

## Adsorption states of the self-assembly of NH<sub>3</sub> molecules on the Si(001) surface

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Condens. Matter 21 064237

(<http://iopscience.iop.org/0953-8984/21/6/064237>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 17:48

Please note that [terms and conditions apply](#).

# Adsorption states of the self-assembly of NH<sub>3</sub> molecules on the Si(001) surface

Yong-Sung Kim<sup>1</sup>, Ja-Yong Koo<sup>1</sup> and Hanchul Kim<sup>2</sup>

<sup>1</sup> Korea Research Institute of Standards and Science, PO Box 102, Yuseong, Daejeon 305-600, Korea

<sup>2</sup> Department of Physics, Sookmyung Women's University, Seoul 140-742, Korea

E-mail: [yongsung.kim@kriss.re.kr](mailto:yongsung.kim@kriss.re.kr)

Received 19 July 2008

Published 20 January 2009

Online at [stacks.iop.org/JPhysCM/21/064237](http://stacks.iop.org/JPhysCM/21/064237)

## Abstract

Adsorption states of the self-assembly of NH<sub>3</sub> molecules on the Si(001) surface are investigated using density-functional theory calculations. H-bond interactions between incoming and adsorbed NH<sub>3</sub> molecules produce a strong attractive potential field for the incoming molecules. Induced by the H bonds, physisorption states are formed on the adsorbed NH<sub>3</sub>. Molecular adsorption states are formed on a buckled-down Si atom near the adsorbed NH<sub>3</sub>. Various physisorption, molecular and dissociative adsorption configurations are discussed.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

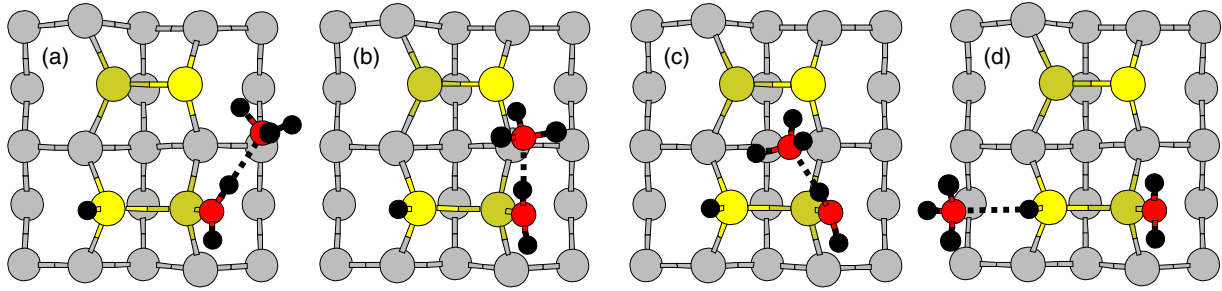
The ammonia (NH<sub>3</sub>) molecule is a common nitrating agent in the Si nitridation process [1]. As an initial stage of the nitridation, adsorption of NH<sub>3</sub> molecules has been extensively studied. For a single NH<sub>3</sub> molecule, the adsorption process on the Si(001) surface is known to be the following [2–4]. (i) An NH<sub>3</sub> molecule adsorbs on a buckled-down Si atom on the Si(001) surface. The lone-pair electron of the NH<sub>3</sub> molecule prefers to form a dative bond with the electron-deficient buckled-down Si atom. This is the molecular adsorption state and has a Si–NH<sub>3</sub> bonding configuration. (ii) Then, an H atom of the Si–NH<sub>3</sub> is dissociated and chemisorbs on a nearby buckled-up Si atom. An NH<sub>2</sub> fragment is left behind and a new Si–H bond forms closely. When the NH<sub>2</sub> and H fragments are located on the same dimer, it is called an on-dimer (OD) configuration. When they are on neighboring dimers in the same dimer row, it is called an inter-dimer (ID) configuration. These are the dissociative adsorption states in the adsorption of a single NH<sub>3</sub> molecule on the Si(001) surface.

