

Formation of a Surface-Mediated Donor–Acceptor Complex: Coadsorption of Trimethylamine and Boron Trifluoride on the Silicon (001) Surface

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The interaction of trimethylamine and boron trifluoride on the Si(001) surface has been investigated using X-ray photoelectron (XP) spectroscopy. XP spectra show the TMA forms a dative bond with the clean Si(001) surface, while on the clean surface BF_3 bonds dissociatively, yielding $\text{Si}-\text{BF}_2$ and $\text{Si}-\text{F}$ species. If the surface is first “saturated” with TMA, however, BF_3 will continue to adsorb, giving rise to new F(1s) XP peaks. Based on an analysis of the energies and thermal behavior of these peaks, we propose that the adsorption of TMA and BF_3 on the Si(001) surface leads to the formation of a novel surface-mediated donor–acceptor complex of the structure $\text{TMA}-\text{Si}-\text{Si}-\text{BF}_3$.

The (001) surface of silicon consists of “dimers”, formed by pairs of Si atoms linked with a strong σ bond and a weak π bond.¹ Recently, we have shown that trimethylamine (TMA) can form surprisingly stable dative-bonded complexes with the Si(001) surface.² The stability of these complexes arises from the fact that when the N lone pair interacts at one end of a $\text{Si}=\text{Si}$ dimer, the electron density is largely transferred to the “nonbonded” Si atom within the same dimer. The remaining Si dimer atom is extremely electron rich and presumably should be a good electron donor (Lewis base). Boron trifluoride (BF_3) is a good Lewis acid that forms donor–acceptor complexes with electron-rich molecules, such as trimethylamine.^{3,4} In this paper, we show that preadsorption of TMA on Si(001) dramatically modifies the interaction of BF_3 molecules with the surface, and we propose that sequential adsorption of TMA followed by BF_3 leads to the formation of a novel surface-mediated donor–acceptor complex $\text{TMA}-\text{Si}-\text{Si}-\text{BF}_3$.

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of $<1 \times 10^{-10}$ Torr. Si(001) samples ($0.07\text{--}0.13 \Omega\cdot\text{cm}$, P-doped) were cleaned as described previously and then annealed to 1400 K in UHV to produce a clean, well-ordered (2×1) reconstructed Si(001) surface.⁵ TMA and BF_3 (purity $>99\%$) were introduced to the UHV chamber through a variable leak valve, using the rise in chamber background pressure to estimate the exposure. Reagent purity was verified with an in situ mass spectrometer. Exposures are given in langmuirs ($1 \text{ langmuir} \equiv 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$). X-ray photoelectron (XP) spectra were obtained using Al $\text{K}\alpha$ radiation (1486.6 eV). The Si(2p) peaks were used as an internal standard for both energy and intensity. Spectra reported here have been adjusted to yield a constant 99.4 eV binding energy for the bulk Si($2p_{3/2}$) line.

Before presenting the data from the coadsorption of TMA and BF_3 on the surface, we first summarize the main features associated with the individual molecules.

Figure 1 shows the N(1s) (Figure 1a) and C(1s) (Figure 1b) XP spectra obtained when a cold (190 Kelvin) Si(001) surface

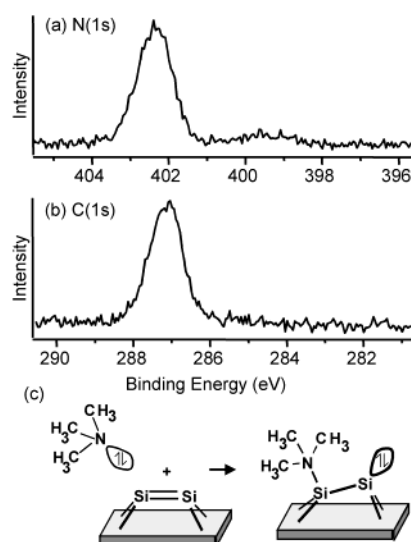


Figure 1. XP spectra of Si(001) surface exposed to 20 langmuirs TMA at 190 K: (a) N(1s); (b) C(1s); (c) bonding of TMA on the surface.

was exposed to 20 langmuirs TMA. The N(1s) spectrum (Figure 1a) is dominated by a large, narrow (fwhm = 1.0 eV) peak with a binding energy of 402.3 eV. A tiny peak is also observed at 399.2 eV ($\sim 7\%$ of total peak area). The C(1s) spectrum (Figure 1b) shows a single peak at 287.0 eV with a fwhm of 1.0 eV.

