containing species were not determined.

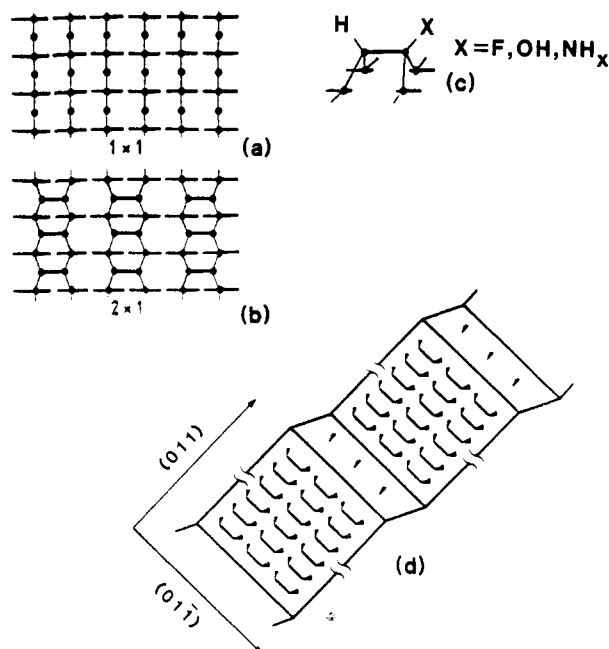
We present the results of an ESDIAD (electron-stimulated desorption ion angular distributions) study of  $\text{HF}$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$  on Si(100) and interpret our results in terms

- (1) Ignatiev, A.; Jona, F.; Debe, M.; Johnson, D. E.; White, S. J.; Woodruff, D. P. *J. Phys. C* 1977, 10, 1109.
- (2) Jona, F.; Shih, H. D.; Jepsen, D. W.; Marcus, P. M. *J. Phys. C* 1979, 12, L455.
- (3) Kaplan, R. *Surf. Sci.* 1980, 93, 145.
- (4) Yang, W. S.; Jona, F.; Marcus, P. M. *Solid State Commun.* 1982, 43, 847.
- (5) Yang, W. S.; Jona, F.; Marcus, P. M. *Phys. Rev. B: Condens. Matter* 1983, 28, 2049.
- (6) Koke, P.; Goldmann, A.; Mönch, W.; Wolfgarten, G.; Pollmann, J. *Surf. Sci.* 1985, 152/153, 1001.
- (7) Goldmann, A.; Koke, P.; Mönch, W.; Wolfgarten, G.; Pollmann, J. *Surf. Sci.* 1986, 169, 438.
- (8) Tromp, R. M.; Hamers, R. J.; Demuth, J. E. *Phys. Rev. Lett.* 1985, 55, 1303.
- (9) Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Phys. Rev. B: Condens. Matter* 1986, 34, 5343.
- (10) Yin, M. T.; Cohen, M. L. *Phys. Rev. B: Condens. Matter* 1981, 24, 2303.
- (11) Chadi, D. J. Proc. IVC-IX and ICSS-V, de Segovia, J. L., Ed.; Libreria Castañeira, Santiago Rusiñol, Madrid, 1983, p 80.
- (12) Allan, D. C.; Mele, E. J. *Phys. Rev. Lett.* 1984, 53, 826.
- (13) Brink, R. S.; Verwoerd, W. S.; *Surf. Sci.* 1988, 154, L203.
- (14) Saxena, A.; Gawlinski, E. T.; Gunton, J. D. *Surf. Sci.* 1985, 160, 618.
- (15) Abraham, F. F.; Batra, I.; *Surf. Sci.* 1985, 163, L752.
- (16) Tiersten, S.; Ying, S. C.; Reinecke, T. L. *Phys. Rev. B: Condens. Matter* 1986, 33, 4062.
- (17) Aspnes, D. E.; Ihm, J. *Phys. Rev. Lett.* 1986, 57, 3054.
- (18) Tabata, T.; Aruga, T.; Murata, Y. *Surf. Sci.* 1987, 179, L63.
- (19) Chabal, Y. J. *Phys. Rev. B: Condens. Matter* 1984, 29, 3677.
- (20) Chabal, Y. J.; Christman, S. B. *Phys. Rev. B: Condens. Matter* 1984, 29, 6974.
- (21) Ibach, H.; Wagner, H.; Bruchmann, D. *Solid State Commun.* 1982, 42, 457.
- (22) Oellig, E. M.; Butz, R.; Wagner, H.; Ibach, H. *Solid State Commun.* 1984, 51, 7.
- (23) Chabal, Y. J. *J. Vac. Sci. Technol. A* 1985, A3, 1448.
- (24) Fujiwara, K. *Surf. Sci.* 1981, 108, 124.
- (25) Ranke, W.; Schmeisser, D. *Surf. Sci.* 1985, 149, 485.
- (26) Bozso, F.; Avouris, Ph. *Phys. Rev. Lett.* 1986, 57, 1185.
- (27) Hiil, E. L.; Kubler, L.; Bischoff, J. L.; Bolmont, D. *Phys. Rev. B: Condens. Matter* 1987, 35, 5913.
- (28) Bozack, M. J.; Dresser, M. J.; Choyke, W. J.; Taylor, P. A.; Yates, J. T., Jr. *Surf. Sci.* 1987, 184, L332.

