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Multiple adsorption configurations of NH_3 molecules on the Si(001) surface

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Initial adsorption configurations of NH_3 molecules on the Si(001) surface are studied by using scanning tunneling microscopy (STM) and *ab initio* pseudopotential calculations. In contrast to the previous consensus of single configuration, we demonstrate that there exist *two* distinct STM features. One is found to be the existing model of on-dimer configuration, that is characterized by the previously unreported "U-shape" empty-state feature. The other is identified to be NH_2 and H adsorbed at the same side of two adjacent dimers along the dimer row. The identification of all the adsorption configurations would be useful for the quantitative analysis of Si nitridation.

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The interaction of NH_3 molecules with the Si(001) surface has attracted much attention in relation to the synthesis of silicon nitride film for microelectronic components. In one of the early studies, it was claimed that the NH_3 molecules fully dissociated on Si(001) even at temperatures as low as 90 K, with N atoms occupying subsurface sites and H atoms binding to the surface Si dangling bonds.[1] This view was challenged by the suggestion that NH_3 molecules partially dissociated into NH_x and H on Si(001) at room temperature (RT).[2] Later, NH_3 molecules were shown to dissociate into NH_2 and H to form Si-NH_2 and Si-H bonds at 120 K from thermal desorption spectroscopy with preadsorbed atomic deuterium.[3] This has been confirmed by subsequent experiments employing such techniques as electron-energy-loss spectroscopy,[4,5] secondary ion mass spectroscopy,[6] and angle-resolved photoemission spectroscopy.[7]

The atomic structure of a single NH_3 molecule on Si(001) has been studied both experimentally[4,8] and theoretically,[9–14] and a consensus seems to have been reached: an NH_3 molecule initially adsorbs on the "down" atom of a Si dimer, and then spontaneously dissociates into NH_2 and H through the path I in Fig. 1(a) to form the H-Si-Si-NH_2 configuration on one Si dimer. This arrangement will be designated as the on-dimer (OD) configuration and is depicted in Fig. 1(b). In addition to the path I, however, one can imagine two more dissociation paths such as II and III in Fig. 1(a). Dissociation through these paths would result in the inter-dimer (ID) and the inter-dimer-row (IDR) configurations shown in Figs. 1(c) and 1(d), respectively. The ID was recently claimed to be overpopulated to the OD owing to proton tunneling mechanism,[15] while the IDR had been theoretically discarded due to the small adsorption energy and the high dissociation barrier.[12] These two configurations has not been experimentally verified yet.

It is important to identify all the possible adsorption configurations of NH_3 on Si(001), for it can be used to quantify the incorporated N atoms and to understand the microscopic mechanism of the Si nitridation.[16] If the absolute quantity of the foreign atom is known, high-resolution scanning tunneling microscopy (STM) images can be used to draw plausible atomic structure, since a foreign atom often induces a noticeable STM feature on Si(001).[17,18] For instance, this approach has been successfully applied to understand the initial carbonization of Si(001) using C_2H_2.[18,19]

Adsorption of molecules can be best studied with real-space probes such as STM at very low coverage. There exist only a limited number of STM studies on $NH_3/Si(001)$,[20,21] but they do not provide information on the initial stage. Moreover, several molecules have recently been reported to take multiple adsorption configurations of different adsorption energies on Si(001).[22–25] It indicates that the adsorption of molecules are often subject to kinetics, not solely to energetics. Thus it is worth while to explore the possibility of multiple adsorption configurations for $NH_3/Si(001)$ using high-resolution STM.

