Interplay of Hydrogen-Bond and Coordinate Covalent-Bond Interactions in Self-Assembly of NH_3 Molecules on the Si(001) Surface

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An exchange of hydrogen-bond and coordinate covalent-bond (dative-bond) interactions is found to play a critical role in the self-assembly of NH_3 molecules on the Si(001) surface. An NH_3 molecule in the height of ∼3–10 Å above the surface is attracted toward the preadsorbed NH_2 moiety through the long-range H-bond interaction. Within ∼3 Å, the H-bond interaction becomes repulsive, and instead the dative bond with the buckled-down Si atom governs the adsorption process. The interplay of the two interactions induces the clustering and the zigzag feature of the dissociatively adsorbed NH_3 molecules on the Si(001) surface.

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Adsorption of molecules on a semiconductor surface has been studied intensively for several decades, in relation with atomic control of semiconductor processes and fabrication of molecular electronic and chemical devices [1–3]. In particular, the adsorption process of strongly interacting molecules has attracted much attention due to the complicated interactions between the molecules themselves in addition to those between the molecule and the surface [4,5].

Ammonia (NH_3) is widely used as a common nitriding agent in silicon technology [6]. Because of the polar property, the NH_3 molecules adsorbed on the Si(001) surface can form a strongly interacting channel of hydrogen (H) bonds. The adsorption process of a single NH_3 molecule on the Si(001) surface is now well established: first the incoming NH_3 forms a coordinate covalent (dative) bond with a buckled-down Si atom on the surface (the molecular adsorption state), and then one H atom is dissociated from the NH_3 and adsorbs on a nearby buckled-up Si atom (the dissociative adsorption state) [7–9]. In higher coverage, the NH_3 molecules self-assemble and form clusters in zigzag pattern on the Si dimer rows [10–12]. However, the microscopic origin and the detailed interaction mechanism for the self-assembly of NH_3 molecules on the Si(001) surface are still controversial.

Theoretically, the parallel linear chain was calculated to have the minimum formation energy due to the H bond between the adsorbed NH_2 fragments along one side of the dimer row [13,14]. However, experimental studies claimed the zigzag chain to be the dominant state over the linear one, in which the dissociated NH_2 fragments are arranged alternatively on the opposite sides of adjacent dimers along a dimer row. Infrared absorption spectroscopy measurements suggested that the zigzag chain structure is more favored, and the indirect interaction model of the adsorbate-induced modification in the electronic structure of neighboring dimers was proposed [15]. The STM study also observed that the adsorption of NH_3 forms a zigzag chain structure dominantly [12]. Another theoretical study reported that the zigzag chain structure is higher in adsorption energy than the linear chain structure due to the adsorbate-adsorbate repulsion [16]. Thus far, the theoretical studies have focused mainly on the energetics and the electronic structures of the adsorption configurations [11,13–16].

In this Letter, we address the essential role of the adsorption kinetics in the self-assembly of NH_3 molecules on the Si(001) surface. The detailed potential energy surfaces (PES) are investigated for an NH_3 molecule under the interaction with the preadsorbed NH_3. We find that (i) an unexpectedly strong attractive interaction is induced by the H bond between the impinging NH_3 and the preadsorbed NH_2, (ii) the exchange of dominant attractive interactions occurs between the H bond and the dative bond during the adsorption process near the surface, and (iii) as a result, the NH_3 adsorbs preferentially on a buckled-down Si atom next to the preadsorbed NH_3, leading to the experimentally observed zigzag chain structure [12,15].

We performed density-functional theory calculations as implemented in the VIENNA *ab initio* simulation package code [17]. The ultrasoft pseudopotentials [18] with a kinetic energy cutoff of 350 eV were used and the generalized gradient approximation was used for the exchange-correlation energy [19]. The **k**-point set equivalent to an 8×8 mesh within a 1×1 surface Brillouin zone was used. The substrate was modeled using a six-layer slab with a 14-layer-thick vacuum space. The dangling bonds at the bottom surface were passivated by H atoms. A 4×4 surface cell was mainly used, and 4×8 and 8×4 cells were adopted when the long-range interaction between NH_3 molecules was considered.

