Highly Selective Surface Lewis Acid−Base Reaction: Trimethylamine on Si(100)c(4×2)

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Adsorption of trimethylamine (TMA) on Si(100)c(4×2) has been studied using scanning tunneling microscopy (STM), valence photoelectron spectroscopy (PES), and high-resolution electron energy spectroscopy (HREELS) between 80 and 300 K. The TMA molecule is adsorbed nondissociatively only on the down dimer atom and appears as a triangle shaped bright protrusion in the occupied state STM image. The saturation coverage of TMA on Si(100) is estimated to be ∼0.25 ML (ML = one molecule per surface Si atom). The PES and HREELS results suggest that TMA is adsorbed through the N lone pair by forming an Si−N dative bond. The HREELS spectra indicate that the symmetry of adsorbed TMA is C_s and the molecular C_3 axis is tilted from the surface normal. The stretching mode of the SiN dative bond is observed at 525 cm^{-1}. Thus the combined STM, PES, and HREELS results indicate that the chemisorption of TMA on Si(100)c(4×2) occurs selectively on the down dimer atom via dative bonding. Hence, the TMA adsorption on Si(100)c(4×2) is purely site-specific on the down dimer atom and can be categorized in Lewis acid−base reaction. The acidity of the down dimer atom is also discussed according to the analysis of vibrational spectra.

I. Introduction

Since the concept of Lewis acid and Lewis base was introduced by Gilbert Lewis in 1938, a large number of investigations have reported on the chemistry of Lewis acid−base complexes.[1,2] Although the concept has been widely utilized in aqueous and nonaqueous systems, direct real-space observation of Lewis acid−base reaction at the atomic scale has been barely available so far.

The Si(100) clean surface undergoes reconstruction into the c(4×2) structure with the alternate arrangement of buckled dimers at low temperature (<200 K).[3] In the buckled dimer on Si(100)c(4×2), a partial charge transfer occurs from a down dimer atom to an up dimer atom and thereby the up and down atoms become negatively and positively charged, respectively.[4] Hence, the up and down dimer atoms can behave like a Lewis base and Lewis acid, respectively. Recently, the interaction of organic molecules with silicon surfaces has drawn much attention from both fundamental and technological points of view.[5−7] One of the fundamental interests is how the Lewis acid and Lewis base character in the buckled dimer atoms controls the reaction toward different molecules.

Trimethylamine (TMA) is an ideal Lewis base molecule having a lone pair at the N atom. Different organic amines have been studied on the Si(100) surface using several experimental techniques.[6,8−11] Bent and co-workers have investigated some simple amine molecules including TMA using multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy and density functional theory (DFT) calculation.[6,9] Cao and Hamers have studied TMA and dimethylamine on Si(100) using X-ray photoelectron spectroscopy (XPS), FTIR at 300 K, and DFT calculation.[8] These studies about the TMA adsorption on Si(100) at 300 K suggest that TMA is molecularly chemisorbed

on Si(100) through the dative bonding with a silicon atom.[6,8,9] Computational studies on small clusters have predicted molecular adsorption of TMA at the down atom of silicon dimer.[6,8,9] Recently, we have reported a direct observation of adsorbed TMA at the down dimer atom on Si(100) using low-temperature scanning tunneling microscopy (STM).[12]

In this paper, we report the adsorption of TMA on Si(100)c(4×2) by STM, valence band photoelectron spectroscopy (PES), and high-resolution electron energy loss spectroscopy (HREELS) between 80 and 300 K. The combined STM, PES, and HREELS results clearly indicate that TMA is adsorbed only on the down dimer atom of the buckled Si dimer through the N lone pair.

II. Experimental Section

The Si(100) substrate was obtained by cutting an Si wafer. The clean surface was prepared by repeated flashing at 1500 K under ultrahigh vacuum (UHV) with a base pressure better than 1.5×10^{-8} Pa. The sample was cooled using liquid N$_2$. STM measurements were carried out using JEOL SPM-4500 at 80 and 300 K. Valence band PES measurements were carried out at BL-16B with an undulator radiation source of Photon Factory (PF) in KEK under the PF-PAC approval (No. 00-G198 and 01-G209). The photoelectrons were collected with a hemispherical analyzer (SPECS PHOIBOS100). The HREELS measurement was performed using ELS-5000 by LK technology. In EELS measurements, the full width at half-maximum (fwhm) of the elastic peak was 56−70 cm^{-1}. Gaseous TMA molecules were introduced onto the surface through a pulse gas dosing system. The amount of exposure is given in the number of shots (1 shots ≅ 0.05 langmuir; 1 langmuir = 1×10^{-6} Torr. s).

