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Microscopic observation of precursor-mediated adsorption process of NH_3 on $Si(100)c(4\times 2)$ using STM

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Adsorption process of NH_3 on $Si(100)c(4\times 2)$ has been studied using scanning tunneling microscopy (STM) at 65 K. The dissociated species of NH_3 are adsorbed on the same dimer, since the depression on a dimer site is observed in the STM image. A small amount of molecular precursor species of NH_3 are observed as bright protrusions. The precursor species undergo dissociative chemisorption upon interaction with another mobile molecule, resulting in the depression on two adjacent dimers. The reactivity of the dimer adjacent to the already reacted dimer is largely enhanced resulting in the formation of two-dimensional islands of dissociated species. The C defect is found to be an active site for the dissociation of NH_3.

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I. INTRODUCTION

Numerous studies in the past decades have been reported about the existence of a weakly bound intermediate (i.e., precursor) in the course of gas-surface reaction.[1] The precursor state in a surface reaction plays a central role in steering the forward and backward reaction processes and thus controls the dynamics of the gas-surface interaction. However, only a few studies have succeeded in the direct observation of such precursor species and their decay into the reaction products.[2,3] Here we present a direct observation of such a precursor species and the dissociation process for NH_3 on $Si(100)c(4\times 2)$.

Atomic level understanding of chemical reactions on Si(100) is important for the controlled modification of the surface properties. NH_3 is a common nitriding agent for producing ultrathin silicon nitride films, which play an important role in the microelectronic industries as insulator, oxidation masks, diffusion barriers, and gate dielectrics.[4–8] A number of studies have been reported regarding the NH_3 adsorption on Si(100) using various experimental and theoretical methods.[9–18] The dissociation of NH_3 upon adsorption on Si(100) have been reported by most of these studies. The proposed dissociated species are (i) NH_2 and H,[12,13,18] (ii) NH and H,[19] or (iii) H and N (N goes into the bulk).[9–11] In the vibrational studies, the adsorbed NH_2 and H species were clearly identified.[12,13] Thus it has been unambiguously determined that NH_3 dissociates on Si(100) and NH_2 and H species are formed above 90 K. However, it is not clear whether the dissociation occurs on the same dimer[18] or across the dimers as predicted by calculations.[20] In the early scanning tunneling microscopy (STM) study by Hamers *et al.*,[10,11] the experiments were conducted at nearly saturation coverage, and thus it seemed difficult to get the information about the microscopic dissociation process.

In addition to the dissociated species, some studies have suggested that molecular NH_3 species may exist on Si(100). An ultraviolet photoemission spectroscopy (UPS) study reported the existence of physisorbed molecular NH_3 on Si(100) at 80 K.[17] Takaoka and Kusunoki indicated the existence of molecular NH_3 as a precursor using the molecular-beam technique.[14] Recently, Queeney *et al.* have studied the dissociation of NH_3 on $Si(100)(2\times 1)$ by a combination of infrared- (IR) absorption spectroscopy and density-functional (DFT) cluster calculation; the vibrational peaks related to the molecular NH_3 were observed at 220 K.[13] Despite these studies, direct and strong experimental evidence is still lacking in understanding the microscopic adsorption process of NH_3 on $Si(100)c(4\times 2)$.

In this paper, we report an experimental study about NH_3 adsorption on $Si(100)c(4\times 2)$ using STM at 65 K. The NH_3 molecule is found to be dissociated on the same dimer resulting in a single dimer depression in both occupied and unoccupied state images. The molecular precursor species are observed as bright protrusions. The precursor species is dissociated upon interaction with another mobile NH_3 molecule resulting in the depressions on two adjacent dimers. In addition to the dissociation on the clean dimer, NH_3 preferentially dissociates at the C defect. The dissociated species grow into two-dimensional islands with increasing exposure, suggesting the existence of a mobile precursor species and the adsorbate-enhanced reactivity of the neighboring dimers.

II. EXPERIMENT

The Si(100) substrate was obtained from a cut of a Si wafer (phosphorous doped, resistivity $=0.05\ \Omega$ cm). The clean surface was prepared by repeated flashing to 1500 K under UHV with a base pressure better than 1.5×10^{-8} Pa. Using a cryopump, a thus prepared clean surface contained $<1\%$ defects. The sample was cooled down to 65 K using liquid N_2 followed by pumping. Gaseous NH_3 molecules were introduced through a pulse-valve doser. The amount of exposure was expressed by the number of shots (one shot is ~ 0.1 L). STM measurements were carried out using a JEOL SPM-4500. Hereafter, the fractional coverage θ is estimated from the ratio of the number of reacted dimers to the total number of dimers in the scanning area.