First, the interaction between a single NH_3 molecule and the clean Si(001) surface is investigated. The potential energy surfaces of the NH_3 are calculated at various heights. The height Z is defined as the distance between the planes of the N atom of the NH_3 molecule and the uppermost buckled-up Si atoms of the clean surface, which are parallel to the Si(001). We divide the planes with the mesh spacing of $\sqrt{2}a/4$, as shown in Fig. 1(a), where a is the lattice constant. The N atom is fixed at each grid point on the plane, and all the other atoms are relaxed except those in the fixed bottom layers of the Si slab. The reference of the potential energy is an isolated NH_3 and the clean Si(001) surface.

When the NH_3 molecule is located at 4 Å above the surface, the potential energy is -0.05 eV either above the buckled-up or the buckled-down Si atom (see Fig. 2). Above the buckled-down Si atom, the N atom of the NH_3 is directed to the surface, indicating the attraction is induced by the dative-bond formation between the lone-pair electrons of the NH_3 and the electron-deficient buckled-down Si atom. On the other hand, above the buckled-up Si atom, the H atom of the NH_3 faces the surface, attracted toward the nucleophilic buckled-up Si atom. When the height is less than 4 Å, the NH_3 molecule is driven toward the buckled-down Si atom. Above the buckled-up Si atom, the potential energy increases as the result of the nuclear-nuclear repulsion between the interacting atoms, as shown in Fig. 2. Above the buckled-down Si atom, as the NH_3 approaches the surface, the potential energy decreases to -0.11 eV at $Z = 3.4$ Å and finally to -1.31 eV at $Z = 1.3$ Å, forming the molecular adsorption state.

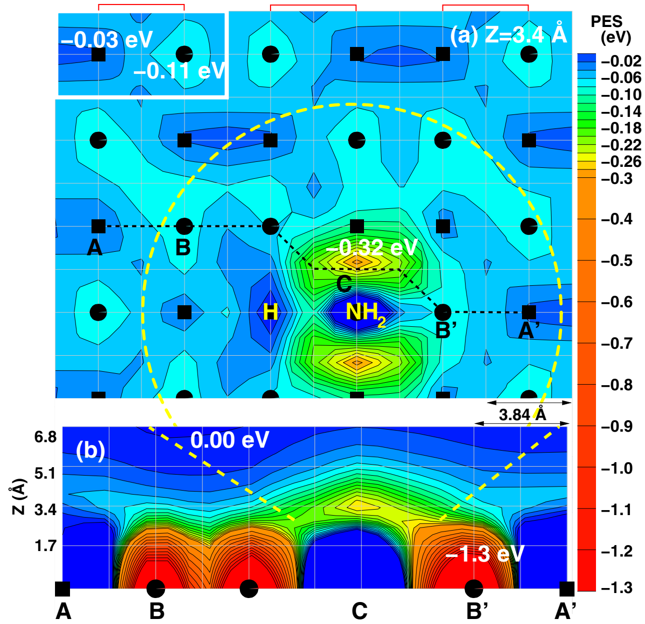

FIG. 1 (color online). (a) Calculated potential energy surfaces (PES) for an impinging NH_3 molecule near the preadsorbed NH_3 at the height of 3.4 Å. The inset in the top-left corner shows the calculated PES on the clean surface at the same height. (b) The vertical section of the PES along the black dashed line in (a). Filled boxes (circles) at the grid points indicate the nearby site of the buckled-up (-down) Si atoms. The red brackets on the top indicate the dimer rows. The contour spacing is 0.02 eV in the range of 0.0 to -0.3 eV and 0.1 eV in -0.3 to -1.3 eV. The gray (yellow) dashed lines represent the estimated attraction range of the H bond, where the lateral force fields for the impinging NH_3 exist.