III. Results

**A. STM Observation at 80 and 300 K.** Figure 1 shows the occupied state STM image of the Si(100)c(4×2) surface exposed

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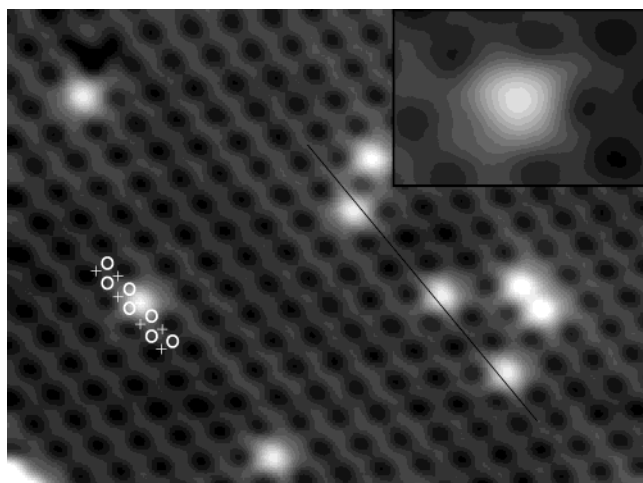
Figure 1. STM images of Si(100)c(4×2) surface exposed to trimethylamine (TMA) at 80 K. The bright protrusions are adsorbed TMA. A zoomed-in image is shown in the inset, where the shape of the protrusions is clearly resolved. $V_{sample} = -2.2$ V, $I = 0.1$ nA. Scanning area 15 × 11 nm^2.

to a small amount of TMA at 80 K. The zigzag pattern due to the c(4×2) structure is clearly observed over the entire scanning region.[13] The randomly distributed bright protrusions are assigned to adsorbed TMA molecules.[12] All the bright protrusions are located at either side of the center (indicated by the line) of the dimer row. By registering the silicon dimer atoms, we determined that the center of the bright protrusion located on the down atom site of the buckled dimer.[12] On the basis of the visual inspection of hundreds of bright protrusions, we have estimated that almost all of bright protrusions are located on the down atom sites. A few dark sites may be due to the surface defects; the Si(100)c(4×2) surface contains different types of defects, which appear as dark depressions in the occupied state image.[14] It is noted that the STM image acquired with negative and positive sample bias represents the distribution of up and down dimer atoms of the Si(100)c(4×2) surface, respectively.[4]

A zoomed-in image of the TMA adsorbed Si(100)c(4×2) surface is shown in the inset, where the shape of the bright protrusion can be identified. We have found that most of the protrusions located on the c(4×2) region are triangle-shaped.[12] One of the three corners of triangle shape protrusion is pointed toward the dimer bond direction. The direction of triangle-shaped protrusion with respect to the underlying dimer does not change during STM measurement at 80 K.

Parts a and b of Figure 2 show the STM images of TMA exposed surface in the occupied state and unoccupied state, respectively, at 80 K. Both images were taken at the same scanning area. The bright protrusions in Figure 2a are ascribed to adsorbed TMA molecules. In the unoccupied state image, the TMA adsorbed sites appear as depressions. A single adsorbed TMA in both images is encircled. An adsorbed TMA causes the depression over five dimers in a row. Some dark sites in Figure 2a are due to intrinsic missing dimer defects. The bright protrusions in Figure 2b may be due to the C-defects.[14,15]

