Imaging of Chemical-Bond Formation with the Scanning Tunneling Microscope: NH_3 Dissociation on Si(001)

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We have directly observed chemisorption-induced changes in surface chemical bonding using a scanning tunneling microscope (STM). The dissociative adsorption of NH_3 on Si(001) preserves the (2×1) local symmetry, but STM images reveal changes in the spatial distribution of occupied electronic states which allow us to distinguish reacted and unreacted Si(001) dimers. The STM results on the reacted surface are interpreted in terms of tunneling through localized Si-H bonding orbitals of a Si(001)-(2×1)H monohydride.

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Since its development by Binnig *et al.*,[1] scanning tunneling microscopy (STM) has become an important technique for imaging surfaces on the atomic scale. Recent studies have also shown that the STM can be used in a spectroscopic mode to reveal the energies and spatial location of the surface electronic states.[2-4] Since electronic structure and chemical reactivity are intimately related, this suggests that the STM has great potential as a tool for the study of *chemistry* at surfaces. This requires the ability to observe and interpret adsorbate-induced changes in localized electronic states associated with chemical bonding at the surface, which has not been previously demonstrated. In a recent study of oxygen adsorption on GaAs,[5] long-range band bending prevented details of the adsorption and bonding from being studied. In studies of metal adsorbates on Si(111),[6,7] adsorption was accompanied by a change in surface symmetry so that changes in the surface geometric and electronic structures could not be distinguished.

In this Letter, we report the first use of STM as an *in situ* probe for studying a surface chemical *reaction* at the atomic level, using the interaction of NH_3 with Si(001)[8,9] as a prototypical gas-surface reaction system. We use STM to probe both the atomic structure and the density of states of the surface before and after reaction with NH_3. While the (2×1) surface symmetry is maintained, we find pronounced differences between the spatial distribution of the occupied surface states on the clean and NH_3-dosed surfaces which we interpret in terms of electronic states associated with Si-Si and Si-H bonding interactions. Our results support a model for the mechanism of NH_3 dissociation on Si(001)[8] and the formation of a Si(001)-(2×1)H monohydride surface layer.

The STM used in this study has been described previously.[2,10,11] Constant-separation I-V curves were recorded simultaneously to provide density-of-states information.[2] After predosing of the vacuum chamber with NH_3, the Si(001) wafer (n type, 6 mΩ cm) was cleaned by annealing to 1330 K for 3 min at a pressure of $<10^{-9}$ Torr and then cooled to 300 K. After tunneling (1 nA current) on the clean Si(001) surface[10,11] the sample was pulled back from the tungsten tip and dosed with typically 1-10 L [1 L (langmuir) $=10^{-6}$ Torr sec] NH_3 or ND_3 (the sticking coefficient[8] is $\simeq 1$). In some experiments, the NH_3 was allowed to dose the sample continually at a background pressure of 10^{-9}-10^{-8} Torr, with equivalent results.

In Fig. 1 we show STM images of the clean Si(001) surface at negative [Fig. 1(a), -2 V] and positive [1(b), $+1.2$ V] sample bias and of the NH_3-dosed surface at negative [Figs. 1(c),1(d), -2 V] bias. Images of the NH_3-dosed surface at positive bias (not shown) look nearly identical to those at negative bias. Polarity-dependent changes in STM images reflect differences in the spatial contribution of occupied and unoccupied electronic states. To bring out fully the electronic symmetry of these surfaces, in Fig. 2 we show corrugation profiles measured along the $\langle 110\rangle$ direction (perpendicular to the dimer rows) for the clean surface at negative (Fig. 2, curve a, -2 V) and positive (curve b, $+1.2$ V) bias and for the NH_3-dosed surface at -2 V bias (curve c). The presence of missing-dimer defects[11-13] allows us to determine unambiguously the positions of the dimers on clean and NH_3-dosed samples under various biasing conditions. The corrugation profiles in Fig. 2 have been aligned such that they start and end *between* the dimer rows and pass directly above the centers of the dimers as indicated.