In this paper, we report a combined study of STM and *ab initio* calculations on the initial stage of $NH_3/Si(001)$, and demonstrate that there exist two dissociative adsorption configurations. One is the OD that has been generally accepted hitherto [Fig. 1(b)]. For OD, we observed the previously unreported empty-state feature spanning three dimers, which enables clear distinction of OD from the normal dimer vacancy (DV). The other is identified to be the ID, and characterized by the two-dimer spanning STM feature that appears almost identical to the *C* defect on the clean surface.[26]

The experiments were carried out using a homemade STM in an ultrahigh vacuum (UHV) chamber with a base pressure better than 5×10^{-11} Torr. The samples were phosphorus doped Si(001) wafers with the resistivity of $1-10\ \Omega$ cm. Atomically flat clean surfaces were obtained by repeated flashing up to 1450 K maintaining the pressure below 5×10^{-10} Torr.[27] Ammonia gas was introduced to the

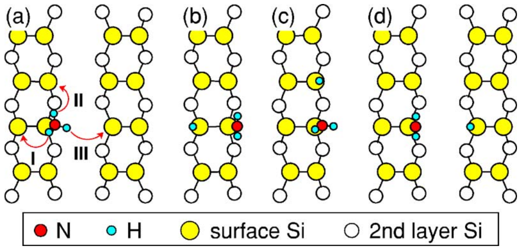

FIG. 1. (Color online) Schematic diagrams of NH_3 adsorption on Si(001). (a) Geometry of the molecular adsorption through a dative bond and possible H-dissociation pathways indicated by arrows. Dissociative adsorption cases (b) on-dimer, (c) inter-dimer, and (d) inter-dimer-row configurations.

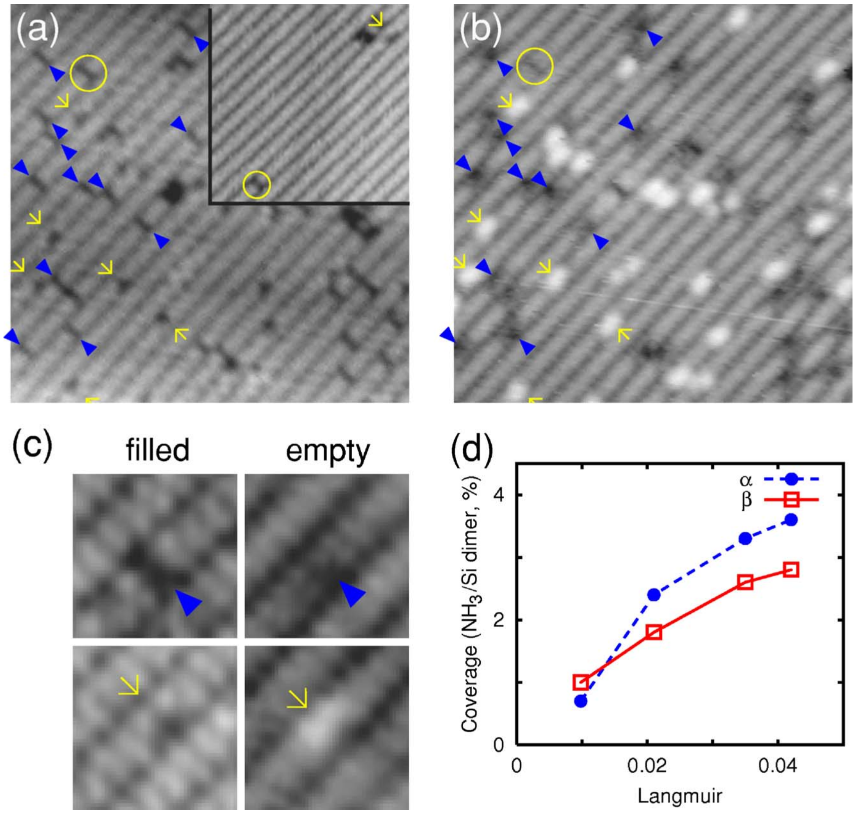

FIG. 2. (Color online) STM images of the same region of $NH_3/Si(100)$ after dosing 0.04 L of NH_3 molecules: (a) filled state ($V_s = -2.0$ V) and (b) empty state ($V_s = +0.7$ V). In the left part of the images, the normal DV and α and β features are indicated by a circle, arrowheads, and arrows, respectively. Inset in (a) is a filled-state image of the clean surface showing a DV and a C defect. (c) Enlarged STM images of the α and β features. (d) The density change of α and β features with respect to the NH_3 dosage (see text).

sample surface at RT by backfilling the chamber at 1.5×10^{-10} Torr. The resulting $NH_3/Si(001)$ was investigated by STM at RT.