To get the information about the saturation coverage, STM measurements were performed with larger exposure at 300 and 80 K. The image shown in Figure 3a was taken after the Si(100) surface was exposed to a large amount of TMA at 300 K. The bright protrusions in the entire scanning area are adsorbed TMA species. Although the homogeneous layer of adsorbed TMA molecules is not observed over extended area, we can identify
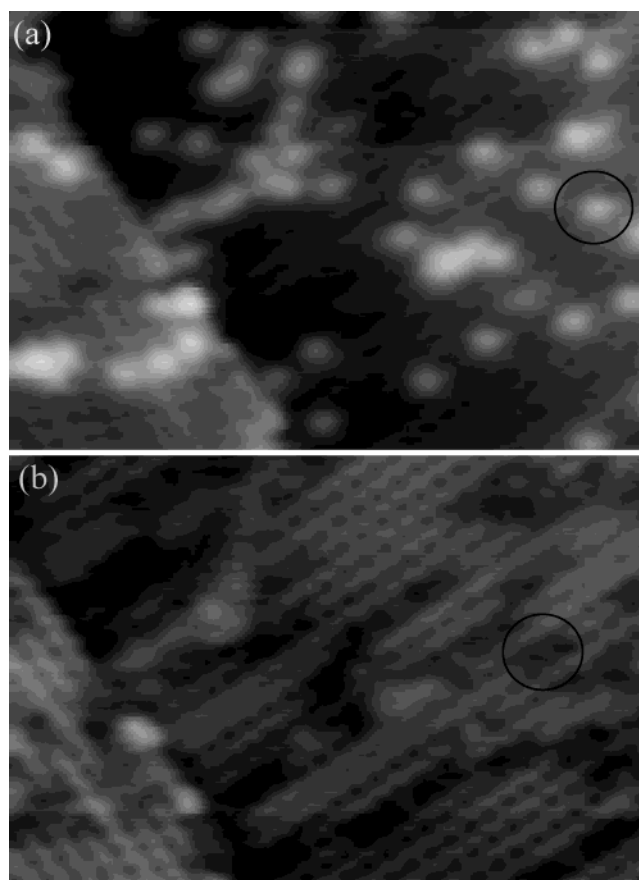

Figure 2. STM images at the same scanning area of trimethylamine (TMA) exposed Si(100)c(4×2) surface in the (a) occupied state and (b) unoccupied state at 80 K. A typical adsorbed TMA is encircled in both images. $V_{sample} = -2.0$ V (a) and 2.0 V (b), $I = 0.1$ nA. Scanning area 21 × 14 nm^2.

the unit cell of locally ordered structure of adsorbed TMA molecules in some region of Figure 3a. Two different arrangements of adsorbed TMA are identified as indicated by the unit cell "A" and "B". The shapes of "A" and "B" are rectangular and parallelogram, respectively. Here, the underlying dimer rows are along [01$\bar{1}$] direction. The similar unit cells of adsorbed TMA were also observed at 80 K. We have estimated that perpendicular distances between two sides of rectangle and parallelogram along the dimer row are 8.5 and 7.6 Å, respectively. It is noted that the distance between two neighboring dimers in a (2×1) structure is 7.7 Å. Thus, the STM images suggest that TMA does not adsorb on every down dimer atom. Schematic models for the structure "A" and "B" are shown in Figure 3b. The details about the arrangement and conformation of adsorbed TMA will be discussed later. Note that the formation of homogeneously ordered structure of adsorbed TMA seems to be disturbed by the presence of C defects. In room temperature STM images, C-defects (a few percent) were usually observed on the clean surface. The C-defect having two free dangling bonds with a single electron for each may not be suitable site for TMA adsorption.[15] As a result, many dark areas are observed, where TMA does not adsorb.