For tunneling out of the occupied states of the clean Si(001) surface [Fig. 1(a)] STM topographs reveal rows of bean-shaped protrusions with a (2×1) local symmetry. Previous studies[3,10,11] have demonstrated that each of these protrusions is a dimer and that under these conditions, tunneling occurs through the occupied π dangling bond state associated with the dimer bonding. The corrugation profile (Fig. 2, curve a) shows a maximum above the center of each dimer and a minimum between dimers. Conversely, Fig. 1(b) shows an STM topograph taken at $+1.2$ V sample bias where electrons tunnel

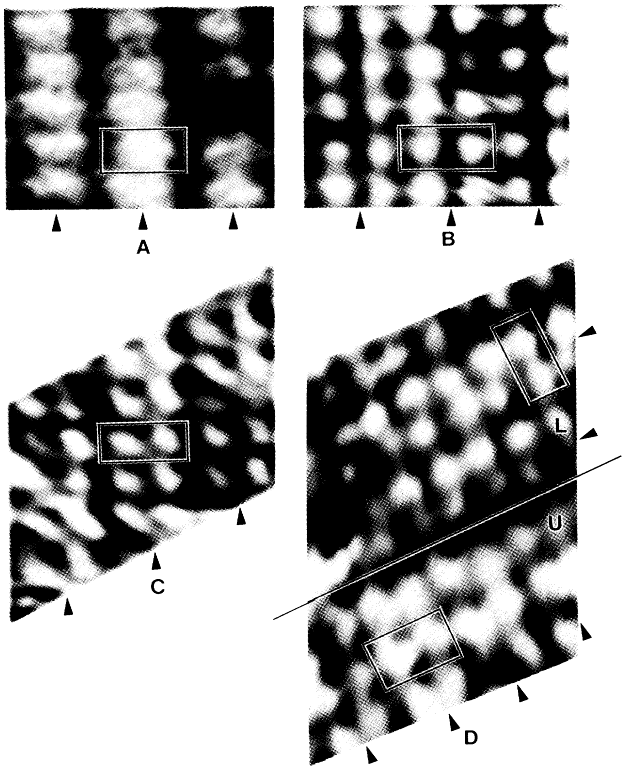

FIG. 1. STM topographic images probing the (a) occupied (-2 V bias) and (b) unoccupied ($+1.2$ V bias) surface states of clean Si(001) and the (c),(d) occupied (-2 V sample bias) states of NH_3-dosed Si(001). In each figure, the arrows point in the $\langle 1\bar{1}0\rangle$ direction and point directly at the center of the dimer rows. Each box outlines a (2×1) unit cell with a dimer centered in the box. (a) contains a single "missing-dimer defect" (Ref. 12). In (d), the position of a single atomic step is indicated by the solid line, and the upper and lower terraces are identified by "*U*" and "*L*".

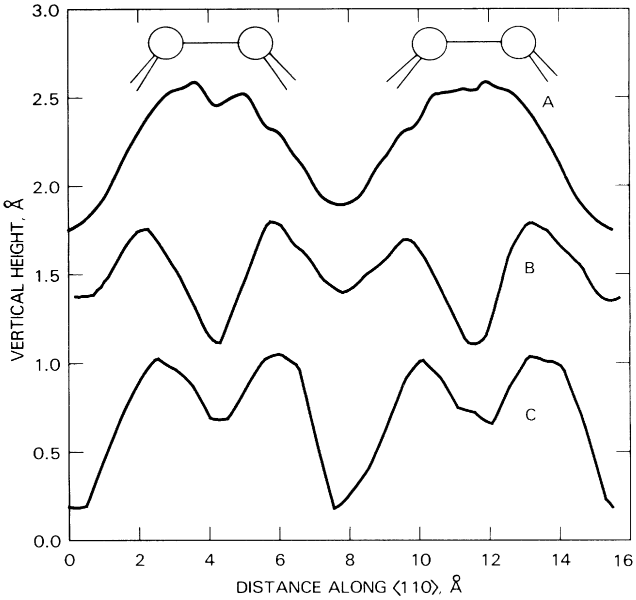

FIG. 2. STM corrugation profiles along the $\langle 110\rangle$ direction on clean Si(001) at -2 V bias (curve *a*), clean Si(001) surface at $+1.2$ V bias (curve *b*), and NH_3-dosed Si(001) at -2 V bias (curve *c*). Each profile starts between two dimer rows, passes over the centers of two dimers, and ends between two rows.

from the tip into the unoccupied states of the sample. In this case translation along $\langle 110\rangle$ shows both a minimum between the dimer rows, and a second, even *deeper* minimum along the *center* of each dimer row, as can be clearly seen in Fig. 2, curve *b*. The overall symmetry remains (2×1).