III. RESULTS

Figures 1(a)–1(d) show a series of STM images in the occupied state at almost the same scanning area with increas-

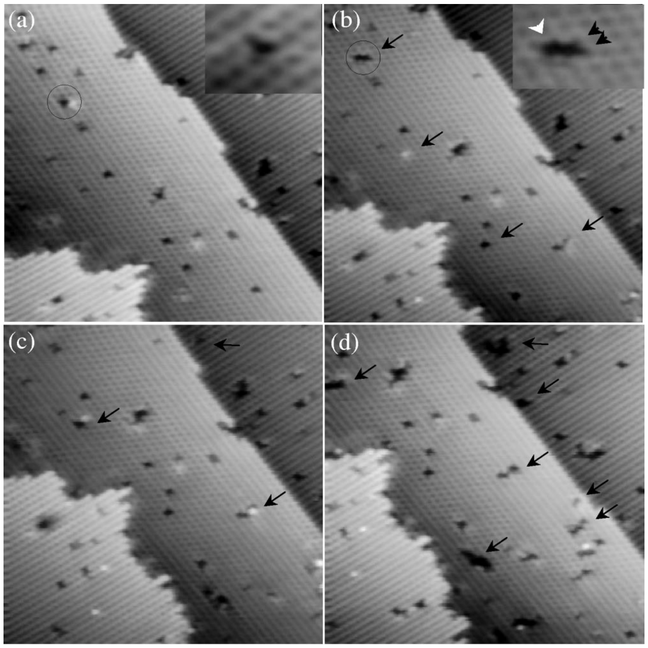

FIG. 1. A series of STM images of the Si(100)$c(4\times2)$ surface exposed to increasing amount of NH_3 at 65 K. All the occupied state images were recorded at almost the same scanning area. The images (a), (b), (c), and (d) were measured after the clean surface was exposed to three, four, five, and seven shots of NH_3, respectively. The arrows in (b)–(d) indicate the sites where some changes were observed as compared with the previous image. The inset in (a) shows a single dimer depression by NH_3 adsorption. The inset in (b) shows a depression converted from a bright protrusion after an additional exposure [see the circles in (a) and (b) also]. The two arrow heads indicate that two adjacent dimers are involved in such a reaction. Note that a white arrow head indicates the already reacted site. $V_{sample}=-2.0$ V and $I_{tunnel}=0.1$ nA. Scan area is 38×38 nm^2. The coverage in (d) $\theta=\sim0.02$.

ing NH_3 exposure at 65 K. The images (a), (b), (c), and (d) were measured after the clean surface was exposed to three, four, five, and seven shots of NH_3, respectively. Below the substrate temperature of 200 K, the flip-flop motion of the Si dimer is frozen and the alternate arrangement of buckled dimers is formed on the surface resulting into the $c(4\times2)$ structure.[21] In the buckled dimer, a partial charge transfer from a lower to an upper dimer atom occurs. Hence, the upper atom and the lower atom of a buckled dimer become negatively and positively charged, respectively.[22,23] Thus the STM images measured with negative (occupied state) and positive (unoccupied state) sample bias reflect the distribution of upper and lower atoms of the buckled dimers, respectively. Note that the defects on the clean surface ($<1\%$ in the present study) appear as dark depressions in the occupied state image.[24,25] Since the initial surface [Fig. 1(a)] was already exposed to three shots of NH_3, the increased number of depressions ($\sim1.6\%$) may be due to NH_3 adsorption (as discussed below).

The $c(4\times2)$ structure consisting of the alternate arrangement of buckled dimers is clearly observed in the images shown in Fig. 1(a)–1(d).[21] The arrows in Figs. 1(b)–1(d) indicate the sites where some changes are observed due to additional NH_3 exposure as compared with the previous image. Among the NH_3-induced changes, most are dark depressions and a few are bright protrusions. We have found that a minimum size of dark depression caused by NH_3 adsorption involves only a single dimer, as shown in the inset of Fig. 1(a). The bright protrusions were quite stable during STM measurements at 65 K. However, with an additional exposure of NH_3, the bright protrusion became a dark depression [see two adjacent dimers shown by two arrow heads in the inset of Fig. 1(b)]. The existence of a bright protrusion due to NH_3 exposure and its conversion to a dark site by an additional exposure were confirmed by several cycles of controlled experiments.