Next, the interaction between an NH_3 molecule and the Si(001) surface with a preadsorbed NH_3 molecule is examined. The preadsorbed NH_3 is considered to be dissociated in the on-dimer (OD) configuration, where the H is on the buckled-up Si atom and the NH_2 is on the buckled-down Si atom of the same dimer [9]. When an approaching NH_3 molecule is in the height of 3–4 Å above the surface, there is a deep potential well near the adsorbed NH_2 [see Figs. 1(a) and 1(b)]. The minimum value on the PES at $Z = 3.4$ Å is -0.32 eV, which is much lower than that (-0.11 eV) on the clean surface. This indicates that the preadsorbed NH_3 provides a basin of strong attraction for another incoming NH_3 molecule. In the minimum of the PES, the lone-pair orbital of the NH_3 molecule faces the H atom of the adsorbed NH_2 [see Fig. 3(a)]. This means that the H bond between the N atom of the incoming NH_3 and the H atom of the adsorbed NH_2 is responsible for the attraction. Figure 1(b) shows a vertical section of the PES. The dashed gray (yellow) line represents the attraction range where the lateral force field attracts an incoming NH_3 molecule toward the preadsorbed NH_2. The estimated attraction range of the H bond is approximately 10 Å, which spans about 5 dimers and 3 dimer rows in a circle with a radius of the interaction range [see the gray (yellow) dashed circle in Fig. 1(a)].

At the height from 10 to ~3 Å, the H-bond attraction exceeds the dative-bond attraction as shown in Fig. 2. The interaction range of the H bond is found to be long enough to cluster NH_3 molecules even in low coverage; we esti-

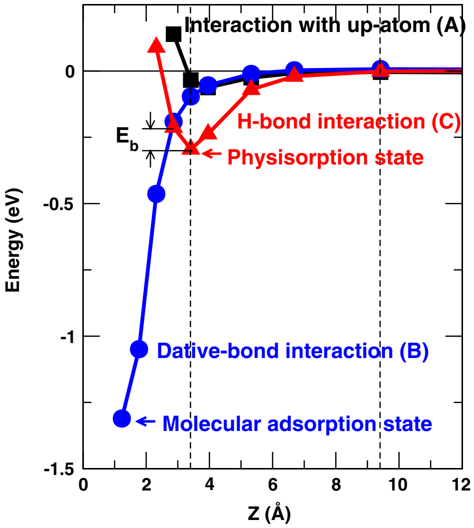

FIG. 2 (color online). Calculated potential energies above a buckled-up Si atom (■), a buckled-down Si atom (●), and the preadsorbed NH_2 moiety (▲) as a function of the height Z.

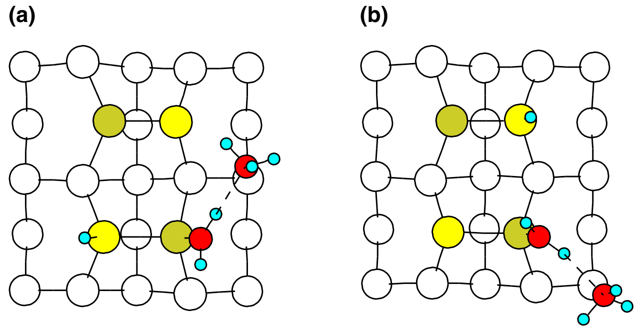

FIG. 3 (color online). Atomic structures of the physisorption states of NH_3 near (a) OD and (b) ID. The bright gray (bright yellow) and medium gray (dark yellow) large balls represent the buckled-up and buckled-down Si atoms, respectively. The dark gray (red) and medium gray (blue) small balls indicate the N and H atoms, respectively.

mate that the clustering of the NH_3 molecules can occur if the coverage of the NH_3 is higher than 0.07 monolayer (ML), i.e., one NH_3 molecule per 15 dimers. Experimentally, the clustering of NH_3 molecules has been observed when the concentration is higher than ~0.07 ML [12].