Subsequent adsorption of NH<sub>3</sub> molecules is more interesting. The NH<sub>3</sub> molecules are polar molecules and strongly interact with each other. Therefore, the subsequent adsorption is under the influence of the preadsorbed species and tends to be self-assembled on the Si(001) surface [5–8]. The self-assembly of NH<sub>3</sub> molecules on the Si(001) surface occurs both along the dimer row and across the dimer rows. Along the dimer row, the NH<sub>2</sub> fragments are arranged in

a zigzag configuration. They are located on buckled-down Si atoms along the dimer row on the Si(001) surface. The simple H-bond interaction model which considers only the adsorption energies fails to explain the zigzag feature of the self-assembly of NH<sub>3</sub> molecules [9, 10]. Instead, the indirect interaction model, adsorbate-induced charge polarization of the neighboring dimers, can partially explain the zigzag feature [11]. However, the long-range interaction to attract the molecules towards the adsorbed NH<sub>3</sub> cannot be clearly understood from the indirect interaction model. Recently, it was proposed that the interplay of the H- and dative-bond interactions plays an important role in the self-assembly of NH<sub>3</sub> molecules [12]. In this paper, the adsorption states of physisorption, molecular and dissociative adsorption are investigated in the self-assembly of NH<sub>3</sub> molecules on the Si(001) surface.

## 2. Calculation method

We performed density-functional theory calculations as implemented in the VIENNA *ab initio* simulation package code [13]. The ultrasoft pseudopotentials were used [14]. The electron wavefunctions were expanded in a plane-wave basis set with a kinetic energy cutoff of 350 eV. The electron exchange–correlation energy was approximated using the generalized gradient approximation (GGA) [15]. The surface structure was modeled by a slab geometry, which was



**Figure 1.** Atomic structures of the physisorption states of an  $\text{NH}_3$  molecule near the adsorbed  $\text{NH}_3$ . The adsorbed molecule is in the OD configuration. (a)–(c) The OD- $P_{\text{NH}_2}$  states and (d) the OD- $P_{\text{H}}$  state. The dark and bright yellow (medium and bright gray) balls are the buckled-down and -up Si atoms on the Si(001) surface, respectively. The red (small dark gray) and black balls are the N and H atoms, respectively. The gray balls below the dimers are the sub-surface Si atoms. The H bonds are indicated by the dashed lines.

**Table 1.** Calculated binding energies and H-bond lengths of the physisorption states of an  $\text{NH}_3$  molecule on the adsorbed  $\text{NH}_3$  molecule in the OD configuration.

| Physisorption states      | Binding energy (eV) | H-bond length ( $\text{\AA}$ ) |
|---------------------------|---------------------|--------------------------------|
| OD- $P_{\text{NH}_2}$ (a) | 0.320               | 1.987                          |
| OD- $P_{\text{NH}_2}$ (b) | 0.311               | 1.985                          |
| OD- $P_{\text{NH}_2}$ (c) | 0.272               | 1.993                          |
| OD- $P_{\text{H}}$        | 0.093               | 2.774                          |

composed of six Si layers with H termination at the bottom and 14-layer-thick vacuum space. A  $4 \times 4$  surface supercell was mainly used, and  $4 \times 8$  and  $8 \times 4$  cells were adopted when the long-range interaction between molecules was considered. The  $\mathbf{k}$ -point sampling was equivalent to an  $8 \times 8$  mesh within the  $1 \times 1$  surface Brillouin zone. Geometry optimization was done with force criteria less than  $0.01 \text{ eV \AA}^{-1}$ .