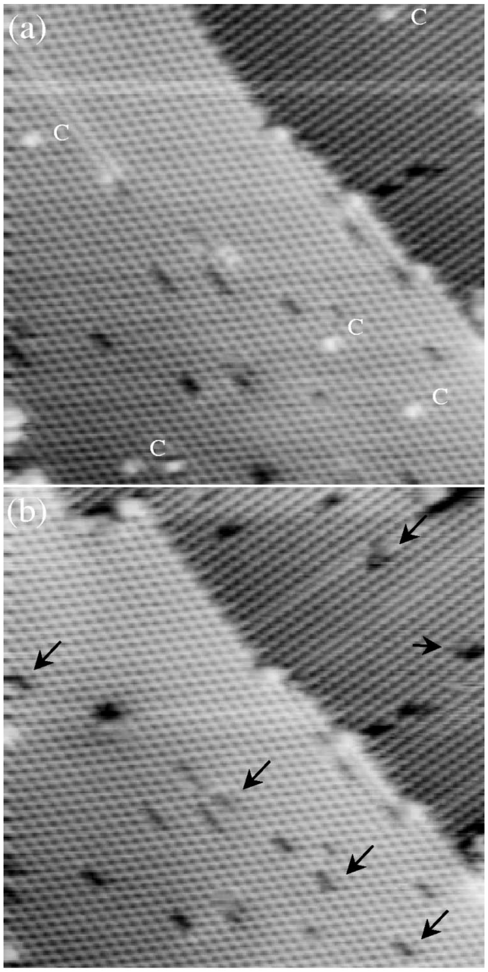

FIG. 2. STM images in the unoccupied state (a) before and (b) after a shot of NH_3 exposure at 65 K. Both images were recorded at the same scanning area. The bright protrusions indicated by C in (a) are the C defects on Si(100). The arrows in (b) indicate the sites where NH_3 induced changes were observed. $V_{sample}=2.0$ V and $I_{tunnel}=0.1$ nA. Scan area is 34×34 nm^2.

In order to investigate the reactivity of the C-type defect[24,25] towards NH_3, STM images including C defects were taken at the same scanning area before and after a shot of NH_3 exposure. Figures 2(a) and 2(b) show the STM images in the unoccupied state after the clean surface is exposed to one and two shots of NH_3 exposure, respectively, at 65 K. In Fig. 2(a), some depression sites and bright protru-

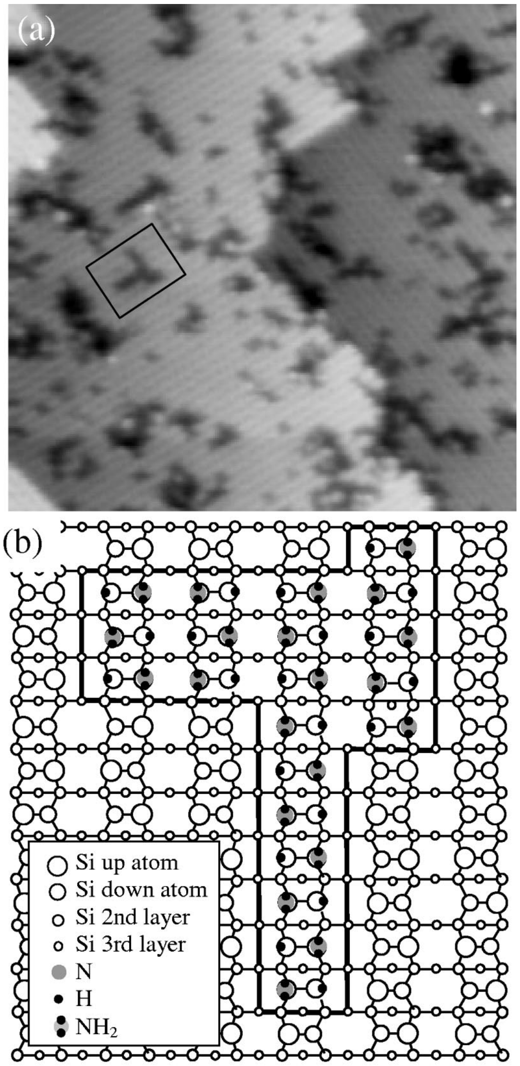

FIG. 3. (a) The STM image of NH_3 exposed Si(100) surface at a higher coverage at 65 K. The depressed areas are due to the dissociated species of NH_3. The fractional coverage $\theta = \sim 0.2$. $V_{sample} = -2.0$ V and $I_{tunnel} = 0.04$ nA. Scan area is 36×36 nm^2. (b) The island model consisting of the dissociated species ($NH_2 + H$).

sions are observed. The depression sites are due to preadsorbed NH_3 and/or a defect on the surface.[24] The bright protrusions indicated by ‘‘C’’ are the C defects. A C defect is created by the adsorption of a single water molecule on two adjacent dimers leaving two free dangling bonds.[25] In Fig. 2(b), arrows indicate the sites where adsorption of NH_3 occurs. Similar to the occupied state images, adsorbed species appear as dark depression in the unoccupied state image also. In addition, it is clearly observed that the bright protrusions of C defect become depressed upon NH_3 exposure.