<sup>†</sup> Presented at the symposium entitled "Molecular Processes at Solid Surfaces: Spectroscopy of Intermediates and Adsorbate Interactions", 193rd National Meeting of the American Chemical Society, Denver, CO, April 6-8, 1987.

<sup>‡</sup> NBS/NRC Postdoctoral Research Associate.

<sup>§</sup> Visiting Scientist. Permanent address: Department of Chemistry, Iowa State University, Ames, Iowa 50011.



**Figure 1.** (a) Model of the unreconstructed Si(100) surface. (b) Model showing the formation of the rows of silicon dimers. (c) Model of the silicon dimer, showing dangling bonds and a model of the dissociative chemisorption of HF, H<sub>2</sub>O, and NH<sub>3</sub>. (d) Model of the stepped surface. Note the terraces of dimer rows, 22 in our case, with the dimers terminated by dangling bonds.

of dissociative chemisorption models. ESDIAD allows the determination of the *local* structure of an adsorbate by directly imaging the ensemble average of the directions of the chemical bonds that cleave to form the observed ions.

The ESDIAD mechanism and experimental techniques used have been described in detail previously.<sup>29,30</sup> Briefly, ESDIAD is the study of the angular distribution of ion emission observed when an electron beam excites a surface and causes desorption. The ion emission is not isotropic for an array of oriented adsorbed molecules but rather consists of beams of ions in specific directions. The angular anisotropy in ion emission is characteristic of the distribution of bond angles in the adsorbate; i.e., the initial desorption direction of an ion is believed to be along the bond vector of the state that fragments to generate the ions.<sup>31,32</sup> The observed ion distribution is the ensemble average of the ion emission of the populated vibrational, rotational, and similar states. This leads to the observation of reversible temperature dependence in beam profiles and patterns.

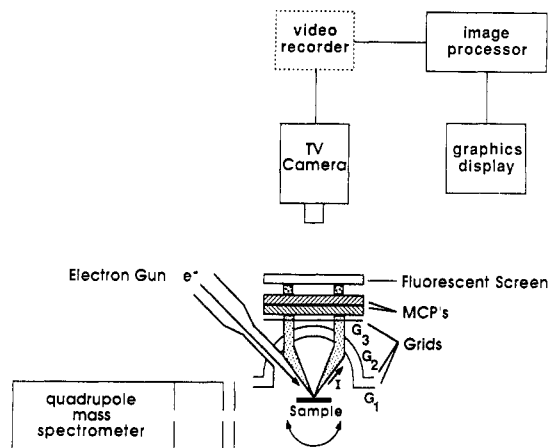
As is discussed in detail below, we have found evidence that HF, H<sub>2</sub>O, and NH<sub>3</sub> chemisorb dissociatively on the stepped, reconstructed Si(100) surface. We have determined the Si-F bond polar angle after HF chemisorption.

(29) Madey, T. E.; Ramaker, D. E.; Stockbauer, R. *Ann. Rev. Phys. Chem.* 1984, 35, 215.

(30) Johnson, A. L.; Stockbauer, R.; Barak, D.; Madey, T. E. *Proceedings of DIET-III*; Shelter Island, NY, May 1987.

(31) Czyzewski, J. J.; Madey, T. E.; Yates, J. T., Jr. *Phys. Rev. Lett.* 1974, 32, 777. Madey, T. E.; Yates, J. T., Jr. *Surf. Sci.* 1977, 63, 203.

(32) Madey, T. E. *Inelastic Particle-Surface Collisions*; Heiland, W.; Taglauer, E., Eds.; Springer Series in Chemical Physics 17; Springer-Verlag: Berlin, 1981; 80. Madey, T. E.; Netzer, F. P.; Houston, J. E.; Hanson, D. M.; Stockbauer, R. *Desorption Induced by Electronic Transitions, DIET-I*; Tolk, N. H.; Traum, M. M.; Tully, J. C.; Madey, T. E., Eds.; Springer Series in Chemical Physics 24; Springer-Verlag: Heidelberg, 1983; p 120. Madey, T. E.; Benndorf, C.; Shinn, N.; Miskovic, Z.; Vukanic, J. *Desorption Induced by Electronic Transitions, DIET-II*; Brenig, W.; Menzel, D., Springer Series in Surface Sciences 4; Springer-Verlag: Heidelberg, 1985; p 104. Madey, T. E. *J. Vac. Sci. Technol. A* 1986, A4, 257. Madey, T. E. *Science (Washington, D.C.)* 234, 316.



**Figure 2.** Experimental apparatus. The TV camera and video data acquisition system are outside the vacuum chamber. The mass spectrometer is used for thermal desorption measurements and residual gas analysis, as well as for the identification of the ESD ions. G<sub>2</sub> may be biased to allow retarding field analysis of the ion energy distribution.

We also find evidence of interactions for chemisorbed H<sub>2</sub>O and NH<sub>3</sub> fragments that cause the ZH bond to be inclined away from the (Si-Si)<sub>dimer</sub>-Z plane (Figure 1c). (Note that "Z" refers to the O in OH and the N in NH<sub>3</sub>.)