Near the height of $Z = 3.4$ Å, the physisorption states of NH_3 with the preadsorbed NH_2 are found. The atomic structure of the most stable physisorption state is shown in Fig. 3(a). The other physisorption states are found at different positions of the NH_3 with different orientations of the NH_2 (not shown). The fact that the N atom of the NH_3 faces the H atom of the adsorbed NH_2 indicates that the binding character is H bond. The binding energy and the H-bond length are calculated to be 0.32 eV and 1.98 Å, respectively. For a free NH_3 dimer, the strength of the H bond is calculated to be 0.15 eV, which is close to the experimental value of 0.12 eV [20], and the H-bond length is calculated to be 2.43 Å. It should be noted that the H bond between the NH_3 and the NH_2 moiety is unexpectedly strong. The strong H bond can be understood from the charge redistribution near the preadsorbed NH_2 moiety; Fig. 4 shows the calculated total charge densities near the preadsorbed NH_2 and the isolated NH_3 molecule. The difference of the total charge densities [Fig. 4(c)] clearly shows that the electrons are transferred from the H atoms to the N atom. The electron-deficient H of the NH_2 can effectively attract the lone pair of the NH_3 molecule. Therefore, the wide interaction range observed on the calculated PES (Fig. 1) originates from the strong H bond between the NH_3 and the NH_2 moiety.

The height near 3 Å above the surface is an important region where the dominant attraction mechanism changes from the H-bond to the dative-bond interaction (see Fig. 2). Down to $Z = 3.4$ Å, the potential energy continues to decrease and reaches -0.32 eV near the preadsorbed NH_3, as shown in Fig. 2. This value is much lower than that (-0.11 eV) on the clean surface (above the buckled-down Si atom) at the same height. However, below $Z = 3.4$ Å, the potential energy of the NH_3 starts to increase (i.e., interaction becomes repulsive) near the preadsorbed NH_2. On the other hand, the potential energy above the buckled-down Si atom rapidly decreases because a dative bond begins to form between the NH_3 and the buckled-down Si atom. Therefore, the exchange between the two attractive interactions occurs in this region. There exists an energy barrier (E_b) for the transition from the physisorption states (induced by the H bond) to the molecular adsorption state (by the dative bond). The E_b is calculated using the dimer method [21], and found to be only a few tens of meV, which is close to the E_b estimated from Fig. 2. At $Z = 1.32$ Å, the NH_3 molecule forms the molecular adsorption state with the potential energy of -1.24 to -1.55 eV, depending on the adsorption sites near the preadsorbed NH_3.

Based on the above calculational results, we can figure out the process of the self-assembly of NH_3 on the Si(001) surface: (i) a single NH_3 molecule adsorbs on a buckled-down Si atom and dissociates into H and NH_2; (ii) another NH_3 molecule impinging in the range of the H-bond attraction from the adsorbed NH_2 is attracted toward the NH_2; (iii) when an incoming NH_3 approaches within 3 Å