Figures 2(a) and 2(b) show the filled- and the empty-state images of Si(001) after dosing 0.04 L of NH_3 molecules respectively. In both images, two different features, α (arrowheads) and β (arrows) are observed. The α feature appears as a missing dimer in the filled-state image resembling the intrinsic DV.[17] However, in the empty state, it spans three dimer sites clearly discriminating itself from the DV. It takes a "U" shape, which is composed of a dimer with a missing atom and two slightly depressed adjacent dimers. To our best knowledge, this "U-shaped" feature has not been reported. The β feature spans two dimers and appears as two missing atoms on the same side of two adjacent dimers in a dimer row in the filled-state images. It looks very similar to the C defect which is frequently observed on the clean Si(001) surface [e.g, see the inset in Fig. 2(a)]. It is also indiscernible from the C defect in the empty-state images, characterized by an asymmetric tear-drop-like bright protrusion.

In order to examine whether these two features are related with the adsorption of NH_3, we counted the two features in the empty-state STM images at several different NH_3 dosages. The number of the α feature can be counted directly from the empty-state images, for it is clearly differentiated from the intrinsic DV. On the other hand, the number of the β feature is determined by subtracting the number of C defects on the clean surface from the total number of C-defect-like features. In our samples, the density of the C defect on the clean surface was around 0.5%. The populations of α and β increased with the dosage of NH_3 molecules, showing that both α and β features are due to NH_3 adsorption [Fig. 2(d)].

We assign the α feature as the OD in Fig. 1(b), since this configuration is expected to appear as the depression of a single dimer in the filled-state images due to the saturated Si dangling bonds. As for the β feature, the filled- and empty-state features are reminiscent of those for the C_2H_2 adsorbed in the end-bridge configuration on Si(001).[22,28] The end-bridge configuration of C_2H_2 is a natural counterpart of the ID [Fig. 1 in Ref. 22 vs Fig. 1(c)] in the case of dissociated NH_3. Thus we associate the β feature to the ID.

To examine the above assignments and to understand the unprecedented STM observations including the U-shaped empty-state feature and the C-defect-like feature, we have performed the *ab initio* pseudopotential calculations[29] within the generalized gradient approximation[30] of the exchange-correlation functional. We used the energy cutoff of 350 eV, the theoretical lattice constant of 5.46 Å, the **k**-point sampling equivalent to 8×8 mesh within the 1×1 surface Brillouin zone, and ultrasoft pseudopotentials.[31,32] The substrate is modeled by the repeated slab geometry with a 4×8 surface supercell. The slab is composed of six Si layers with the $c(4 \times 2)$-reconstructed top surface and the H-passivated bottom surface. Such a slab alternates with a fourteen-layer-thick vacuum region. All the atoms, except for those in the two bottom Si and the H layers, were relaxed so that atomic forces are $\leqslant 0.001$ eV/Å. The calculated results are presented in Table I, and some of the relaxed structures are shown in Fig. 3.

The molecular adsorption, which has been believed to be a precursor state, is found to be an exothermic reaction with the adsorption energy (E_{ads}) of 1.31 eV. This occurs preferentially on the "down" atom of a Si dimer, due to the attraction between the lone pair electrons in NH_3 and the empty

TABLE I. Adsorption energies E_{ads} (in eV) and structural parameters for NH_3 adsorption configurations. $d_{\text{Si-Si}}$ and θ are the bond length and the buckling angle of the reacted Si dimers, respectively. $d_{\text{Si-N(H)}}$ is the Si-N(H) bond length. $\phi_{\mathrm{N(H)}}$ is the bond angle of Si-Si-N(H). Lengths and angles are presented in Å and degree, respectively.