### Experimental Section

The stepped silicon surface was prepared from an electronic-grade silicon wafer (n-type, phosphorus doped, 350 Ω-cm resistivity) and measured approximately 1 cm × 1 cm. The stepped sample was a vicinal (100) surface cut 5° toward the (011) direction. At various points in the investigation different sample-mounting techniques were used. Each sample was mounted on a tantalum foil holder, and a thermocouple was either spot-welded to the tantalum above the crystal or glued to the crystal by using a zirconia-based cement.<sup>33</sup> The crystal was heated either resistively or by electron bombardment and was cooled with liquid nitrogen to base temperatures of 125–140 K. The crystal was cleaned by argon ion bombardment at 500 and 1000 V followed by annealing to 1300 K for up to 1 h. The surface purity was monitored by Auger spectroscopy, and the surface order was checked by LEED (low-energy electron diffraction).

The ion angular distributions are imaged by using a dual microchannel plate electron multiplier and phosphor assembly, and the ion masses are monitored by using a quadrupole mass spectrometer located in the region of the sample (Figure 2). The ESDIAD data are collected and analyzed with a video data acquisition system. Our digital data acquisition system for ESDIAD can be used at all count rates, in contrast to position-sensitive anodes. Similarly, "bright spots" due to imperfections in the multichannel plates can be ignored in our apparatus if the spot is not in a region where the data are displayed, whereas such spots can give false counts with a position-sensitive anode and can contribute to the count rate limit. Finally, our method allows the retrofit of existing display-type ESDIAD apparatus to digital acquisition with relatively low cost and no vacuum modifications. The video data system is built around an IP 512 video system in a LSI-11/73 microcomputer.<sup>34</sup> The video signal is digitized to 8 bits (256 levels) of gray scale. The images were obtained either directly from the phosphor by using the video camera (in real time or off-line by using video tape data storage) or from previously obtained photographic negatives. All of the present results are derived from direct digitization of phosphor-screen images. The digitization of the data allows subsequent generation of intensity plots (see below). The images are smoothed by using an  $n \times n$  point

(33) Bozack, M. J.; Muehlhoff, L.; Russell, J. N., Jr.; Choyke, W. J.; Yates, J. T., Jr. *J. Vac. Sci. Technol. A* 1987, 5, 1.

(34) Specification of a manufacturer is included to identify experimental conditions and does not imply endorsement for the product by NBS.

equally weighted boxcar-smoothing algorithm to remove granularity due to the grids (we generally use  $8 \times 8$  points for analysis, although the degree of smoothing is modified to fit the circumstances of count rate and presentation format). To give a feeling for the degree of smoothing,  $8 \times 8$  points is  $1/64$  of the full screen width. For the ESDIAD experiments, electron energies were typically 230 eV; this includes the effects of an 80-V crystal bias potential used to compress the ion trajectories.<sup>29</sup>

The HF used in these experiments was obtained from Air Products<sup>34</sup> and used without further purification. The  $\text{NH}_3$  was obtained from Matheson<sup>34</sup> and purified by freezing in liquid nitrogen and pumping off the uncondensed gases just before dosing. The water used in these experiments was purified by distillation and deionization and degassed by repeated freeze/pump/thaw cycles.

The molecules were introduced through stainless steel lines connected to  $1/4$ -in. dosing tubes in UHV. The HF and  $\text{NH}_3$  samples required extensive preconditioning of the sample lines before dosing. The HF was dosed from an independent manifold pumped with a sorption pump; at the UHV end, the dosing tube was terminated by a cone-shaped nozzle 1 cm in diameter located 1 cm from the sample. The  $\text{H}_2\text{O}$  and  $\text{NH}_3$  were dosed from the background. Unless otherwise indicated, the doses were calculated with uncorrected ion gauge pressures.

The identity of the ions is determined by using the mass spectrometer with the ionizer filament off (Figure 2). For both  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on  $\text{Si}(100)$ , under our experimental conditions (in particular with 230-eV primary electron beam energy), the majority ion species is  $\text{H}^+$ , whereas in the case of HF on  $\text{Si}(100)$  we observe strong ion emission due to  $\text{F}^+$ . While there is evidence for  $\text{H}^+$  emission from the  $\text{Si}(100)2 \times 1$ -HF surface, the  $\text{F}^+$  emission clearly dominates, as is seen by comparison with experiments where we dosed atomic hydrogen onto the clean surface.

Studies were undertaken to determine the adsorbate features that are the source of the ESD ion emission (e.g., is  $\text{H}^+$  due to adsorbed molecular fragments, such as OH or  $\text{NH}_x$ , or to Si-H species?). We have adsorbed hydrogen atoms (prepared from a molecular hydrogen background, by turning on the mass spectrometer ionizer with the crystal facing the filament) and found only weak  $\text{H}^+$  ion emission, much less than that seen from water. For the adsorption of HF,  $\text{NH}_3$ , and  $\text{H}_2\text{O}$  onto  $\text{Si}(100)$  we attribute the strong ion emission and the ESDIAD patterns to surface species other than Si-H.

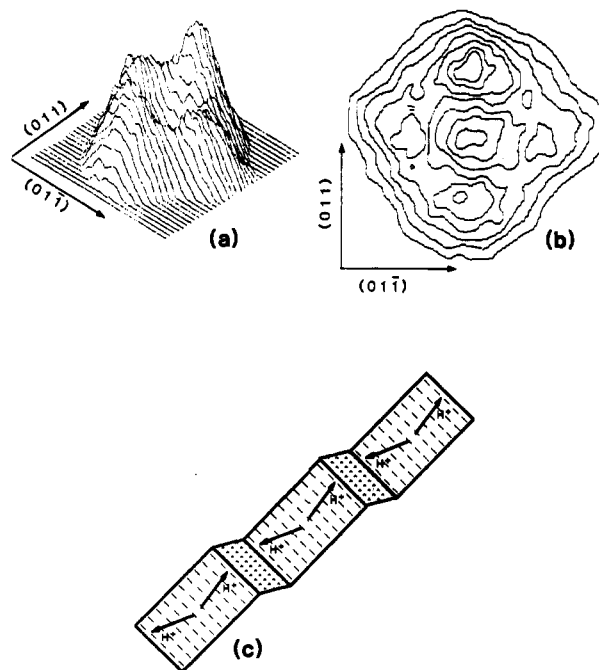
It is important to note that there is a falloff in gain of the ESDIAD optics toward the lower right that appears in all of the patterns and is not due to adsorbate structure.