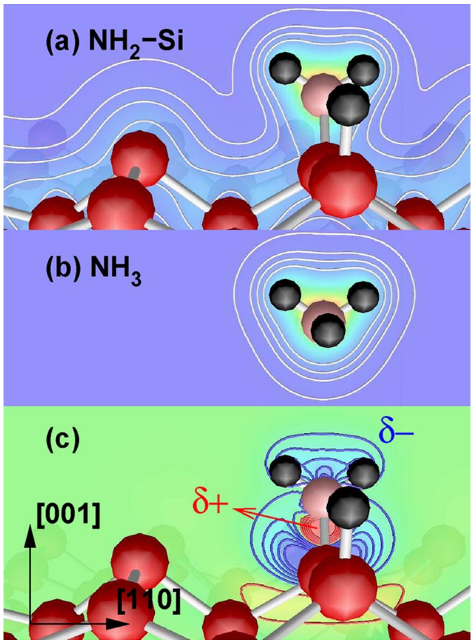

FIG. 4 (color online). Total charge densities of (a) the adsorbed NH_2 in the OD configuration [ρ(OD)] and (b) the NH_3 molecule [$\rho(NH_3)$] are shown on the planes of the N and the two H atoms. (c) The difference of the charge densities [ρ(OD)-$\rho(NH_3)$-ρ(surface)] is shown with the bright gray (red) (positive; increase of the charge) and the dark gray (blue) (negative; decrease of the charge) contours. In (a) and (b), the contours are drawn for 0.015, 0.077, 0.154, and 0.307e/Å^3. In (c), the bright gray (red) contours begin from +0.015 to +0.077e/Å^3, and the dark gray (blue) ones from -0.015 to $-0.077e$/Å^3, with the increment of 0.0155e/Å^3.

above the surface, the NH_3 is attracted not by the H bond but by the buckled-down Si atom. The direction of the NH_3 adsorption pathway is then turned toward the buckled-down Si atom on the surface, instead of the adsorbed NH_2; (iv) finally, the NH_3 molecule adsorbs on a buckled-down Si atom near the adsorbed NH_3, and subsequently dissociates into H and NH_2.

According to this mechanism, the molecular adsorption site is determined by the dimer buckling near the adsorbed NH_2. At room temperature, the buckled dimers can flip and affect the adsorption of the NH_3 on the clean surface. However, the preadsorbed NH_2 induces charge polarization on the buckled-up atoms of the neighboring dimers [15,16], and the two H atoms of the NH_2 tend to be oriented toward the neighboring nucleophilic buckled-up Si atoms. Therefore, the impinging NH_3 adsorbs on the buckled-down Si atoms next to the H along the dimer row in a zigzag configuration, as observed in experiments [12,15]. In contrast, due to weaker inter-dimer-row correlation, the adjacent dimers in the neighboring dimer row will undergo flipping motion at room temperature. Hence the adsorption site in the neighboring dimer row should depend on the instantaneous buckling of the corresponding dimers [22].

Another dissociated configuration of NH_3 on the Si(001) surface is the interdimer (ID), where H is on a buckled-up Si atom of the adjacent dimer on the same side of the dimer row [9]. The adsorption process of an NH_3 molecule near the ID is also investigated. The attractive potential energy by the H bond between the impinging NH_3 and the preadsorbed NH_2 is found to be close to that calculated for the OD configuration. The physisorption states of the NH_3 are also found near the ID configuration, as shown in Fig. 3(b). The binding energy of the physisorption state (H bond) in the ID is calculated to be 0.32 eV, which is the same as that in the OD. The H-bond distance (2.02 Å) in the ID is close to that (1.98 Å) in the OD. When $Z < 3$ Å, the adsorption of the NH_3 is also dominated by the dative-bond formation with the surface buckled-down Si atom. As a result, the NH_3 molecule adsorbs onto the buckled-down Si atoms adjacent to the ID, as demonstrated in the recent STM experiment [12].

In conclusion, the kinetic nature of the self-assembly of NH_3 molecules on the Si(001) surface is investigated. The impinging NH_3 molecule is attracted toward the preadsorbed NH_2 through the H bond in the height of $\sim$3–10 Å, and within $\sim$3 Å the dative bond partakes to drive and adsorb the NH_3 on the buckled-down Si atom. Therefore, the NH_3 prefers to adsorb on a buckled-down Si atom next to the preadsorbed NH_3. The exchange of the dominant attractive interactions between the H bond (between the molecules) and the dative bond (between the molecule and the surface) plays an essential role in clustering the NH_3 molecules and forming the characteristic zigzag patterns on the Si(001) surface.

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