		Structural parameters					
Configuration	E_{ads}	$d_{\text{Si-Si}}$	θ	$d_{\text{Si-N}}$	$d_{\text{Si-H}}$	ϕ_{N}	ϕ_{H}
clean		2.35	18.5				
molecular	1.31	2.42	12.4	1.98		100	
on-dimer	2.06	2.45	0.0	1.73	1.49	116	113
inter-dimer[a]	1.79	2.45	4.3	1.73		106	
		2.39	−9.5[b]		1.49	113	
inter-dimer-row[a]	1.56	2.44	−6.0[b]	1.72		116	
		2.41	0.1		1.49		108

[a] Upper (lower) row is for the Si dimer reacted with NH_2 (H).

[b] The negative buckling angle implies that the unreacted Si atom of the reacted dimer is "down."

dangling bond at the "down" Si atom. The Si-N bond length is 1.98 Å, longer than 1.73 Å for the dissociative adsorption cases. This reflects the weaker Si-N dative bond in the precursor state. It is notable that the Si-N bond is tilted by ~5° to an adjacent dimer on the same dimer row as seen in Fig. 3(a). An important consequence of the tilted geometry is that the H transfer distance during the NH_3 dissociation is shorter for the ID than for the OD, which in turn result in the smaller energy barrier for the ID.[15]

Among the considered dissociative adsorption structures, the OD is the ground-state configuration with $E_{\mathrm{ads}}=2.06$ eV. In the OD, the reacted Si dimer becomes symmetric and the bond length is elongated to 2.45 Å. The NH_2 possesses the mirror symmetry with respect to the reacted dimer[12,33] as shown in Fig. 3(b), differently from the *gauche* model proposed by some previous calculations.[13,15] The ID is found to be the next stable geometry having $E_{\mathrm{ads}}=1.79$ eV. The NH_2 in the ID, in contrast to the OD case, adsorbs in the *gauche* geometry with the lone-pair of N directed towards the H atom on the adjacent dimer. The Si dimers reacted with NH_2 (H) are elongated to 2.45 (2.39) Å, and are oppositely buckled although the buckling is significantly reduced compared with the normal dimers. The IDR is the least stable one having $E_{\mathrm{ads}}=1.56$ eV. In fact, the IDR had been discarded in Ref. 12 due to its high dissociation barrier.

The constant-current STM images were simulated using the fully relaxed geometries within the Tersoff-Hamann approximation.[34] The simulated images for the OD and ID are shown in Figs. 3(d) and 3(e), respectively. The simulation of the OD reveals that the reacted dimer appears as a DV in the filled state. In the empty state, the Si atom reacted with NH_2 appears as a dark depression and the two adjacent dimers as weakly depressed split dimers constituting the U shape. All these are in agreement with the α feature in the experiment, confirming the assignment of the α feature to the OD. Splitting of the two adjacent dimers is related with their shortened bonds. They are shorter by 0.02 Å compared to the normal dimers. The shorter dimer bond implies stronger interaction between the constituent Si atoms, and thus ends up with spatially more separated antibonding orbitals that are observed in the empty-state image. These two dimers are also lower by 0.05 Å in height, consistent with their weak depression.

For the case of the ID, the two reacted Si atoms manifest as two neighboring dark depressions in the filled state. In the empty state, however, a bright tear-drop-like protrusion appears shifted towards the unreacted atoms of the two reacted dimers. It is asymmetric with the wider part (i.e., the head of the teardrop) at the dimer reacted with NH_2 and the tail at the dimer reacted with H. All these well reproduce the experimental β feature, evidencing the existence of the ID.