## Results

We observe essentially no positive ion emission from clean stepped  $\text{Si}(100)$  when the surface is bombarded by a primary electron beam with an energy of 230 eV. The LEED pattern from the stepped surface shows predominantly a single domain of  $2 \times 1$  reconstruction with the dimer bonds parallel to the step edges (i.e., see Figure 1d), as has been seen earlier.<sup>3</sup> The LEED patterns for the stepped  $\text{Si}(100)$  surface are unchanged by the adsorption of HF,  $\text{H}_2\text{O}$ , or  $\text{NH}_3$  at up to monolayer coverages, suggesting that the  $\text{Si}(100)2 \times 1$  reconstruction is not perturbed by the adsorption of these molecules.

**$\text{H}_2\text{O}$ .** Some of the results of our investigations of the adsorption of  $\text{H}_2\text{O}$  onto stepped and planar  $\text{Si}(100)$  have been published previously,<sup>35</sup> where more details of the experimental results and discussion of the proposed interactions may be found.

The ESDIAD of 0.5 langmuir of  $\text{H}_2\text{O}$  on stepped  $\text{Si}(100)$  at 140 K is shown in Figure 3a,b. The only ion observed is  $\text{H}^+$ , and the hydrogen-dosing experiments mentioned earlier demonstrate that the  $\text{H}^+$  emission is from the surface OH groups. The  $\text{H}^+$  signal increases in proportion to the oxygen (KVV) Auger signal, consistent with the



**Figure 3.** ESDIAD of 0.5 langmuir of  $\text{H}_2\text{O}$  on stepped  $\text{Si}(100)$  at 140 K. (a) Perspective plot. (b) Contour plot of the ESDIAD data. (c) Model indicating that the ion emission is perpendicular to the Si-Si bond axes. In C, (—) indicates the dimer bonds.

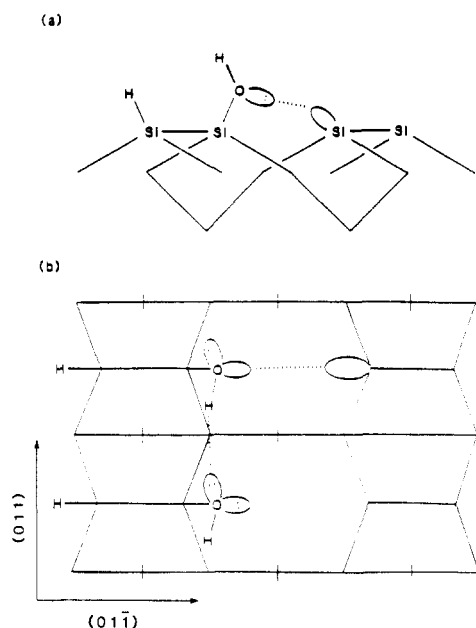
ESDIAD coming from the majority surface state. The crystal orientation for all of the figures is such that the step edges and dimers are as indicated. Note that the primary beams of ion emission are perpendicular to the step edges and, thus, perpendicular to the dimer axes.

We have also studied the chemisorption of  $\text{H}_2\text{O}$  on planar  $\text{Si}(100)$ .<sup>35</sup> Unlike the stepped  $\text{Si}(100)$  crystal, which is dominated by dimers oriented parallel to the step edges, the planar  $\text{Si}(100)$  surface contains two types of domains in which the dimer axes are orthogonal, and therefore the surface as a whole is fourfold symmetric. For the planar  $\text{Si}(100)$ - $\text{H}_2\text{O}$  surface we find a four-beam pattern at low temperature, with the beams along the primary crystal axes. The four-beam pattern is reversibly temperature dependent, becoming azimuthally disordered at  $T \geq 200$  K. These observations lead us to propose the models in Figure 4. The OH group is inclined nearly perpendicular to the silicon-silicon-oxygen plane by interaction of the OH group with the surface, by either a dative interaction between the oxygen lone-pair orbitals and predominantly empty silicon dangling bond (Figure 4a), a dipole-image dipole interaction, or a hydrogen bond between adjacent OH groups (Figure 4b). The dative bond interaction model is supported by the observation of a decrease in the apparent ordering at low temperature for higher coverages, since higher coverages have fewer empty dangling bonds to interact with the oxygen lone pairs. However, the azimuthal ordering does not disappear until a multilayer is formed.

