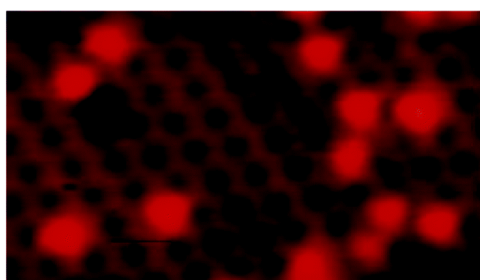


Purely Site-Specific Chemisorption and Conformation of Trimethylamine on Si(100)c(4 × 2)

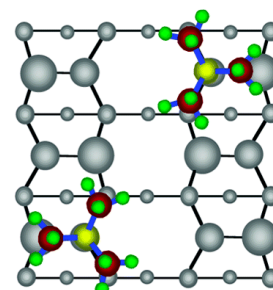
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Occupied state STM image of TMA on Si(100)c(4x2)



Schematic model for TMA on Si(100)c(4x2)

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Purely Site-Specific Chemisorption and Conformation of Trimethylamine on Si(100)c(4 × 2)

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Recently, the interaction of organic molecules with silicon surfaces has drawn much attention from both fundamental and technological points of view.^{1–3} One of the fundamental points of interest is how the spatial localization of electron density on the silicon surface controls the reactivity of the surface toward different molecules. 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).⁴ In the buckled dimer on Si(100)c(4×2), a partial charge transfer occurs from a down to an up dimer atom, and thereby the up and down atoms become partially negatively and positively charged, respectively.⁵ Hence, the reactivity of up and down dimer atoms is expected to be highly selective toward Lewis acid and Lewis base molecules.

Different organic amines on the Si(100) surface have been studied using several experimental techniques.^{2,6–9} Bent and co-workers have investigated some simple amine molecules, including trimethylamine (TMA), using multiple internal reflection Fourier transform infrared spectroscopy (MIR–FTIR) and density functional theory (DFT) calculation.^{2,7} Cao and Hamers have studied TMA and dimethylamine on the Si(100) surface using X-ray photoelectron spectroscopy (XPS), FTIR at 300 K, and DFT calculation.⁶ These studies concerning the TMA adsorption on Si(100) at 300 K suggest that TMA is chemisorbed on Si(100) through dative bonding with a silicon atom.^{2,6,7} Computational studies with small clusters have predicted the molecular adsorption of TMA molecule at the down atom of buckled silicon dimer.^{2,6,7} Recently, we studied the electronic state of adsorbed TMA on Si(100) at 90 K using photoelectron spectroscopy.¹⁰ To our knowledge, there is no direct experimental evidence about the site-specific adsorption as well as the conformation of adsorbed TMA on the Si(100) surface. In this Communication, we report the purely site-specific adsorption of the TMA molecule and its conformation on Si(100)c(4×2), determined using low-temperature scanning tunneling microscopy (STM) at 80 K.

The Si(100) substrate was obtained by cutting Si wafers (phosphorus doped, resistivity = 0.05 Ω cm). The clean surface was prepared by repeated flashing at 1500 K under ultrahigh vacuum with a base pressure better than 1.5×10^{-8} Pa. Using a cryopump, the clean surface thus prepared contained <1% defects. The sample was cooled to 80 K using liquid N₂. TMA molecules were introduced through a pulse-valve doser. STM measurements were carried out using JEOL SPM-4500.

Figure 1 shows the occupied-state STM images at the same scanning area of the Si(100)c(4×2) surface exposed to a small amount of TMA at 80 K. After an additional dose of TMA on the surface shown in Figure 1a, the image in Figure 1b was recorded. The zigzag pattern due to the c(4×2) structure is clearly observed over the entire scanning region. It is noted that, due to a partial charge transfer from the down atom to the up atom of the buckled

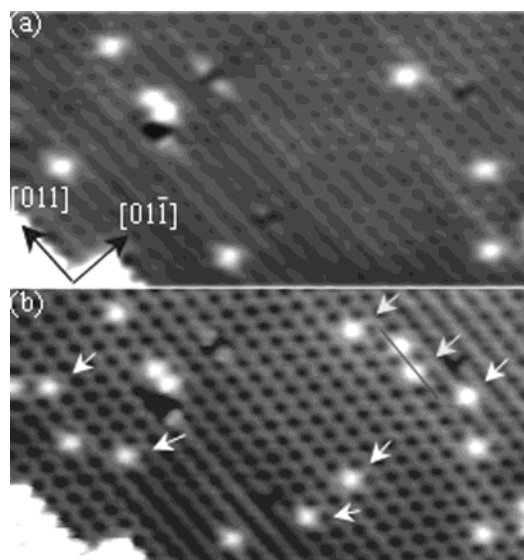


Figure 1. STM images at the same scanning area of Si(100)c(4×2) surface exposed to trimethylamine (TMA) at 80 K. (a) The Si(100)c(4×2) surface exposed to one shot of TMA. (b) After an additional exposure of TMA. The bright protrusions indicated by arrows in (b) have newly appeared after the additional TMA exposure. $V_{\text{sample}} = -2.2$ V, $I = 0.1$ nA. Scanning area is 28×15 nm².

dimer, the STM image acquired with negative sample bias represents the distribution of up dimer atoms of the Si(100)c(4×2) surface.⁵

In Figure 1, several bright protrusions are clearly observed after exposure to TMA at 80 K. The protrusions are randomly distributed on the surface, and the number of protrusions is increased with an additional exposure. The protrusions indicated by arrows in Figure 1b newly appeared due to an additional TMA exposure. Obviously, the newly appearing and already existing protrusions are identical, which suggests that all bright protrusion observed in Figure 1 are due to identical surface species of adsorbed TMA. In addition, all of the bright protrusions are located at either side of the center (indicated by the line) of the dimer row. It is noted that a few dark sites in Figure 1 are 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.¹¹