In Figs. 1 and 2, we have found that the adsorption of NH_3 predominantly occurs near the already reacted dark site, indicating the initial stage of island formation. The island formation of adsorbed species is more clearly observed at higher exposure. Figure 3(a) shows a typical STM image of NH_3 adsorbed on the surface at a higher coverage ($\theta = \sim 0.2$). The depression areas and the bright protrusions are ascribed to the dissociative adsorption of NH_3 and the molecular precursor species, respectively, which will be discussed in detail later. It is clear that adsorbed NH_3 species grow as two-dimensional islands, i.e., the islands grow in both directions along and across the dimer row. A schematic atomic structure of a typical island of adsorbed NH_3 enclosed by a square [Fig. 3(a)] is shown in Fig. 3(b), based on the ‘‘opposed’’ structure of H-Si-Si-NH_2 units originally proposed by Queeney *et al.*[13] The area enclosed by the solid line corresponds to the depressed area in the image. The details of the atomic structure of adsorbed NH_3 will be discussed in the following section. By the inspection of several images at higher coverage, it is observed that the bright protrusions always appear at the edge of the island.

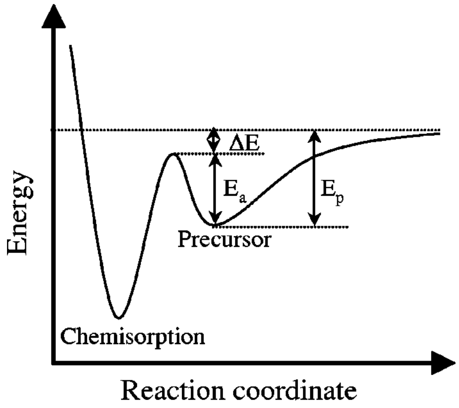

FIG. 4. One-dimensional potential-energy diagram of a precursor-mediated adsorption. E_a and E_p represent the activation barrier for adsorption and desorption from the precursor state, respectively. ΔE, E_a, and E_p are reported to be ~ 17 kJ/mol, 63–100 kJ/mol, and 117–138 kJ/mol, respectively. (Refs. 13–16)

IV. DISCUSSION

It has been reported that NH_3 dissociates upon adsorption on Si(100) above 90 K.[12,13,15] The NH_3 molecule as a typical Lewis base is expected to attack an electrophilic lower dimer atom initially.[15,16] Theoretical calculations have predicted a precursor-mediated dissociation of NH_3 on Si(100).[15,16] The first step is the molecular adsorption of NH_3 at a lower dimer atom (i.e., a precursor state), and the adsorption energy E_p is 117–138 kJ/mol (Fig. 4).[13,15,16] The second step is the dissociation of NH_3 from the precursor state to NH_2 and H. The dissociation from the precursor state has an activation barrier ($E_a = 63$–100 kJ/mol) with respect to the bottom of the precursor state.[16,15] Takaoka and Kunsunoki have experimentally determined that the activation barrier for dissociation is ~ 17 kJ/mol lower than that for desorption from the precursor state (ΔE in Fig. 4).[14] If an incoming molecule directly enters the dissociation path, the molecule is not trapped in the precursor state. The dissociated products (NH_2 and H) were clearly identified by vibrational spectra of the adsorbed species.[12,13] These dissociated species could be bonded on the surface dimer(s) in different ways: NH_2 and H species on the same dimer, on two adjacent dimers in a row, or on two dimers across the dimer row. The present experiments clearly show that the dissociated species (NH_2 and H) are bonded on the same dimer and form a H-Si-Si-NH_2 unit, since a minimum depression occurs on a single dimer due to NH_3 adsorption [the inset of Fig. 1(a)].[12,13]

Although the overall dissociation of NH_3 from gas phase is barrierless on Si(100) (see Fig. 4), there is a probability that some molecules are trapped in the precursor state. When the adsorption energy of NH_3 molecule is dissipated to the vibrational, rotational, and/or translational excitations and finally the substrate phonon on the Si surface, the molecule may be trapped in the precursor state.[16] UPS, molecular-beam, and IR studies have suggested the existence of molecular NH_3 on Si(100).[13,14,17] In agreement with the previous prediction, we ascribe the bright protrusion to a NH_3 molecule in the precursor state. Once a NH_3 molecule is trapped in a precursor state, this species is found to be quite stable and does not migrate during the STM measurement at 65 K. The activation barrier for migration of NH_3 in the precursor state was estimated to be $\sim$44 kJ/mol,[14] which is sufficiently large to prohibit the migration at 65 K. The adsorbed NH_3 in the precursor state remains undissociated until another adsorbing molecule interacts with the precursor NH_3, and both species become dissociated on two adjacent dimers as shown in the inset of Fig. 1(b).