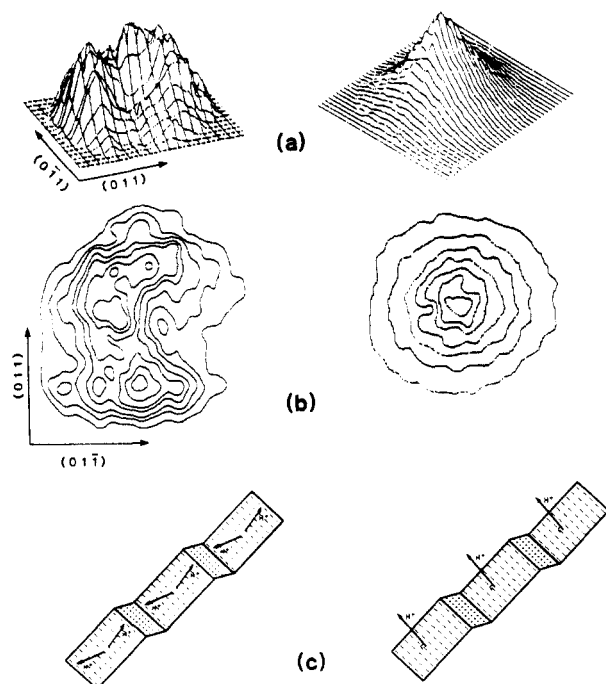
**$\text{NH}_3$ .** To test the model of  $\text{H}_2\text{O}$  chemisorption we examined  $\text{NH}_3$  chemisorption on  $\text{Si}(100)$ .  $\text{NH}_3$  is isoelectronic with  $\text{H}_2\text{O}$ , and in comparison to  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  is a weaker hydrogen bonding liquid but a stronger base. Therefore, if the dative interaction predominates,  $\text{NH}_3$  ESDIAD should show a stronger azimuthal order, but if hydrogen bonding and/or dipole interactions predominate, a weaker ordering would be expected for the  $\text{NH}_3$  ESDIAD.

The ESDIAD of  $\text{NH}_3$  adsorbed on stepped  $\text{Si}(100)$  at 125 K is shown in Figure 5. We observe two characteristic

(35) Larsson, C. U. S.; Johnson, A. L.; Flodström, A.; Madey, T. E. *J. Vac. Sci. Technol. A* 1987, A5, 842.

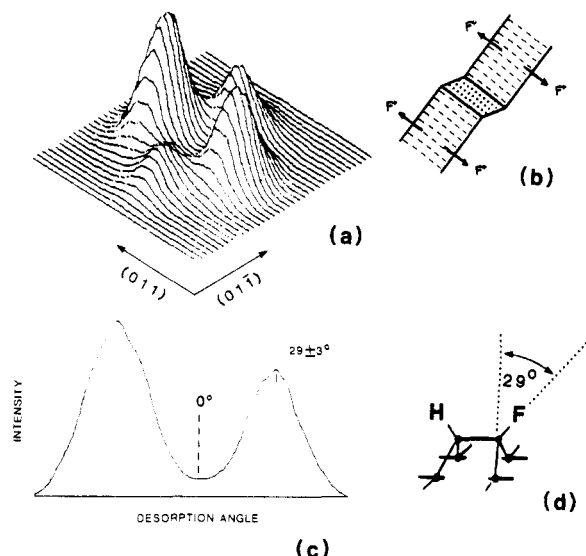


**Figure 4.** Proposed models for the chemisorption of  $\text{H}_2\text{O}$  on  $\text{Si}(100)$ . (a) Model showing the dative interaction, in which the oxygen lone pair donates electron density to the (partially) empty silicon dangling bond. (b) Model showing the dative interaction together with the hydrogen-bonding interaction. Note that the OH bonds are inclined nearly perpendicular to the Si dimer axes.



**Figure 5.** ESDIAD of  $\text{NH}_3$  on stepped  $\text{Si}(100)$  at 125 K: left column, ESDIAD data and model for 0.1-langmuir dose; right column, ESDIAD data and model for 2.0-langmuir dose. (a, b) Perspective and contour plot of the ESDIAD, respectively. (c) Ion directions: at low coverages (in this case corresponding to a dose of 0.1 langmuir) perpendicular to the dimer axes (as in the case of OH); at higher coverages (here corresponding to a dose of 2.0 langmuirs), normal to the surface.

ESDIAD patterns. At doses below  $\sim 0.3$  langmuir the  $\text{NH}_3$  ESDIAD shows a very weak halo, with emission predominantly in the same directions as is seen for  $\text{H}_2\text{O}$ , i.e., perpendicular to the dimer bond. Above 0.5 langmuir the emission is a strong peak along the surface normal. These ESDIAD patterns are due to  $\text{H}^+$  only—we see only  $\text{H}^+$  for monolayer coverages of  $\text{NH}_3$ . Bozso<sup>26</sup> has proposed on the basis of XPS and ISS spectroscopies that  $\text{NH}_3$  completely



**Figure 6.** (a) ESDIAD of a saturation doses of HF on stepped  $\text{Si}(100)$  at 230 K. (b) Model showing that the  $\text{F}^+$  emission is parallel to the surface dimers, i.e., along the azimuth of the Si-Si dimer bond. (c, d) The polar angle of the ion emission at 130 K (and thus the Si-F bond) is  $29 \pm 3^\circ$  and the fwhm is  $19^\circ$ . Note that the ion emission peaks are sharp, indicating the silicon dimer is not in two different asymmetric forms. The intensity versus desorption angle plot, c, was taken with a compression field (due to a 80-V bias applied to the sample) and is a "slice" through the perspective plot a. The polar angle was determined in other experiments where there was no compression field.