The 402.3 eV binding energy of the large N(1s) peak is nearly 3 eV higher than that typically encountered in Si-bonded nitrogen compounds in which the N atom has the tertiary coordination. For example, aniline, ammonia, and dimethylamine all bond to Si(001) via cleavage of one N–H bond, yielding 3-fold coordination for N and giving rise to N(1s) binding energies of 399.5–400.2 eV.^{2,6,7} The 402.3 eV binding energy is close to that observed for ammonium salts such as NH_4Cl (403.2 eV),² $(\text{CH}_3)_4\text{NBr}$ (401.6 eV),⁸ and $(\text{CH}_3)_4\text{NCl}$ (402.5 eV).⁹ In a detailed experimental and computational study,² we recently showed that these high N(1s) and C(1s) binding energies arise because TMA forms a highly ionic dative-bonded complex with the Si(001) surface. The N atom of the

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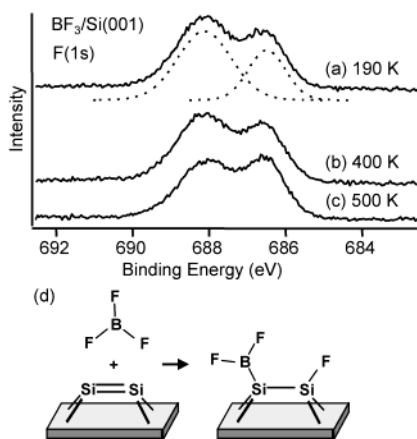


Figure 2. XP spectra of Si(001) surface exposed to 20 langmuirs BF_3 at 190 K: (a) F(1s); (b) bonding of BF_3 on the surface.

TMA donates electron density to the Si(001) surface and adopts a quaternary coordination like that depicted in Figure 1c, with a strong positive charge on the N atom and a partial negative charge on the exposed Si atom; this Si atom essentially has a "lone pair" orbital centered on it.

Figure 2a shows the F(1s) XP spectrum of a clean Si(001) surface exposed to 20 langmuirs BF_3 at 190 K, and after subsequent annealing to 400 K and then to 500 K. Because the sensitivity to boron is low and the most intense B peak has a strong overlap with a Si plasmon loss feature, the chemistry of BF_3 is inferred from the F(1s) spectra. The spectrum shows two peaks at 688.1 (fwhm = 1.6 eV) and 686.5 eV (fwhm = 1.2 eV). The area of the 688.1 eV peak is almost exactly twice that of the 686.5 eV peak, indicating the presence of two distinct forms of F in a 2:1 ratio. Warming to 400 or 500 K induces a decrease in the area of the 688.1 eV peak and a corresponding increase in the 686.5 eV peak, leaving the total area unchanged. Si–F species typically yield F(1s) binding energies of 685.6–686.4 eV.^{10–14} Therefore, we attribute the 686.5 eV peak to Si–F species formed by dissociative adsorption of BF_3 . The dissociation of BF_3 would be expected to produce species such as Si– BF_2 and (Si) $_2$ –BF. Since B is more electronegative than Si is (Pauling electronegativity = 2.04 for B, 1.9 for Si), F atoms in BF_x species are expected to have higher binding energies than F atoms bonded to Si atoms. On the basis of these electronegativity considerations and the observed peak areas, we attribute the 688.1 eV peak to Si– BF_2 species. These XP data show that when a clean Si(001) surface at 190 K is exposed to BF_3 , the BF_3 molecules dissociate to form Si– BF_2 and Si–F species (Figure 2d), with F(1s) binding energies of 688.1 and 686.5 eV, respectively.

The data in Figure 1 and Figure 2 were obtained with an exposure of 20 langmuirs. More detailed measurements of the N(1s) intensity (for TMA) and the F(1s) intensity (for BF_3) show that when these molecules are exposed separately to the Si(001) surface, saturation is achieved at exposures less than 20 langmuirs. Even though a 20 langmuir exposure of TMA is sufficient to completely saturate the Si(001) surface toward further adsorption of TMA, the TMA-"saturated" surface will continue to adsorb BF_3 .

Figure 3 shows XP spectra after a Si(001) sample at 190 K was exposed to 20 langmuirs TMA and then to 20 langmuirs BF_3 . Also shown are spectra after this sample was warmed to 400 K for 5 min and then returned to 190 K. Immediately after dosing the cold surface, the N(1s) spectrum (Figure 3a) shows a single peak at 402.3 eV, while the corresponding C(1s) spectrum (Figure 3c) shows a single peak at 287.0 eV.