### 3. Results

#### 3.1. Physisorption states

The physisorption states of an  $\text{NH}_3$  molecule on the adsorbed  $\text{NH}_3$  are described here. We first consider the OD configuration for the adsorbed  $\text{NH}_3$  molecule, which consists of  $\text{NH}_2$  and H fragments on the same dimer. The calculated atomic structures of the physisorption states are shown in figure 1. The physisorption state on the  $\text{NH}_2$  fragment of the OD is denoted by OD- $P_{\text{NH}_2}$ , and that on the H fragment is denoted by OD- $P_{\text{H}}$ . Depending on the position of the  $\text{NH}_3$  molecule and the orientation of the  $\text{NH}_2$  fragment, several stable states of the OD- $P_{\text{NH}_2}$  are found as shown in figures 1(a)–(c), and one OD- $P_{\text{H}}$  state is found as shown in figure 1(d). The calculated binding energies and the H-bond lengths are listed in table 1. The lowest energy state is the OD- $P_{\text{NH}_2}$  (a) state, which is shown in figure 1(a), where the  $\text{NH}_3$  molecule is located above the interstitial region between the dimer rows. The binding energy is 0.32 eV. As the  $\text{NH}_3$  molecule moves towards above the dimer row, as shown in figures 1(b) and (c), the binding energies are found to be slightly decreased to 0.31 and 0.27 eV, respectively. The binding energy of the OD- $P_{\text{H}}$  state is only about 0.09 eV. The H bond of the OD- $P_{\text{H}}$  state is much weaker than those of the OD- $P_{\text{NH}_2}$  states. The H-bond length is

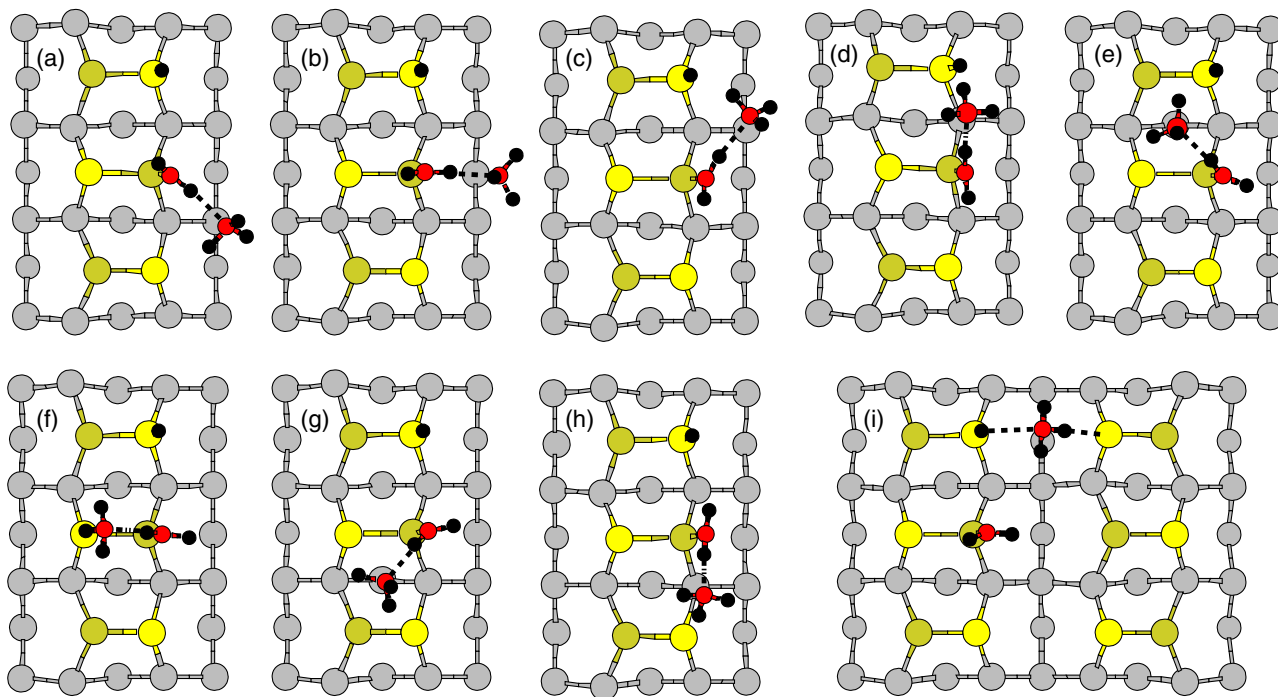
**Table 2.** Calculated binding energies and H-bond lengths of the physisorption states of an  $\text{NH}_3$  molecule on the adsorbed  $\text{NH}_3$  molecule in the ID configuration.