The differences between these images at positive and negative bias can be understood in terms of the bonding and antibonding states involved in tunneling. As discussed by Appelbaum, Baraff, and Hamann,[14] the occupied π_b bonding state of Si(001) has A_1 symmetry and is therefore even under reflection through both the (110) and $(1\bar{1}0)$ planes, leading to the "bean-shaped" dimer structures in Fig. 1(a). In contrast, the unoccupied π_a antibonding state has B_1 symmetry, so that *this* state has a *node* along the center of the dimer bond, which is clearly observed in the STM image in Fig. 1(b) and the corrugation profile (Fig. 2, curve *b*). We conclude that these STM images of clean Si(001) reflect the symmetry properties of the bonding and antibonding states.

Figure 1(c) shows an STM image of the NH_3-dosed Si(001) surface at -2 V bias. From a comparison of this image with that of the clean Si(001) surface shown in Fig. 1(a) (also -2 V bias), we reach two important conclusions: (1) The reacted surface preserves the (2×1) symmetry, and (2) while on the clean surface we observed bean-shaped dimers, on the NH_3-dosed surface we observe tunneling primarily from the *ends* of the dimers. Thus, the corrugation profile in Fig. 2, curve *c*, shows that translation along $\langle 110\rangle$ reveals a strong minimum between the dimer rows with a second shallower minimum along the center of the dimer rows. Figure 1(d) shows another region of the surface which includes a single atomic step; here the gray scale has been adjusted to reveal the (2×1) atomic structure on both the lower and upper terraces. The upper part (lower terrace) is slightly disordered and the dimers adjacent to the step edge are apparently buckled; the slight disorder likely results from defects present on the clean surface or from strain associated with the step.[11] We shall concentrate on the ordered (2×1) structure, which comprises the vast majority of the surface. We also note the similarity between *occupied-state* images of the NH_3-dosed surface [Figs. 1(c),1(d)] and *unoccupied-state* images of the clean surface [Fig. 1(b)].

In order to study changes in the surface density of

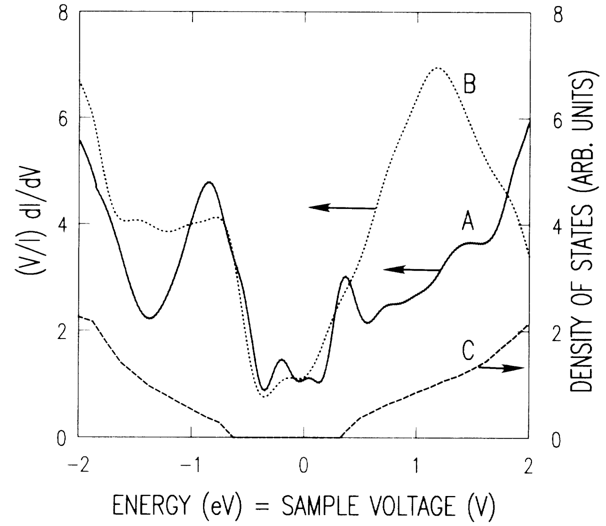

FIG. 3. Tunneling spectroscopy measurements on ordered (2×1) regions of clean (curve *a*) and NH_3-dosed (curve *b*) Si(001) surfaces. Curve *c* shows the calculated silicon bulk density of states (after Ref. 15).

states (DOS) induced by the reaction, we have also measured the tunneling I-V characteristics on clean and NH_3-dosed Si(001) surfaces and have averaged them over well-ordered (2×1) regions. DOS information is the obtained by our calculating the quantity $(V/I)dI/dV$, which is approximately proportional to the surface DOS, normalized such that at $V=0$, $(V/I)dI/dV=1$.[4] Figure 3 shows this quantity plotted versus sample bias before (curve *a*) and after (curve *b*) reaction with NH_3, along with the calculated bulk density of states for silicon (curve *c*).[15] For the clean surface (Fig. 3, curve *a*), we find a gap extending down to $\simeq -0.35$ eV with a pronounced peak at 0.8 eV below the Fermi level (E_F). Above the Fermi level, the DOS increases starting at 0.2 eV above E_F with a sharp peak near 0.35 eV. We assign the peak at -0.8 eV to the "dangling bond" π_b level and the peak at $+0.35$ eV to the corresponding π_a antibonding level on the basis of the original theoretical work of Appelbaum, Baraff, and Hamann[14] for the symmetric dimer model. Our values are also in agreement with photoemission[16] and inverse photoemission[17] spectra, which reveal states at -0.7 and $+0.3$ eV. After dosing, Fig. 3, curve *b*, shows that the π_b state of the clean surface is replaced by a broad unstructured shoulder. The DOS[15] for bulk Si (Fig. 3, curve *c*) shows a similar onset, leading us to associate this structure with tunneling from valence-band states. We also find that the unoccupied π_a state is eliminated, and we instead find a broad peak with a maximum around 1.0 eV above E_F. We attribute this peak to a Si-H antibonding state, on the basis of calculations by Ciraci *et al.*[18] and the energy-loss spectroscopy data at Maruno *et al.*[19]