dissociates on  $\text{Si}(100)$  to form surface nitrogen and hydrogen and that at room temperature the nitrogen goes subsurface. Hlil<sup>27</sup> infers the existence of surface  $\text{NH}_x$  groups on the basis of photoelectron spectroscopy at room temperature. Our results are consistent with the existence of surface  $\text{NH}_x$  fragments at low coverages. The low-coverage emission is not due to Si-H bonds, since the results of the HF adsorption studies (see below) indicate that the  $\text{H}^+$  emission would be peaked along the dimer bonds (similar to the  $\text{F}^+$  emission from the Si-F bonds). The weakness of the emission, while not quantitative, suggests that the  $\text{NH}_x$  species is a minority state. The structure of the high-coverage state is difficult to interpret. Any  $\text{NH}_x$  species on a  $2 \times 1$  surface would have to be greatly perturbed from its normal bond angle to give a N-H bond aligned along the surface normal. However, a novel metastable hydrogen chemisorption state<sup>36</sup> has been identified recently with  $\text{H}^+$  ESDIAD emission along the surface normal for hydrogen-dosed  $\text{Si}(100)$ .<sup>37</sup> The above difficulties, and the possibility of the formation of a bulk nitride-like state (that still must preserve the  $2 \times 1$  LEED pattern), keep us from further analysis of the ESDIAD of the high-coverage state at the present time.

**HF.** The ESDIAD of an apparent (see below) 1 langmuir of HF dosed at 130 K onto a stepped  $\text{Si}(100)$  surface is shown in Figure 6. The primary ion is  $\text{F}^+$ , with minor  $\text{H}^+$  contributions.

The difficulties of dosing HF deserve further comment. HF displaces  $\text{N}_2$  and  $\text{H}_2$  from the doser and vacuum system walls (the  $\text{N}_2$  and  $\text{H}_2$  flux is less than the HF flux for the data shown here but varies depending on the preconditioning of the doser), and thus the observed pressure rise (and apparent dose) is an upper bound for the HF partial pressure. We believe neither  $\text{N}_2$  nor  $\text{H}_2$  adsorb onto  $\text{Si}(100)$

(36) Appelbaum, J. A.; Hamann, D. R.; Tasso, K. H. *Rev. Phys. Lett.* 1977, 39, 1487.

(37) Rowe, J. E. *Proceedings of DIET-III*; Shelter Island, NY, May 20-22, 1987, in press.

in significant amounts at 130 K. Further, the dosing arrangement for HF increases the HF pressure in the region of the crystal, compensating for the dilution effects. The ESDIAD intensity increases monotonically as a function of dose, reaching saturation at an apparent dose of 0.02 langmuir. Auger spectroscopy of the surface after a saturation dose of HF shows adsorbed fluorine (which rapidly decreases with electron beam dose, making quantitative measurements of fluorine by this technique difficult) and no evidence of adsorbed nitrogen or oxygen. In experiments in which the surface is dosed with hydrogen activated by the proximity of the mass spectrometer ionizer filament, we find that hundreds of langmuirs of dose are required to produce significant coverage. This behavior has been seen by other workers.<sup>38-40</sup> For the current situation, the hydrogen is unactivated and the dose is, at most, tens of langmuirs. Thus we feel confident that the ESDIAD pattern of Figure 6 represents a saturation dose of HF on Si(100) with no coadsorbed material.

The most intense beams of  $F^+$  emission desorb along azimuths *parallel* to the step edges and thus parallel to the dimers (the beams in the up- and downstairs directions are mostly due to residual minority dimer domains). The ESDIAD pattern persists following heating to at least 600 K, showing only reversible beam broadening. This behavior is expected from the dissociative chemisorption model, where the ion direction is controlled by the Si-F bond directions.

The correlation of polar ion emission angle with polar bond angle is complicated by image charge forces and ion reneutralization effects.<sup>41,42</sup> Calculations<sup>42</sup> indicate that the maximum in the ion angular distribution is within a few degrees of the bond direction, when the emission direction is not too far from the surface normal ( $\leq 30-40^\circ$ ) and the ion has more than a few electronvolts of kinetic energy. A retarding field analysis of the  $F^+$  ions demonstrates that the maximum of the ion energy distribution is  $\geq 4$  eV. Thus, we determine a polar angle of  $29 \pm 3^\circ$  for the  $F^+$  emission, with a full width at half-maximum of  $19^\circ$  at 130 K (Figure 6c); this implies a polar angle of  $\sim 29^\circ$  for the Si-F bond (Figure 6d). Measurements of angles are made under field-free conditions, in which the bias voltage used to "compress" the ESDIAD patterns<sup>29,31,32</sup> is reduced to zero.

### Discussion

We have presented ESDIAD patterns of  $H_2O$ ,  $NH_3$ , and HF adsorbed on stepped Si(100)2 $\times$ 1. At low coverages all of these chemisorption states exhibit emission directed away from the surface normal, indicating that the bonds that cleave to form the ions are inclined away from the surface normal. The relative angles and directions of ion emission allow one to derive characteristics of the chemisorption states, in particular, the bonds being formed at the surface and the existence of interactions that induce local ordering in the surface species. In each case, irreversible changes in the patterns (loss of signal intensity, changes in symmetry) due to desorption or reaction are found only after heating to temperatures greater than 600 K, indicating that the chemical state of the adsorbed species is not strongly perturbed below 600 K. Reversible changes (ion beam broadening, azimuthal ordering) are seen from 125-600 K.