| Physisorption states      | Binding energy (eV) | H-bond length ( $\text{\AA}$ ) |
|---------------------------|---------------------|--------------------------------|
| ID- $P_{\text{NH}_2}$ (a) | 0.322               | 2.024                          |
| ID- $P_{\text{NH}_2}$ (b) | 0.277               | 2.031                          |
| ID- $P_{\text{NH}_2}$ (c) | 0.292               | 2.056                          |
| ID- $P_{\text{NH}_2}$ (d) | 0.293               | 1.997                          |
| ID- $P_{\text{NH}_2}$ (e) | 0.259               | 2.038                          |
| ID- $P_{\text{NH}_2}$ (f) | 0.280               | 2.042                          |
| ID- $P_{\text{NH}_2}$ (g) | 0.289               | 2.060                          |
| ID- $P_{\text{NH}_2}$ (h) | 0.297               | 1.983                          |
| ID- $P_{\text{H}}$        | 0.095               | 2.853                          |

calculated to be 2.77  $\text{\AA}$  in the OD- $P_{\text{H}}$  state, while it is 1.99  $\text{\AA}$  in the OD- $P_{\text{NH}_2}$  states, which also indicates the strong H bond of the OD- $P_{\text{NH}_2}$  states and the weak bond of the OD- $P_{\text{H}}$  state.

Next, we consider the ID configuration for the adsorbed  $\text{NH}_3$  molecule. In the ID configuration, the  $\text{NH}_2$  and H fragments are located on neighboring dimers in the same dimer row. It has a lower symmetry than the OD configuration, and thus there are more numbers of inequivalent sites for the physisorption states of the  $\text{NH}_3$  molecule. The chemical nature is, however, similar to the OD configuration. The physisorption state on the  $\text{NH}_2$  fragment of the ID is denoted by ID- $P_{\text{NH}_2}$ , and that on the H fragment is denoted by ID- $P_{\text{H}}$ . Several stable ID- $P_{\text{NH}_2}$  states and an ID- $P_{\text{H}}$  state are found as shown in figure 2. The calculated binding energies and the H-bond lengths are listed in table 2. The most stable physisorption state is the ID- $P_{\text{NH}_2}$  (a) state, which is shown in figure 2(a), where, similar to the most stable OD- $P_{\text{NH}_2}$  (a) state, the  $\text{NH}_3$  molecule is located above the interstitial region between the dimer rows. The binding energy is 0.32 eV, the same as the OD- $P_{\text{NH}_2}$  (a) state. The binding energies of the ID- $P_{\text{NH}_2}$  states are in the range 0.26–0.32 eV, quantitatively similar to the OD- $P_{\text{NH}_2}$  states. The ID- $P_{\text{H}}$  state forms a weak H bond, similar to the OD case, with the binding energy of 0.09 eV. The H-bond lengths are about 2.0  $\text{\AA}$  in the ID- $P_{\text{NH}_2}$  states, while they are 2.85  $\text{\AA}$  in the ID- $P_{\text{H}}$  state.

The H-bond strengths of the physisorption states are compared with those of a free  $\text{NH}_3$  dimer, which consists of an H bond. The calculated H-bond strength of the  $\text{NH}_3$  dimer is 0.15 eV in the GGA, which is close to the experimental value



**Figure 2.** Atomic structures of the physisorption states of an  $\text{NH}_3$  molecule near the adsorbed  $\text{NH}_3$  molecule. The adsorbed molecule is in the ID configuration. (a)–(h) The various ID- $P_{\text{NH}_2}$  states and (i) the ID- $P_{\text{H}}$  state. The atom indexes are the same as in figure 1. The H bonds are indicated by the dashed lines.

of 0.12 eV [16, 17]. It is noted that the H-bond strength of the  $P_{\text{NH}_2}$  states, 0.32 eV, is much higher than that of the free  $\text{NH}_3$  dimer. The bond length of the  $\text{NH}_3$  dimer is 2.43 Å in our calculations, which is longer than those of the  $P_{\text{NH}_2}$  states (2.0 Å).