B. Valence Band Photoelectron Spectroscopy at 90 K. Figure 4 shows a series of valence PES spectra of the Si(100) surface as a function of TMA exposure. For the clean surface a sharp peak is observed at 0.7 eV below the Fermi level. This peak is assigned to the occupied surface state of the buckled dimer, which is localized around the up dimer atom (D_{up}).[16,17]
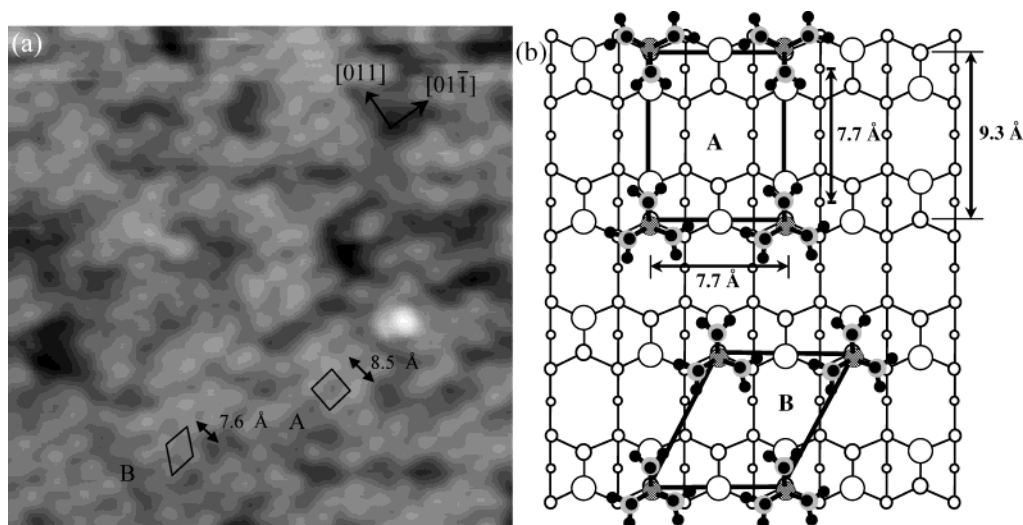
Figure 3. (a) STM image of the Si(100) surface exposed to large amount of TMA at 300 K. The protrusions observed all over the scanning region are adsorbed TMA. Two different unit cells of adsorbed TMA are indicated by rectangle ("A") and parallelogram ("B"). (b) Schematic model for TMA adsorbed structure indicated by "A" and "B" in (a). The c(4×2) structure is shown for the substrate.
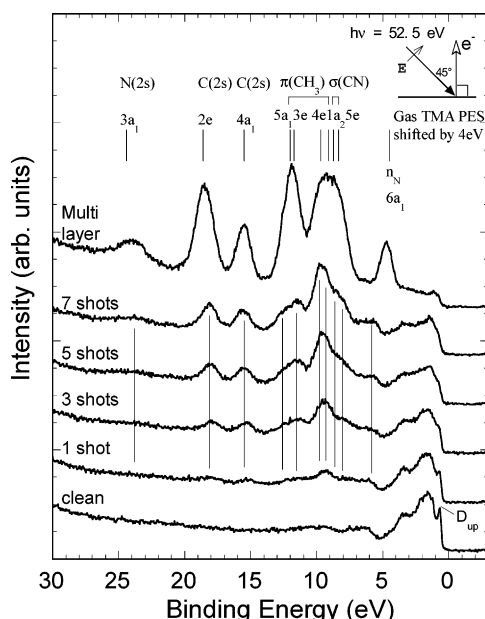
Figure 4. Valence band PES spectra of the Si(100)c(4×2) surface exposed to increasing amounts of TMA at 90 K. Incident angle 45°. Normal emission. $h\nu = 52.5$ eV. The peak positions for gaseous TMA and their assignment are also shown.[18−21]

With increasing the exposure of TMA, adsorbate derived peaks and shoulders are observed at 5.6, 7.9, 8.5, 9.2, 9.7, 11.4, 12.5, 15.5, 18.1, and 23.9 eV, as indicated by thin vertical lines. The intensities of these peaks are monotonically increased with increasing exposure. The saturation coverage was achieved at 7 shots. The surface and bulk Si peaks are decreased in intensity with increasing TMA exposure. The D_{up} peak is slightly shifted to 0.9 eV.

For the multilayer, the spectral feature changes; dominant peaks are observed at 4.7, ~9, 11.9, 15.6, 18.5, and 24.0 eV. These peaks can be compared with those in the photoelectron spectra for gas-phase TMA; the assignments of peaks are indicated in Figure 4.[18−21]

A distinct difference between the spectra for adsorbed TMA and the multilayer spectrum is observed for the peak originated from the lone-pair state of N atom in TMA (highest occupied molecular orbital: HOMO, $6a_1$). For the multilayer

TMA the peak is clearly observed at 4.7 eV, but for the chemisorbed TMA the peak becomes smaller and broad, and its position is shifted to 5.6 eV. Other peaks are still clearly observed and the energy shifts are smaller than 0.4 eV, although the relative intensities are different from those of multilayer TMA.