The observation of a precursor state in the STM images suggests that the lifetime of precursor state is longer than the time of STM measurement. The lifetime of a precursor state depends on the activation barrier for dissociation and desorption from the precursor state.[14] Assuming the activation barrier for dissociation to be 17 kJ/mol (34 kJ/mol–17 kJ/mol)[14] or 63 kJ/mol (by theory)[16], we have estimated the lifetime of the precursor to be $\sim$166 sec or 4×10^{50} sec at 65 K. Thus the estimated lifetime is consistent with the present STM observation.

At very low coverage, where the area of clean terraces is large, some precursor species (bright protrusion) are found at the dimer in the clean terrace or at the neighboring dimer of an already reacted one. At relatively higher coverage, the precursor species are always found at the edge of reacted island. These phenomena can be explained by considering that an impinged NH_3 molecule is mobile on the surface prior to the adsorption in the precursor state or the dissociation. It should be noted that the number of precursor species in the STM images is very small ($\theta_p\sim2\times10^{-3}$ in Fig. 3) even at higher coverage. We think that only a part of impinged molecules are trapped in the precursor state. Queeney *et al.* have reported the existence of a small amount of molecular NH_3 using infrared spectroscopy.[13]

With increasing NH_3 exposure, the number of H-Si-Si-NH_2 units grows as two-dimensional island as observed in Fig. 3(a), i.e., the island grows in both direction along and across the dimer row. Based on the IR studies and DFT calculation, Queeney *et al.* have suggested that the H-Si-Si-NH_2 units are arranged in similar fashion as the dimers in the $c(4\times2)$ structure, where NH_2 is bound to a down atom as shown in Fig. 3(b).[13] The island formation of H-Si-Si-NH_2 units suggests that once an isolated H-Si-Si-NH_2 unit is formed, a mobile molecule is predominantly dissociated on the neighboring dimers, i.e., the reactivity of the dimer adjacent to the already reacted dimer is higher as compared to the dimer on the clean terrace.

The origin of the enhanced reactivity of the dimer next to the reacted one may be related to the charge polarization on the dimer atoms induced by the H-Si-Si-NH_2 unit, as predicted in the previous studies.[13] It is observed that the presence of a H-Si-Si-NH_2 unit, where NH_2 is adsorbed on the lower Si atom, stabilizes the opposed buckling in an adjacent dimer by $\sim$4.2 kJ/mol.[13] Thus the reactivity of the down dimer atom next to the H-Si-Si-NH_2 unit towards NH_3 is enhanced. The adsorbate-induced enhanced reactivity of the neighboring dimers may play an important role in the formation of desired nanostructures on the surface. In the present STM study, the island formation and the precursor species near the island are clearly visualized.

Finally, the unoccupied state images clearly indicate that dissociation of NH_3 occurs preferentially at the C defect (Fig. 2). The half-filled free dangling bonds of C defects are more reactive compared with the bare buckled dimer.[25] Therefore, the NH_3 dissociation at the C defect occurs on two adjacent dimers. Even at very low coverage ($\theta\sim0.01$) all the C defects appear to be reacted with NH_3 molecule. In addition to NH_3, the higher reactivity of C defect has also been observed in the case of CO and O_2 adsorption on Si(100).[26,27]

V. CONCLUSIONS

The microscopic adsorption process of NH_3 on Si(100) has been investigated using low-temperature STM. The NH_3 molecule is found to be dissociated on the same dimer. Molecular precursor species of NH_3 are also observed as bright protrusions. NH_3 in the precursor state is stable during STM measurement at 65 K and dissociates upon the interaction with another mobile NH_3 molecule. The reactivity of the dimer adjacent to the N_2H-Si-Si-H unit is enhanced. The mobile NH_3 species play an important role in the formation of two-dimensional island as a result of the dissociation on the dimer adjacent to the N_2H-Si-Si-H unit. The C defect is also a reactive adsorption site for NH_3.

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