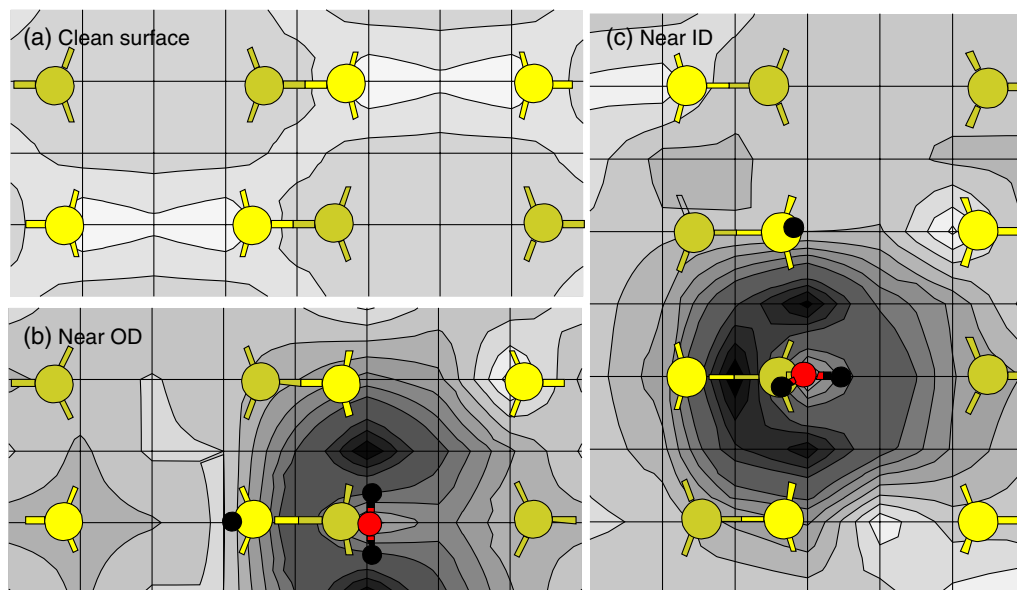
### 3.2. Potential energy surfaces

The existence of the strong H bond in the  $P_{\text{NH}_2}$  states implies that the impinging  $\text{NH}_3$  molecule can be attracted toward the adsorbed  $\text{NH}_3$  effectively. In order to estimate the interaction range of the attraction, we calculate the potential energy surfaces (PES) of the  $\text{NH}_3$  molecule at the height ( $Z$ ) of about 4 Å above the Si(001) surfaces. The height  $Z$  is defined as the distance between the planes of the N atom of the  $\text{NH}_3$  molecule and the uppermost buckled-up Si atoms of the clean surface, which are parallel to the Si(001). Figure 3 shows the calculated PES above the clean surface and near the adsorbed  $\text{NH}_3$  in the OD and ID configurations. As shown in figure 3(a), above the clean surface, the PES is relatively flat. There is only a slight potential energy difference between the buckled-up and -down Si atoms. However, near the adsorbed  $\text{NH}_3$ , either in the OD or ID configuration, at the same height, we find there is a deep and wide basin of strong attraction near the adsorbed  $\text{NH}_3$ . The potential energy on the local minima on the PES is about  $-0.25$  eV, which is much lower than that on the clean surface (about  $-0.05$  eV). The deep potential well near the adsorbed  $\text{NH}_3$  provides a strong lateral force field to the incoming  $\text{NH}_3$  molecules, attracting them towards the adsorbed  $\text{NH}_3$ . The origin of the strong attractive potential is the strong H bond between the N atom of the incoming

$\text{NH}_3$  molecule and the H atoms of the adsorbed  $\text{NH}_3$ . The attraction range is estimated to be about 10 Å from the PES. It corresponds to about 15 dimers in range. Therefore, the critical coverage for the self-assembly of  $\text{NH}_3$  molecules can be estimated to be about 1  $\text{NH}_3$  molecule per 15 dimers, which is approximately 0.07 monolayers (ML). Experimentally, the self-assembly of  $\text{NH}_3$  molecules is really observed when the concentration is higher than about 0.07 ML [8].