We find the evidence most consistent with dissociative chemisorption of HF,  $H_2O$ , and  $NH_3$  (to form  $H + F$ ,  $H + OH$ , and  $H + NH_x$ , respectively) on stepped Si(100). Dissociative chemisorption is controversial primarily in the case of  $H_2O$  adsorption on Si(100).<sup>19-25</sup>  $H_2O$  adsorption on silicon (as well as on a number of other surfaces) has been recently reviewed.<sup>43</sup> In brief, studies using vibrational spectroscopies<sup>19-23</sup> are interpreted in terms of dissociative chemisorption whereas several UPS<sup>24,25</sup> studies have been rationalized in terms of molecular adsorption. On comparison of the past results of studies of  $H_2O$  chemisorption,<sup>43</sup> the evidence for dissociative chemisorption of  $H_2O$  on Si(100) is compelling. Further, our ESDIAD studies find no irreversible change between 145 and 700 K in the observed pattern, suggesting a single (e.g., dissociative) chemisorption state. Lastly, studies of  $H_2O$  and silicon co-condensed in Ar matrices at 15 K<sup>44</sup> contain IR spectra that show initially formation of the complex  $Si(H_2O)$  that rearranges spontaneously to form  $HSiOH$ . This models the dissociative chemisorption of  $H_2O$  on silicon surfaces and shows that dissociation is expected even at 15 K.

We also found a reversible temperature-dependent azimuthal ordering in the ESDIAD pattern of OH on the planar Si(100) surface.<sup>35</sup> While determination of the barrier toward azimuthal disordering would require a detailed model of the probability density for the ensemble of excited states at various temperatures, an order-of-magnitude estimate of the energy can be obtained from the temperature at which the ordering is lost. This estimate is 1.6 kJ/mol (0.4 kcal/mol, or 200 K). This information, along with the observation that the  $H^+$  emission is *perpendicular* to the dimer direction, leads us to propose<sup>35</sup> the models in Figure 4.

$NH_3$  chemisorption on Si(100) has been studied previously by LEED, Auger, TDS, STM, ISS, and photoemission methods.<sup>26,27,45-48</sup> Dissociative chemisorption is the accepted model of  $NH_3$  chemisorption on Si(100). We were interested in  $NH_3$  silicon surface chemistry both for its practical and scientific merits and to test the interactions proposed for the Si(100)- $H_2O$  system. If  $NH_3$  dissociates to  $NH_x$  and adsorbs in the same manner as  $H_2O$ , and if the dative interaction is predominant, then the azimuthal ordering would be weaker. If the hydrogen-bonding interaction is dominant, then the ordering would be stronger for the  $NH_x$ .

Our results indicate the presence of  $NH_x$  fragments (see above) consistent with the results of Hlil.<sup>27</sup> The azimuthal ordering is less evident than that seen for Si(100)- $H_2O$ , which would indicate the predominance of the hydrogen-bonding interaction, if the chemisorption environment is the same. However, the model proposed by Bozso and Avouris<sup>26</sup> requires that the adjacent sites be filled for any  $NH_x$  species to survive. If sites adjacent to the  $NH_x$  are all filled, the dative interaction should be shut off, since there is no acceptor orbital to interact with the lone pair. However, if the dative interaction is predominant and the interaction becomes too strong, one would expect that the adsorbate would deprotonate and yield the nitride, as is seen at higher temperatures.<sup>26</sup> For these reasons the

(38) Law, J. T. *J. Chem. Phys.* **1959**, *30*, 1568.

(39) Ibach, H.; Rowe, J. E. *Surf. Sci.* **1974**, *43*, 481.

(40) Chung, M. F.; Haneman, D. *Surf. Sci.* **1966**, *37*, 1879.

(41) Mišković, Z.; Vukanić, J.; Madey, T. E. *Surf. Sci.* **1984**, *141*, 285.

(42) Mišković, Z.; Vukanić, J.; Madey, T. E. *Surf. Sci.* **1986**, *169*, 405.

(43) Thiel, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, *7*, 211.

(44) Ismail, Z. K.; Hauge, R. H.; Fredin, L.; Kauffman, J. W.; Margrave, J. L. *J. Chem. Phys.* **1982**, *77*, 1617.

(45) Heckingbottom, R.; Wood, P. R. *Surf. Sci.* **1973**, *36*, 594.

(46) Glachant, A.; Saidi, D.; DeLord, J. F. *Surf. Sci.* **1986**, *168*, 672.

(47) Kubler, L.; Hlil, E. K.; Balmont, D.; Gewinner, G. *Surf. Sci.* **1987**, *183*, 503.

(48) Avouris, Ph.; Bozso, F.; Hamer, R. J. *J. Vac. Sci. Technol. B*, in press (private communication).

question of the operant interaction remains open.