The previous theoretical calculations have indicated that the N lone pair of TMA interacts with the down dimer atom of the buckled dimer on Si(100).[6,8,9] The present STM observation at low temperature clearly indicates that TMA is adsorbed at the down dimer atom site. These results are interpreted to indicate that the N lone pair in TMA is involved in the chemisorption bond formation. Most probably, the occupied state at the N lone pair and the unoccupied state localized at the down dimer atom (D_{down}) above the Fermi level are interacting; the dative bond is formed between TMA and the surface, and this new occupied (bonding) state is observed at 5.6 eV. The shift to larger binding energy (~0.9 eV) may support the bonding interaction between them.

C. HREELS at 90 K. Figure 5 shows the HREELS spectra of (a) the clean Si(100)c(4×2) surface, (b), (c) the TMA adsorbed surfaces as a function of TMA exposure at 90 K, and (d) the condensed TMA. It is noted that TMA exposure was performed at 90 K followed by EELS measurement without annealing. Hence, at higher exposure, islands of condensed TMA may be formed partly. For the clean surface, the loss peaks characteristic of the substrate phonon are observed.[22] In Figure 5b,c, the phonon loss peaks disappear and new loss peaks appear at ~370, 525, 805, 975, 1095, 1240, 1450, and 2945 cm⁻¹. Obviously, the newly appeared losses are due to the adsorbed TMA. Some small peaks are also observed at ~1775, ~1953, ~2050, and ~2207 cm⁻¹, which may be the overtone/combination band of (1240 + 525), (1450 + 525) or 2 × 975, (1240 + 805), and (1240 + 975), respectively. In the spectrum of condensed TMA (Figure 5d), loss peaks are observed at 293, 385, 525, 825, 1040, 1190, 1255, 1450, 2775, and 2945 cm⁻¹.

With increasing coverage, we observed that the loss peaks of adsorbed TMA (Figure 5c) at ~370, 805, 975, and 1240 cm⁻¹ were shifted at 385, 825, 1040, and 1255 cm⁻¹ in the spectrum of condensed TMA (Figure 5d), respectively. The intensities of 385 and 825 cm⁻¹ peaks are enhanced in the multilayer spectrum (d). The loss peaks at 1190 and 2775 cm⁻¹ newly appear in the multilayer TMA. When the multilayer surface was
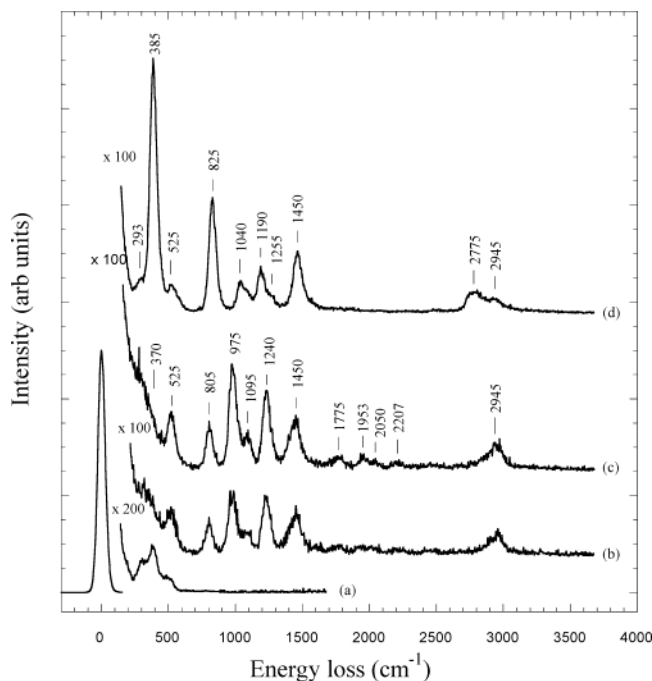
Figure 5. HREELS spectra of (a) the clean Si(100)c(4×2) surface, (b), (c) the surface exposed to increasing amount of TMA at 90 K, and (d) the condensed TMA. All spectra are normalized with their corresponding elastic peak. The baselines of the spectra (b)−(d) are shifted to higher counts for clarity.

annealed to 300 K, the 2775 cm^{-1} peak disappears and a spectrum similar to the adsorbed TMA (Figure 5c) was observed.