### 3.3. Molecular adsorption states

In forming the molecular adsorption state, the buckled-down Si atom attracts the  $\text{NH}_3$  molecule by dative-bond formation. For the  $\text{NH}_3$  molecule attracted towards the adsorbed  $\text{NH}_3$ , the possible molecular adsorption sites are thus on the buckled-down Si atoms near the adsorbed  $\text{NH}_3$ . In figure 4, we show the atomic configurations for the various possible molecular adsorption states. The adsorption energies are listed in table 3. Near the OD configuration, we consider two buckled-down Si atomic sites as shown in figures 4(a) and (b). One is the buckled-down Si atomic site next to the OD in the same dimer row (intra-dimer-row molecular adsorption; figure 4(a)) and the other is the buckled-down Si atomic site next to the  $\text{NH}_2$  of the OD in the neighboring dimer row (inter-dimer-row molecular adsorption; figure 4(b)). The adsorption energy of the intra-dimer-row molecular adsorption state is calculated to be 1.24 eV and that of the inter-dimer-row molecular adsorption state is 1.53 eV. The H bond stabilizes the inter-dimer-row molecular adsorption state. Near the ID configuration, we consider three intra-dimer-row molecular adsorption configurations as shown in figures 4(c)–(e) and one



**Figure 3.** Calculated potential energy surfaces (a) on the clean surface and (b), (c) near the adsorbed  $\text{NH}_3$ . In (b) and (c), the adsorbed  $\text{NH}_3$  molecule is in the OD and ID configuration, respectively. The atom indexes are the same as in figure 1. The impinging  $\text{NH}_3$  molecule is located at the height of 4 Å above the surface. The spacing of the mesh is  $\sqrt{2}a/4$ , here 1.92 Å, where  $a$  is the Si lattice constant. The contour spacing is 0.02 eV from  $-0.04$  to  $-0.24$  eV.

**Table 3.** Calculated adsorption energies of the molecular adsorption states of an  $\text{NH}_3$  molecule near the OD and ID configurations.

| Molecular adsorption states | Adsorption energy (eV) |
|-----------------------------|------------------------|
| Single $\text{NH}_3$        | 1.311                  |
| OD- $\text{NH}_3$ (a)       | 1.240                  |
| OD- $\text{NH}_3$ (b)       | 1.534                  |
| ID- $\text{NH}_3$ (c)       | 1.256                  |
| ID- $\text{NH}_3$ (d)       | 1.211                  |
| ID- $\text{NH}_3$ (e)       | 1.250                  |
| ID- $\text{NH}_3$ (f)       | 1.555                  |

inter-dimer-row molecular adsorption configuration as shown in figure 4(f). The intra-dimer-row molecular adsorption states near the ID have the adsorption energies in the range 1.21–1.26 eV, similar to that near the OD (1.24 eV). The inter-dimer-row molecular adsorption state has a higher adsorption energy (1.55 eV) by the H bond, similar to that near the OD configuration.

It should be noted that the high adsorption energies do not necessarily mean a high population of the molecular adsorption state. In the adsorption process, the kinetics is usually as important as the energetics, especially when the adsorption process is irreversible or not in thermal equilibrium. The  $\text{NH}_3$  molecule attracted towards the adsorbed  $\text{NH}_3$  has a possibility to adsorb on any of the sites shown in figure 4. In experiments, the various adsorption features were really observed in the self-assembly of  $\text{NH}_3$  molecules [8, 18].