Figure 2a shows the high-resolution STM image of TMA adsorbed on Si(100)c(4×2), where the shape of the bright protrusion is clearly resolved. It is observed that most of the protrusions are triangle-shaped. A zoomed-in image of a typical protrusion with the registry of dimer atoms is shown in Figure 2b. The bigger and smaller open circles represent the up and down atoms of the buckled dimer, respectively. It is observed that one of the three corners of the triangle-shaped protrusion is pointed toward the dimer bond direction. By the inspection of hundreds of protrusions, it is

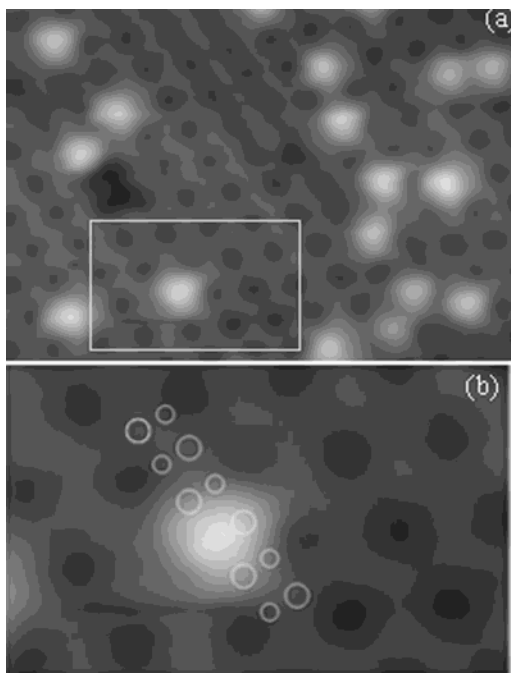


Figure 2. (a) High-resolution STM image of TMA on Si(100)c(4×2) at 80 K. $V_{\text{sample}} = -2.0$ V, $I = 0.1$ nA. Scanning area is 15×10 nm². (b) A zoomed-in image of a typical protrusion. The bigger and smaller open circles represent the up and down atoms of buckled dimer, respectively.

observed that the center of the triangle-shaped protrusion is located on the down atom in all the cases, as shown in Figure 2b. The conformation of the triangle-shaped protrusion with respect to the underlying dimer does not change, at least for several minutes.

The TMA molecule, containing three methyl (–CH₃) groups and one N atom with a lone pair of electrons, has C_{3v} symmetry. 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 the buckled dimer.^{2,6,7} Our recent valence PES measurement clearly indicated that the nitrogen lone pair is involved in chemisorption of TMA on Si(100).¹⁰ If adsorbed TMA remains undissociated, the three-fold symmetry about the N–Si bond may be retained. Since the methyl groups in adsorbed TMA are fully saturated and the N lone pair is involved in the N–Si bond formation, the STM image of adsorbed TMA might be depressed. However, experimentally it was found that a methyl group in an adsorbed organic molecule on Si(100) appears as a bright protrusion in the STM image, which is also supported by ab initio calculations.¹ 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 suggests the molecular adsorption of TMA. The location of the center of the triangle-shaped protrusion indicates that TMA is adsorbed on only the down dimer atom. On the basis of visual inspection of many protrusions, almost 100% of adsorbed TMA molecules are located on the down dimer sites. Therefore, the chemisorption of TMA on Si(100)c(4×2) is *purely site-specific* and can be categorized into Lewis acid–base reaction.

TMA molecules adsorb on the Si(100)c(4×2) surface through the strong dative bond between the N atom and the down atom of the buckled dimer; the three methyl groups are directed to the

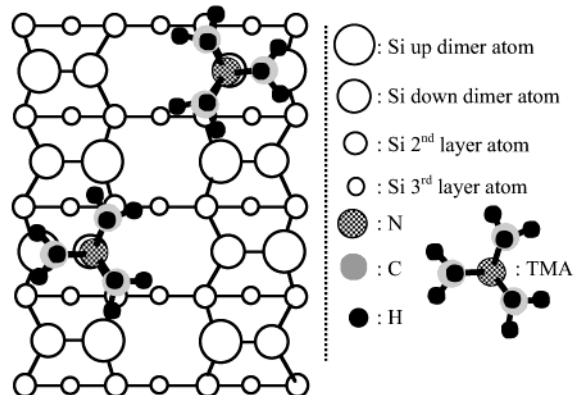


Figure 3. Schematic structural model for chemisorbed TMA on the Si(100)c(4×2) surface.

vacuum side. One of the three methyl groups is directed toward the up dimer atom of the reacted dimer, as schematically shown in Figure 3. Since the dimers are alternately buckled on the c(4×2) surface, two different configurations of adsorbed TMA, as shown in Figure 3, are possible, which is consistent with the experimental findings (Figure 2). The absence of molecular rotation about the N–Si bond during STM measurement at 80 K suggests that the conformation is stable. The conformation of adsorbed TMA in the present study is in disagreement with previous computational calculations.^{2,6,7} The calculated geometry of adsorbed TMA differs by 60° rotation about the N–Si bond axis. This disagreement may originate from the use of a small cluster (Si₆H₁₂) in the calculation, where the interaction with the neighboring dimers and the dimer rows is neglected. The adsorbed states of TMA as a function of coverage at 80 and 300 K have been studied in detail using STM and PES, and we will report them elsewhere.

In summary, we have performed a STM investigation of TMA adsorption on Si(100)c(4×2) at 80 K. The location and the shape of protrusion clearly indicate that the molecular adsorption of TMA is purely site-specific on the down dimer atom, and the TMA adsorption on Si(100)c(4×2) can be categorized into Lewis acid–base reaction.

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