To study more strongly bound electronic states, we have measured normal-emission ultraviolet photoemission (UPS) spectra for the clean and NH_3-dosed Si(001) surfaces and have used the difference spectrum to bring out changes in the DOS caused by NH_3 adsorption.[9] In agreement with our tunneling spectroscopy results, the difference spectrum showed a dip at 0.8 eV below E_F due to the elimination of the π_b surface state upon NH_3 adsorption. Peaks in the difference spectrum near -4.5 eV were attributed to Si-H and Si-N bonding states. UPS spectra of NH_3-dosed and H-dosed Si(001) were nearly identical in the region between E_F and $\simeq -4$ eV, confirming that there are no occupied N-related states near E_F.

We interpret the above findings in terms of the surface electronic structure and the reaction mechanism. UPS studies on Si(001)[9] and on Si(111)[20] have shown that at 300 K, NH_3 dissociates on Si surfaces. Ion scattering and x-ray photoemission spectroscopy experiments[8] on Si(001) showed that the nitrogen atoms reside mostly in subsurface sites, so that the surface consists primarily of hydrogen interacting with the Si(001) dimers. Since STM shows that the (2×1) symmetry is preserved by the reaction, it can be concluded that the dimer bond remains intact and the surface is essentially a silicon monohydride phase (one H atom per surface Si atom). We find no evidence for dihydride formation,[21] which would lead to a (1×1) local symmetry. This indicates that because the monohydride phase has no unsaturated dangling bonds, its chemical reactivity is very low, so that the reaction of Si(001) with NH_3 at 300 K is self-limiting at the monohydride stage.

Since virtually all of the energy decrease achieved by dimerization is associated with the low-lying σ state, rather than the π state, formation of the monohydride has little effect on the Si-Si dimer bond strength. As a result, theoretical calculations[22,23] show that the Si atom positions are nearly *identical* for both Si(001)-(2×1) [Fig. 1(a)] and Si(001)-(2×1)H [Figs. 1(c),1(d)], so that differences between the STM images must be associated with the different spatial locations of Si-Si and Si-H bonding states. To interpret STM images of the NH_3-dosed surface at -2 V sample bias, we must consider the nature of the electronic states lying between E_F and $\simeq 2$ eV below E_F. Since our UPS spectra show that N-related states lie $\simeq 4$ eV below E_F and ion scattering experiments further indicate that the N atoms mostly occupy subsurface positions, we do not expect to detect N atoms at the -2 V bias used in the STM experiments, and indeed, we find no evidence for them.

Appelbaum *et al.*[22] and Ciraci *et al.*[18] demonstrated that the interaction of hydrogen with the π-bond orbitals Si(001) lowers their energy and leads to two new Si(001)-(2×1)H surface state bands whose DOS peak at $\simeq 3$ and $\simeq 4.5$ eV below the valence-band maximum. The band at -4.5 eV derives primarily from the originally occupied π_b state of Si(001) while the band near

-3 eV derives primarily from the originally unoccupied π_a state. Since these states peak far from E_F, we might anticipate that the state density near -2 eV would be low. In fact, extensive hybridization of the H 1*s* level with states *throughout* the valence band[18,22] provides sufficient state density for normal STM operation. One would expect that tunneling out of the Si-H states will be favored because of the spatial extent of the Si-H bonds above the Si surface. Our images indicate that tunneling indeed occurs primarily from the Si-H bonding states, since we see maxima near the ends of the dimers with a minimum along the center of each row. The presence of this minimum and the similarity between the *occupied* state images of the H-covered surface and the *unoccupied* states of the clean surface suggest that the states involved in tunneling from the NH_3-dosed surface are Si-H bond states which are primarily derived from the π_a dangling-bond level for the clean Si(001) surface.