Our Si(100)-HF results are also in accord with the dissociative chemisorption model. The ESDIAD pattern persists following heating to at least 600 K, showing only reversible beam broadening. Furthermore, studies of silicon atoms co-condensed with HF in Ar matrices at 15 K<sup>49</sup> show the formation of HSiF, corroborating a dissociative model. The relatively high energy of the F<sup>+</sup> ions and the desorption angle close to the surface normal allow the determination of the bond angle. The inferred Si-F polar bond angle ( $\sim 29^\circ$ ) is greater than the angle one would expect from tetrahedral bond angles and symmetric dimers, for which a 19–21° polar angle is predicted. This discrepancy can be rationalized either by postulating a relaxation of the dimer into an asymmetric configuration or by lengthening the dimer bond. For the bond lengthening, if one assumes tetrahedral silicon angles except for the dimer bond, and allows only rotations in the second layer, one obtains a model with a silicon-silicon dimer bond length of 2.65 Å (13% longer than the bulk bond length—compare with 2.34 Å<sup>50</sup>). The model of dissociative adsorption of HF across the Si-Si dimer bond to form Si-H and Si-F units is in accord with earlier proposals based on photoemission<sup>50</sup> and EELS evidence.<sup>51</sup>

The ESDIAD beams show no sign of being double-peaked in any of the major directions, which indicates that at least for the dimer bond with fluorine attached there is no evidence for rocked<sup>5</sup> or twisted<sup>13</sup> dimers as has been suggested for the clean surface. It is interesting to note that the ESDIAD pattern is centered when the crystal is rotated  $5 \pm 1^\circ$  toward the upstairs direction away from the

macroscopic surface normal. This indicates that the center of the ESDIAD pattern is normal to the terraces, not the macroscopic surface.

### Summary

In summary, for adsorption temperature between 125 and 300 K, we find evidence for dissociatively chemisorbed states for all of the protic hydrides investigated (H<sub>2</sub>O, NH<sub>3</sub>, HF) on the stepped Si(100) surface. For monolayer coverages of each of the species, the LEED pattern shows no change from that of the clean 2×1 reconstructed surface. The ESDIAD patterns are dominated by emission in directions away from the surface normal in each case.

For H<sub>2</sub>O, the H<sup>+</sup> emission is along azimuths perpendicular to the dimer axes, so that the OH bonds are inclined with azimuths nearly perpendicular to the dimer axes azimuths. Reversible temperature effects (azimuthal order/disorder) are seen for OH on planar Si(100), which we associate with adsorbate-substrate interactions.

NH<sub>x</sub> species are believed to be produced when NH<sub>3</sub> is adsorbed on Si(100). The H<sup>+</sup> emission azimuths (and NH bond azimuths) at low coverages are nearly perpendicular to the dimer axes azimuths.

A saturation coverage of HF on Si(100) is shown to give F<sup>+</sup> ion emission along the azimuths of the silicon dimer bonds, and the polar angle of the Si-F bond measured with respect to the surface normal is  $\sim 29^\circ$ . No evidence is seen for two different asymmetries of the dimers on the Si(100)2×1-HF surface.

**Acknowledgment.** We wish to acknowledge Y. Chabal for the donation of the stepped Si(100) crystal, C. U. S. Larsson and A. Flodström for contributions to the H<sub>2</sub>O work, and P. A. Thiel for valuable discussions. This work was supported in part by the Division of Basic Energy Sciences of the U.S. Department of Energy.

**Registry No.** H<sub>2</sub>O, 7732-18-5; NH<sub>3</sub>, 7664-41-7; HF, 7664-39-3; Si, 7440-21-3.

(49) Ismail, Z. K.; Fredin, F.; Huage, R. H.; Margrave, J. L. *J. Chem. Phys.* **1982**, *77*, 1626.

(50) McFeely, F. R.; Morar, J. F.; Shinn, N. D.; Landgren, G.; Himpsel, F. J. *Phys. Rev. B: Condens. Matter* **1984**, *30*, 764.

(51) Shinn, N. D.; Morar, J. F.; McFeely, F. R. *J. Vac. Sci. Technol. A* **1984**, *2*, 1593.

## A Study of $\pi$ -Bonded CO on Fe(100)<sup>†</sup>

S. D. Cameron

*Exxon Corporate Research Laboratory, Exxon Research and Engineering,  
Annandale, New Jersey 08801*

D. J. Dwyer\*

*Exxon Research and Development Laboratory, Exxon Research and Engineering, Baton Rouge,  
Louisiana 70821*

*Received July 17, 1987. In Final Form: September 22, 1987*

The chemisorption of CO on the Fe(100) surface has been studied by XPS, LEED, TPD, and He II UPS. All data are consistent with earlier suggestions that CO in the  $\alpha_3$  state is bound through both the oxygen and carbon end of the molecule. UPS data reveal extensive rehybridization of the molecule in the  $\alpha_3$  state whereas the  $\alpha_1$ - and  $\alpha_2$ -CO states are more typical of chemisorbed CO. LEED and XPS data reveal that the stoichiometry of the dissociation of the  $\alpha_3$  state is controlled by the availability of c(2×2) sites.

### Introduction

At temperatures below 330 K, CO chemisorbs sequentially into three molecular states ( $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$ ) on the Fe(100) surface.<sup>1,2</sup> High-resolution electron energy loss

spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD) clearly identify the three molecular states as discrete chemical entities with distinct heats of adsorption, carbon-oxygen stretching frequencies, and core level

<sup>†</sup> Presented at the symposium entitled "Molecular Processes at Solid Surfaces: Spectroscopy of Intermediates and Adsorbate Interactions", 193rd National Meeting of the American Chemical Society, Denver, CO, April 6–8, 1987.

(1) Benziger, J.; Madix, R. J. *Surf. Sci.* **1980**, *94*, 119.

(2) Moon, D. W.; Dwyer, D. J.; Bernasek, S. L. *Surf. Sci.* **1985**, *163*, 215.