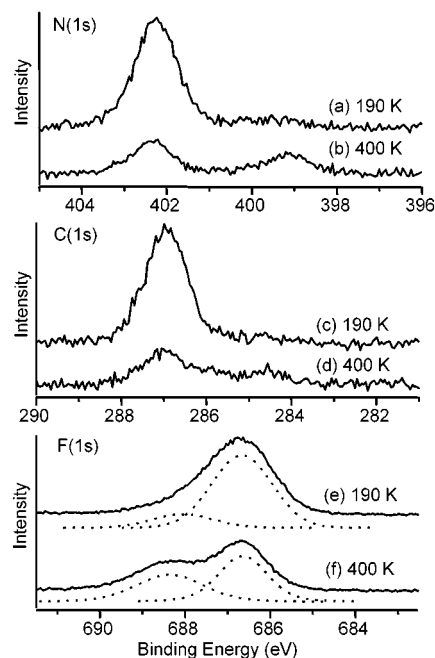


Figure 3. XP spectra of a Si(001) surface exposed at 190 K to 20 langmuirs TMA and then to 20 langmuirs BF_3 , and the same sample after warming to 400 K: (a) N(1s), 190 K; (b) N(1s), 400 K; (c) C(1s), 190 K; (d) C(1s), 400 K; (e) F(1s), 190 K; (f) F(1s), 400 K.

Quantitative comparison of these spectra with those obtained after TMA alone (Figure 1) shows that the position and intensity of the N(1s) and C(1s) peaks are almost identical. The F(1s) spectrum (Figure 3e), however, is very different from that obtained with BF_3 alone (Figure 2a). The TMA + BF_3 sample (Figure 3e) yields a broad peak centered at 686.7 eV (fwhm = 1.7 eV), but the intensity at higher binding energy (688.1 eV) is small, comprising <15% of the total F(1s) peak area. These data show that that predosing with TMA has a large effect on the subsequent behavior of BF_3 , but that BF_3 does not significantly change the preexisting TMA.

When the sample exposed to TMA and BF_3 is annealed to 400 K, the, N(1s) peak at 402.3 eV and the C(1s) peak at 287.0 eV both decrease substantially in intensity, and small new N(1s) (399.1 eV) and C(1s) (284.6 eV) peaks become visible. The pronounced decrease in total area of N(1s) and C(1s) peaks shows that most TMA molecules desorb from the surface, while the small increases in the peaks at low binding energy are consistent with minor dissociation to form Si– $\text{N}(\text{CH}_3)_2$ and Si– CH_3 species such as those observed from TMA alone.² The most significant effects of annealing, however, are observed in the F(1s) spectrum. Especially notable is that annealing causes the F(1s) peak at *higher* binding energy, 688.1 eV, to increase by a factor of ~2.5, while the peak at lower binding energy (686.6 eV) decreases by 50%. The total integrated area of the F(1s) peak changes by less than 12%, demonstrating that only a small fraction of the BF_3 molecules desorb from the surface.

The XP spectra show that predosing with TMA strongly modifies the subsequent chemistry of BF_3 on the surface. In a recent detailed study,² we showed that during dative bonding of TMA to Si(001), the electron donation from N to the Si atom is accompanied by transfer of electron density to the other Si atom of the Si=Si dimer. Consequently, the dative-bonded complex can be described as a TMA–Si–Si–lp ("lp" = lone pair), like that depicted in Figure 1c. These electron-rich Si atoms would appear to be facile sites for bonding of BF_3 . However, measurement of the N(1s) intensities from TMA and comparison with those from NH_3 shows that the saturation N

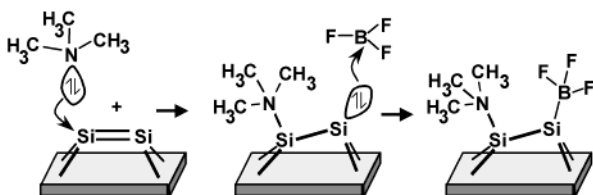


Figure 4. Formation of TMA-Si-Si-BF₃ complex on the Si(001) surface.

coverage from TMA is only ~ 0.25 monolayers (ML), or one TMA molecule per two Si=Si dimers.² Thus, the TMA-saturated surface consists of approximately equal numbers of TMA-Si-Si-lp species and unreacted Si=Si dimers. The subsequent adsorption of BF₃ onto this TMA-saturated surface can then be attributed to bonding either on the unreacted Si=Si dimers or on the Si "lone-pair" orbital of the TMA-Si-Si-lp species.

The low-temperature XP spectrum in Figure 3e is consistent with two interpretations, both hinging on the fact that the XP data at 190 K show only very little intensity at 688.1 eV, where Si-BF₂ species are observed. The first interpretation is that predosing with TMA causes BF₃ molecules to dissociate to a much greater extent than these same molecules would on the clean surface, so that no BF₂ species remain. In this case, the F(1s) XPS peak at ~ 686.6 eV in Figure 3e would arise primarily from F atoms bonded directly to the Si substrate. A second possibility is that the transfer of electron density within the silicon dimer creates a lone-pair orbital on the other Si atoms, which in turn permits formation of a dimer-mediated TMA-Si-Si-BF₃ complex.