In summary, we have studied a prototypical gas-surface reaction, the dissociative chemisorption of NH_3 on Si(001). The STM images clearly show changes in the occupied electronic states of the surface induced by the chemical reaction. Since the Si-atom positions remain virtually unchanged by H adsorption, these changes can be directly attributed to the different spatial distributions of Si-Si and Si-H bonding states.

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[1] G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, Phys. Rev. Lett. **50**, 120 (1983).

[2] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).

[3] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Science **234**, 304 (1986).

[4] R. M. Feenstra, J. A. Stroscio, and A. P. Fein, Surf. Sci. **181**, 295 (1987).

[5] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **58**, 1668 (1987).

[6] E. J. van Loenen, J. E. Demuth, R. M. Tromp, and R. J. Hamers, Phys. Rev. Lett. **58**, 373 (1987).

[7] R. J. Wilson and S. Chiang, Phys. Rev. Lett. **58**, 369 (1987).

[8] F. Bozso and Ph. Avouris, Phys. Rev. Lett. **57**, 1185 (1986).

[9] Ph. Avouris, F. Bozso, and R. J. Hamers, to be published.

[10] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985).

[11] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. B **34**, 5343 (1986).

[12] K. C. Pandey, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors, San Francisco, California, 1984,* edited by D. J. Chadi and W. A. Harrison (Springer-Verlag, New York, 1985), p. 55.

[13] R. J. Hamers, R. M. Tromp, and J. E. Demuth, Surf. Sci. **181**, 346 (1987).

[14] J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. B **14**, 588 (1976).

[15] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **10**, 5095 (1974).

[16] F. J. Himpsel and D. E. Eastman, J. Vac. Sci. Technol. **16**, 1297 (1979).

[17] F. J. Himpsel and Th. Fauster, J. Vac. Sci. Technol. A **2**, 815 (1984).

[18] S. Ciraci, R. Butz, E. M. Oellig, and H. Wagner, Phys. Rev. B **30**, 711 (1984).

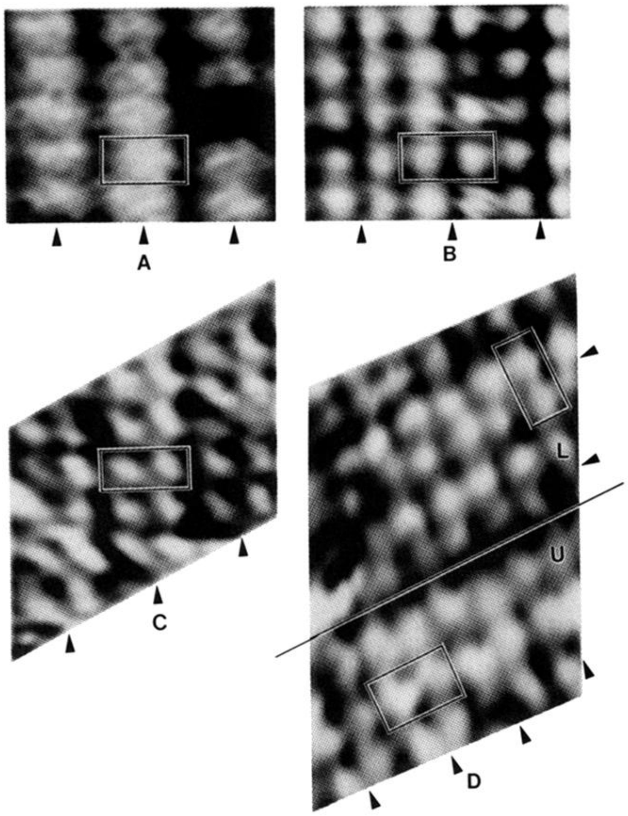
[19] S. Maruno, H. Iwasaki, K. Horioka, S. T. Li, and S. Nakamura, Phys. Rev. B **27**, 4110 (1983).

[20] L. Kubler, E. K. Hlil, D. Bolmont, and G. Gewinner, Surf. Sci. **183**, 503 (1987).

[21] T. Sakurai, and H. D. Hagstrum, Phys. Rev. B **14**, 1593 (1976).

[22] J. A. Appelbaum, G. Baraff, D. R. Hamann, H. D. Hagstrom, and T. Sakurai, Surf. Sci. **70**, 654 (1978).

[23] Y. Chabal and K. Raghavachari, Phys. Rev. Lett. **53**, 282 (1984).



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