### 3.4. Dissociative adsorption states

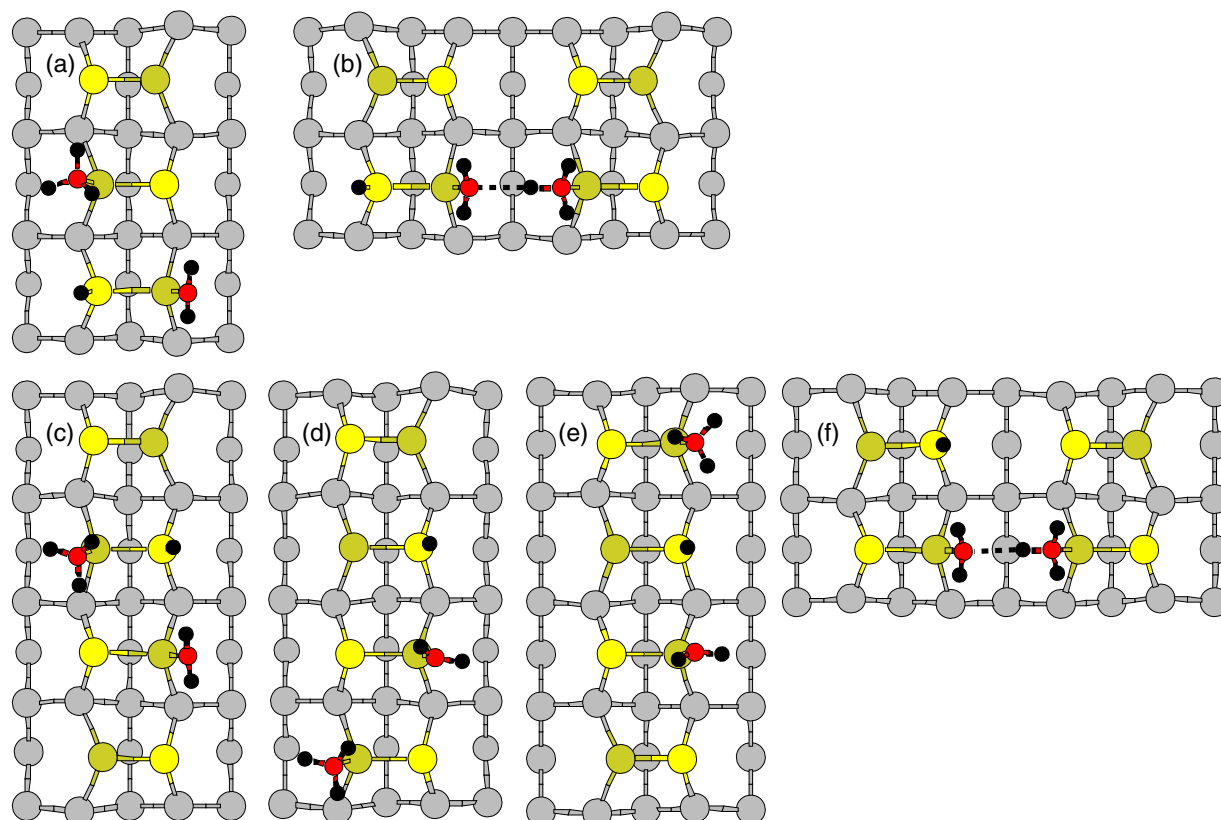
From the molecular adsorption states near the adsorbed  $\text{NH}_3$ , the dissociative adsorption of the molecularly adsorbed  $\text{NH}_3$  occurs. An H atom of the  $\text{NH}_3$  molecule is dissociated to

chemisorb on a nearby buckled-up Si atom forming OD or ID. From the various molecular adsorption states shown in figure 4, there can be a lot of possible dissociative adsorption configurations to be made. We calculated all the possible dissociative adsorption configurations and summarize here only the general tendencies in the adsorption energies and the energy barriers. The adsorption energies for the various OD states are in the range 2.00–2.08 eV, similar to the single OD formation (2.05 eV). The ID formation gives the adsorption energies of 1.71–1.79 eV, similar to the isolated ID formation (1.75 eV). The OD configuration is thus generally more stable than the ID. On the other hand, the energy barriers for the formation of the dissociative adsorption states are lower by about 0.1 eV for the ID formation than for the OD formation, also similar to the single  $\text{NH}_3$  adsorption case. Since the Si dimer is more flexible perpendicular to the direction of the dimer bond, the inter-dimer H transfer is easier. The energy barrier is about 0.78 eV for OD formation and 0.67–0.73 eV for ID formation, when there is no H-bond in the molecular adsorption state (figures 4(a), (c)–(e)). The energy barriers are about 0.3 eV higher when there is an H bond in the molecular adsorption state (figures 4(b) and (f)), 1.07–1.11 eV for OD formation and 0.91–0.94 eV for ID formation. Even though the adsorption energy gives the preference of the OD states, the low energy barrier for the ID states can make the ID formation easier by the kinetic nature of the adsorption process. In experiments, the OD and ID states were both observed [4, 8, 18].