To distinguish between these, we note that when the sample prepared by sequential dosing with TMA and then with BF₃ at 190 K is warmed to 400 K (Figure 3f), there is a pronounced increase in F(1s) intensity at *higher* binding energy, leading to the creation of a distinct peak with a binding energy near 688.1 eV. This energy is identical to that of the Si-BF₂ species formed when clean Si(001) is exposed to BF₃ (Figure 2). Furthermore, the N(1s) data show that the changes in the F(1s) spectrum occur concurrently with desorption of most of the TMA molecules from the surface. We therefore propose that at 190 K the surface is comprised primarily of TMA-Si-Si-BF₃ species such as those shown in Figure 4. When warmed above 400 K, the N(1s) and C(1s) data (Figure 3a-d) show that most TMA molecules desorb into the gas phase. We propose that the loss of TMA from one end of the dimer, and the concurrent increase in the number of available Si surface sites, permits the remaining db-Si-Si-BF₃ species to dissociate into Si-BF₂ (F(1s) at 688.1 eV) and Si-F species (F(1s) at 686.6 eV).

To ensure that formation of a surface-mediated TMA-Si-Si-BF₃ complex is indeed energetically favorable, we also

performed Gaussian 98 total energy calculations using the Becke3LYP density functional and the 6-31+G* basis set.¹⁵ Using a Si₉H₁₂ cluster to mimic the Si(001) surface, these calculations show the formation of the dative-bonded complex TMA-Si-Si-lp is favorable by 104 kJ/mol, and the addition of a BF₃ to this complex to form a TMA-Si-Si-BF₃ adduct further lowers the energy by another 64 kJ/mol, making the TMA-Si-Si-BF₃ adduct 168 kJ/mol lower in energy than the separated Si₉H₁₂, TMA, and BF₃ reactants. Thus, the formation of such a complex appears to be thermodynamically favorable.

The adsorption of TMA on the Si(001) surface has a very significant impact on the subsequent behavior of BF₃. Our data indicate that the sequential adsorption of TMA followed by BF₃ leads to formation of a novel donor-acceptor complex in which the electron transfer from TMA to BF₃ is mediated by the Si=Si dimer bond. The unusual chemistry of the Si(001) surface arises largely because the very weak π bond of the Si=Si dimers permits facile electron transfer between the two Si atoms within each dimer.

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References and Notes

- (1) Chadi, D. J. *Phys. Rev. Lett.* **1979**, *43*, 43-47.
- (2) Cao, X.; Hamers, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 10988-10996.
- (3) Lake, R. F. *Spectrochim. Acta Part A* **1971**, *27*, 1220-1221.
- (4) Sreerkanth, C. S.; Mok, C. Y.; Huang, H. H. *J. Electron Spectrosc. Relat. Phenom.* **1992**, *58*, 129-140.
- (5) Hamers, R. J.; Tromp, R. M.; Demuth, J. E. *Phys. Rev. B* **1986**, *34*, 5343-5357.
- (6) Liu, H.; Hamers, R. J. *Surf. Sci.* **1998**, *416*, 354-362.
- (7) Cao, X.; Coulter, S. K.; Ellison, M. D.; Liu, H.; Liu, J.; Hamers, R. J. *J. Phys. Chem. B* **2001**, *105*, 3759-3768.
- (8) Swartz, W. E., Jr.; Gray, R. C.; Carver, J. C.; Taylor, R. C.; Hercules, D. M. *Spectrochim. Acta* **1974**, *30A*, 1561-1572.
- (9) Lindberg, B. J.; Hedman, J. *Chem. Scripta* **1975**, *7*, 155-166.
- (10) Rieger, D.; Himpsel, F. J.; Karlsson, U. O.; McFeely, F. R.; Morar, J. F.; Yarmoff, J. A. *Phys. Rev. B* **1986**, *34*, 7295-7306.
- (11) Morikawa, Y.; Kubota, K.; Ogawa, H.; Ichiki, T. *J. Vac. Sci. Technol. A* **1998**, *16*, 345-355.
- (12) Mitsuya, M.; Sato, N. *Langmuir* **1999**, *15*, 2099-2102.
- (13) Little, T. W.; Ohuchi, F. S. *Surf. Sci.* **2000**, *445*, 235-242.
- (14) Lozzi, L.; Ottaviano, L.; Santucci, S. *Surf. Sci.* **2001**, *470*, 265-274.
- (15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.