Relying on the degree of agreement between the experiments and the simulations, we conclude that the NH_3 molecule dissociatively adsorbs on Si(001) in *two* configurations, ID as well as OD. We speculate that the metastable ID is kinetically stabilized. A recent theoretical study[15] has suggested the existence of ID employing the proton tunneling mechanism and predicted order-of-magnitude larger amount of the ID than the OD at RT. In contrast to this prediction,

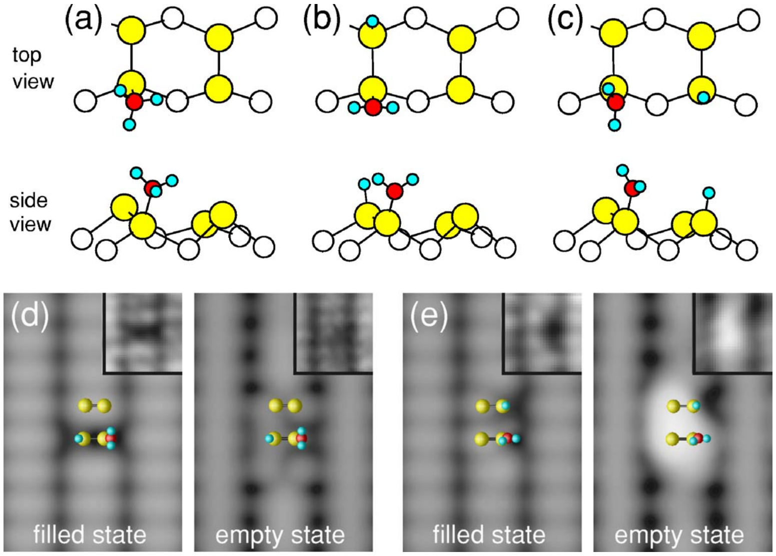

FIG. 3. (Color online) Fully relaxed atomic structures of (a) molecular, (b) on-dimer, and (c) inter-dimer adsorption. Simulated STM images of (d) on-dimer and (e) inter-dimer configurations. Filled- and empty-state images at $V_s=-0.7$ and +0.6 V, respectively, are obtained from the averaged tunneling current of two configurations where dimers are oppositely buckled to simulate the RT fluctuation of dimers. Insets are corresponding experimental images.

our measurement plotted in Fig. 2(d) shows the comparable amount of the OD and the ID. This suggests that the ID is accessed through thermal excitation rather than quantum tunneling.

It is worth while to comment that our findings on $NH_3/Si(001)$ provide a clue to identify the nature of the *C* defect on the clean surface. Recent experimental[35] and theoretical[36] studies suggest that the *C* defect is a dissociated water molecule adsorbed in the ID. However, a definitive conclusion has been hindered by the absence of the more stable OD in contrast to the presence of the metastable ID. Based on our findings of the existence of both OD and ID in $NH_3/Si(001)$, we propose that water molecules may adsorb in both OD and ID on Si(001): the *C* defect is the dissociated H_2O in the ID, while some of the apparent DVs in the filled-state STM images should be the dissociated H_2O in the OD, forming H-Si-Si-OH on one Si dimer. This proposition can be examined by high-resolution empty-state STM images.

In conclusion, based on the STM observations and the first-principles calculations, we have demonstrated that an NH_3 molecule undergoes dissociative adsorption on Si(001) in two configurations. The two dissociated fragments (NH_2 and H) form bonds with two Si atoms either on one Si dimer (OD) or across two adjacent Si dimers in a dimer row (ID). The OD, appearing similar to the normal DV in the filled-state image, shows a distinctive U-shaped three-dimer feature in the empty state. The ID shows almost identical features with the *C* defect on the clean surface. We propose that a water molecule would adsorb in both OD and ID on Si(001) similarly to the present ammonia case. The knowledge of all adsorption structures of $NH_3/Si(001)$ would allow the quantitative measurement of the incorporated N amount and thus be useful to achieve atomistic understanding of the nitridation process of Si(001), as exemplified in the case of the carbon incorporation using $C_2H_2/Si(001)$.[18,19,22]

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