## 4. Summary

We investigated the various adsorption states of the self-assembly of  $\text{NH}_3$  molecules on the Si(001) surface. The





**Figure 4.** Atomic structures of the various molecular adsorption states of an  $\text{NH}_3$  molecule near the adsorbed  $\text{NH}_3$  molecule. The adsorbed molecule is in the OD configuration in (a) and (b), and in the ID in (c)–(f). (a) and (c)–(e) are the intra-dimer-row molecular adsorption configurations, and (b) and (f) are the inter-dimer-row molecular adsorption configurations. The atom indexes are the same as in figure 1. The H bonds are indicated by the dashed lines.

physisorption state of an  $\text{NH}_3$  molecule shows a strong H-bond formation on the adsorbed  $\text{NH}_3$ . The H bond is found to be an important source of attraction to incoming molecules, which can result in the self-assembly of  $\text{NH}_3$  molecules. The  $\text{NH}_3$  molecule is then adsorbed molecularly on a buckled-down Si atom near the adsorbed  $\text{NH}_3$ . The various molecular and dissociative adsorption configurations possibly formed are presented.

## Acknowledgment

YSK acknowledges the support from the Korea Institute of Science and Technology Information under ‘The 8th Strategic Supercomputing Support Program’.

## References

- [1] Belyi V I *et al* 1988 *Silicon Nitride in Electronics* vol 34 (New York: Elsevier)
- [2] Franco N, Avila J, Davila M E, Asensio M C, Woodruff D P, Schaff O, Fernandez V, Schindler K M, Fritzsche V and Bradshaw A M 1997 *Phys. Rev. Lett.* **79** 673
- [3] Xu X, Kang S Y and Yamabe T 2002 *Phys. Rev. Lett.* **88** 076106
- [4] Chung O N, Kim H, Chung S and Koo J Y 2006 *Phys. Rev. B* **73** 033303
- [5] Hossain M Z, Yamashita Y, Mukai K and Yoshinobu J 2003 *Phys. Rev. B* **68** 235322
- [6] Owen J H G, Bowler D R, Kusano S and Miki K 2005 *Phys. Rev. B* **72** 113304
- [7] Bowler D R and Owen J H G 2007 *Phys. Rev. B* **75** 155310
- [8] Chung O N, Kim H, Koo J Y and Chung S 2006 *Phys. Rev. B* **74** 193312
- [9] Cho J H and Kim K S 2000 *Phys. Rev. B* **62** 1607
- [10] Widjaja Y and Musgrave C B 2004 *J. Chem. Phys.* **120** 1555
- [11] Queeney K T, Chabal Y J and Raghavachari K 2001 *Phys. Rev. Lett.* **86** 1046
- [12] Kim Y S, Koo J Y and Kim H 2008 *Phys. Rev. Lett.* **100** 256105
- [13] Kresse G and Joubert D 1999 *Phys. Rev. B* **59** 1758
- [14] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [15] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev. B* **46** 6671
- [16] Rappe A K and Bernstein E R 2000 *J. Phys. Chem. A* **104** 6117
- [17] Fraser G T Jr, Nelson D D, Gerfen G J and Klempner W 1985 *J. Chem. Phys.* **85** 2535
- [18] Chung O N, Kim H, Koo J Y and Chung S 2008 *Surf. Sci.* **602** L69