IV. Discussion

A. Adsorption Site and Binding of TMA on Si(100)c(4×2). The TMA molecule contains three methyl (−CH$_3$) groups and one N atom with a lone pair. The adsorption of TMA on Si-(100) is exothermic (adsorption energy, more than 23.4 kcal/mol) and barrierless.[6,23] It is most likely that the chemisorption of TMA on Si(100)c(4×2) involves the interaction of the lone pair at the N atom with the electron deficient down atom of buckled dimer from an analogy of Lewis acid−base reaction.[6,8,9] In the case of chemisorbed TMA, the peak at 4.7 eV, which is ascribed to the N lone pair in valence PES spectra does not appear (Figure 4). Instead, a new peak is observed at 5.6 eV. We assign this peak to the bonding state of the SiN dative bond. On the other hand, other occupied states including CH bands, and CN band are observed in similar binding energy to the condensed TMA.

The gas-phase TMA has C_{3v} symmetry. If adsorbed TMA remains undissociated, the 3-fold symmetry about the N−Si bond axis may be almost retained. Because the methyl groups in adsorbed TMA are fully saturated and the N lone pair is involved in the N−Si dative bond formation, the STM image of adsorbed TMA might be depressed. However, experimentally it was found that the methyl group in adsorbed organic molecules on Si(100) appeared as a bright protrusion in the STM image, which was also supported by ab initio calculation.[5] Hence, we have ascribed the triangle shaped protrusion to three methyl groups in the adsorbed TMA. The presence of three methyl groups in adsorbed TMA also suggests the nondissociative adsorption of TMA, which is supported by HREELS (discussed later). The location of the center of the triangle protrusion indicates that TMA is adsorbed on the electron

deficient down dimer atom. Thus, the chemisorption of TMA on Si(100)c(4×2) is purely site-specific and can be categorized into Lewis acid−base reaction.[12]

It is obvious that TMA adsorbs on the Si(100)c(4×2) surface through the dative bond between the N atom and the down atom of the buckled dimer; methyl groups are directed to the vacuum side. The STM image of the adsorbed TMA (Figure 1) clearly suggests that one of the three methyl groups is directed toward the up dimer atom of the reacted dimer, as schematically shown in Figure 3b. The absence of molecular rotation about the N−Si bond during STM measurement at 80 K suggests that the rotation along the SiN bond is hindered. The direction of these methyl groups in adsorbed TMA in the present study is in disagreement with previous computational calculations.[6,8,9] The calculated geometry of adsorbed TMA differs by 60° rotation about the N−Si bond axis. This disagreement may originate from the use of small cluster (Si$_9$H$_{12}$) in the calculation, where the interaction with the neighboring dimers and the dimer rows was neglected.

The substrate mediated charge transfer on the neighboring dimer atoms due to the adsorbate has recently been predicted in the case of NH$_3$ on Si(100) using density functional theory and vibrational spectroscopy.[24,25] In the case of TMA adsorption, TMA donates the N lone-pair electrons to the electron deficient down atom of the buckled dimer. The depression over several dimers (Figure 2b) due to the adsorption of a single TMA molecule may be related to the charge transfer from the adsorbed TMA to the neighboring atoms in a row.[25] In valence PES spectra, the occupied surface (D$_{up}$) state is also affected by the adsorption of TMA.

B. Vibrational States of Adsorbed TMA on Si(100)c(4×2). The IR study on gaseous and solid TMA has been done in detail by Murphy et al., where they have shown a comprehensive assignment of the observed peaks.[26] Recently, there are several studies reported on the TMA adsorption on various metal and semiconductor surfaces.[9,27−31] The observed loss peaks for adsorbed TMA on Si(100)c(4×2) (Figure 5b,c) are in good agreement with the previous observation. Comparing with IR spectra of gaseous and adsorbed TMA, the assignment of the observed losses for chemisorbed and condensed TMA in the present study is given in Table 1.

For the chemisorbed TMA (Figure 5b,c), the 2945 cm^{-1} loss is assigned to the C−H stretch in the CH$_3$ groups. The 1450 and 1095 cm^{-1} peaks are due to the CH$_3$ asymmetric and symmetric deformation, respectively. The 1240 and 975 cm^{-1} peaks are ascribed to the CH$_3$ rocking and/or N−C asymmetric stretch and CH$_3$ rocking, respectively. The 805 and 370 cm^{-1} loss peaks are assigned to the symmetric stretching and deformation mode of N−C in the NC$_3$ skeleton. However, the 525 cm^{-1} loss does not match to any of the vibrational frequency reported for TMA. It is observed that the intensity of the 525 and 1240 cm^{-1} (Figure 5c) is drastically decreased in higher exposure (Figure 5d). Note that at higher exposure, the chemisorbed TMA is covered by condensed TMA. Thus, the 525 and 1240 cm^{-1} should be related to the chemisorbed TMA on the Si surface atom. The 1240 cm^{-1} is too high to account for a dative bonded Si−N stretch, and it can be assigned to ν_{18}. Hence, we assign the 525 cm^{-1} peak to the stretching mode of the dative bonded Si−N.

The splitting of C−H stretch peaks at 2775 and 2945 cm^{-1}, in the case of condensed phase spectrum, is due to the trans-lone-pair effect.[32] The interaction of the N lone-pair orbital with the C−H σ orbital oriented trans periplanar to the N lone pair causes an increase in C−H bond length and hence the red shift

TABLE 1: Vibrational Energy (cm^{-1}) for Trimethylamine (TMA) in Gas-Phase and Adsorbed TMA

| | symmetry | | | | | chemisorbed | | | condensed |
mode	C_{3v}	C_s	assignment	gas[26]	solid[39]	Pt(111)[30]	Ni(111)[29]	Si(100)	Si(100)
ν_1	A$_1$	A′	CH$_3$ sym str	2953	2944	2945	2873	2945	2945
ν_2	A$_1$	A′	CH$_3$ sym str	2776	2768	2731	2763		2775
ν_3	A$_1$	A′	CH$_3$ asym def	1459		1455	1463	1450	1450
ν_4	A$_1$	A′	CH$_3$ sym def	1444					(1450)
ν_5	A$_1$	A′	CH$_3$ rock	1186	1196	1187	1205		1190
ν_6	A$_1$	A′	NC$_3$ sym str	828	827	827	812	805	825
ν_7	A$_1$	A′	NC$_3$ sym def	367	389	424		~370	385
ν_8	A$_2$	A″	CH$_3$ asym str	(2977)		2868			
ν_9	A$_2$	A″	CH$_3$ asym def	(1453)					
ν_{10}	A$_2$	A″	CH$_3$ rock	1046		1232			
ν_{11}	A$_2$	A″	torsion	(255)					
ν_{12}	E	A′ + A″	CH$_3$ asym str	2981		2973		2945	2945
ν_{13}	E	A′ + A″	CH$_3$ sym str	2953		2817			
ν_{14}	E	A′ + A″	CH$_3$ asym str	2776		2768			2775
ν_{15}	E	A′ + A″	CH$_3$ asym def	1471		1470			
ν_{16}	E	A′ + A″	CH$_3$ asym def	1444		1043			(1450)
ν_{17}	E	A′ + A″	CH$_3$ sym def	1409		1099, 949		1095	
ν_{18}	E	A′ + A″	NC asym str/CH$_3$ rock	1275		1265, 1271		1240	1255
ν_{19}	E	A′ + A″	CH$_3$ rock	1103		986, 1098		975	
ν_{20}	E	A′ + A″	NC asym str/CH$_3$ rock	1043	1038	949, 1041			1040
ν_{21}	E	A′ + A″	NC$_3$ asym def	424	434	503			
ν_{22}	E	A′ + A″	torsion	281	295				293
			hindered trans			336, 248		525	

in vibrational frequency.[32] The loss peak at 2775 cm^{-1} is ascribed to the symmetric stretch of C–H bond trans periplanar to the N lone pair. Such a low-frequency but high-intensity C–H stretch mode is known as the Bohlmann band. It is remarkable that the 2775 cm^{-1} peak does not appear in the spectra of chemisorbed TMA (Figure 5b,c). This indicates that the N lone pair is no longer available for the trans-lone-pair effect in the case of chemisorbed TMA; i.e., the N lone pair is involved in the chemical bond formation with the Si surface, which is in agreement with the PES results. The trans-lone-pair effect has also been discussed in the previous study by Mui et al.[9]

For the condensed TMA, the peak intensities at 385 (ν_7), 825 (ν_6), 1190 (ν_5), and 2775 (ν_2) cm^{-1} are relatively strong compared with the chemisorbed spectra. All these peaks belong to A$_1$ in C_{3v}. On the other hand, for the chemisorbed TMA on Si(100) the intensities of 975 (ν_{19}), 1095 (ν_{17}), and 1240 (ν_{18}) cm^{-1} peaks are comparable to other peaks. These vibrational modes are originally of E in C_{3v}. These results suggest that the symmetry of adsorbed TMA becomes C_s with some tilt of the C_3 axis with respect to the surface. According to the previous calculation, the N–Si bond is tilted about 18° from the surface normal.[8]

The red shifts of N–C stretches (ν_6 and ν_{18}), in the chemisorbed TMA compared with the gas and multilayer TMA, are in agreement with the increased N–C bond length of TMA (from 1.46 to 1.50 Å) upon adsorption on Si(100).[8,33] The increased bond length in the adsorbed TMA may be related with the donation of N lone pair to the acidic down atom of Si dimer. The lone-pair donation yields some charge depletion around the N and C atoms (as evidenced by higher N 1s and C 1s binding energy)[8] and thus causes the N–C bond weakening. The observed frequencies at 805 (ν_6) and 1240 (ν_{18}) cm^{-1} in the chemisorbed TMA on Si(100) are comparable to those observed (804 and 1250 cm^{-1}) for TMA-I$_2$, which is a typical Lewis acid–base complex.[34]

C. Saturation Coverage of TMA on Si(100)c(4×2). Mui et al. have studied the TMA adsorption on Si(100) at 300 K using MIR-FTIR.[6] Comparing the integrated area of intensity of Si–H vibrational peak of adsorbed TMA with that of methylamine, they proposed the saturation coverage of TMA was only 25% of the saturation coverage of methylamine. It is

noted that the maximum value for the saturation coverage of methylamine would be 0.5 ML (ML = one methylamine per one dimer). However, it may be difficult to estimate the coverage comparing the intensity of vibrational peaks. Cao and Hamers have proposed the saturation coverage of TMA on Si(100) would be 0.25 ML on the basis of their X-ray photoelectron spectroscopy study.[35] The arrangement of adsorbed TMA on Si(100) at higher coverage (Figure 3a) clearly suggests that TMA molecules are adsorbed on the alternate down dimer atom, as shown in Figure 3b. Thus the saturation coverage should be <0.25 ML, where the down dimer atom next to the already reacted one remains unreacted. In the case of NH$_3$ on Si(100)c-(4×2), all the dimers are saturated by Si–NH$_2$ and Si–H species.[24,36,37]

Substrate-mediated charge transfer or the direct interaction between adsorbates through steric repulsion may cause the down atom next to the already reacted one less reactive. Recently, DFT calculations by Widjaja and Musgrave[37] have reported that charge transfer through the substrate affects the neighboring Si dimer atoms on the same side of the dimer row, i.e., the down atom next to the reacted one in a row, is still reactive toward the N lone pair in the case of NH$_3$ on Si(100). However, the charge-transfer effect may not prohibit the occupation of TMA molecule on the down atom next to the reacted one in a row. The diameter of the adsorbed TMA is expected to be similar to that of the tetramethylammonium ion, 5.5 Å.[38] The distance between two nearest down atoms in a row is estimated to be 4.2 Å. Hence, due to the steric hindrance, every down atom cannot be occupied by TMA. Thus the saturation coverage of TMA on Si(100) observed in the present study (~0.25 ML) is reasonable.[33]

V. Conclusions

The adsorbed state of trimethylamine (TMA) on Si(100)c-(4×2) has been studied using STM, PES, and HREELS between 80 and 300 K. The TMA molecule is adsorbed nondissociatively only on the down dimer atom and appears as a triangle-shaped bright protrusion in the occupied state STM image. The saturation coverage of TMA is estimated to be ~0.25 ML. The PES and HREELS results clearly suggest that TMA is adsorbed

through the N lone pair by forming a Si−N dative bond. The combined STM, PES, and HREELS results indicate that chemisorption of TMA on Si(100)c(4×2) is purely site-specific on the down dimer atom. The chemisorbed system between TMA and the down atom on Si(100)c(4×2) is a Lewis acid−base complex, which is comparable to TMA-I$_2$ complex.

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