The initial stage of the dissociative adsorption and the surface electronic state evolution of NH$_3$ on Si(111)-(7 × 7)

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Abstract
Adsorption of NH$_3$ molecules on Si(111)-(7 × 7) has been studied by scanning tunneling microscopy. We find that the dissociative adsorption is site-selective and exhibits two adsorption structures resulting from different reaction channels: NH$_3$ → NH$_2$ + H and NH$_3$ → NH + 2H. To explain the dissociation processes, an adsorption model for these reactions is given. Furthermore, the evolution of the local electronic structures is investigated by means of atomically resolved scanning tunneling spectroscopy to clarify the effect of different fragments on the surface states. Finally, we discuss the adsorption position of H atoms from the NH$_3$ dissociation.

1. Introduction

The adsorption of ammonia on silicon surfaces has received considerable attention for many years due to its importance in the microelectronics industry [1]. It is an important stage in the formation of high quality silicon nitride (Si$_3$N$_4$) film grown by chemical vapor deposition [2]. A number of studies using various surface-sensitive techniques, such as high resolution electron energy loss spectroscopy [3, 4], photoemission spectroscopy (PES) [5] and scanning tunneling microscopy (STM) [6, 7], have been performed at this stage. Early reported results suggested that ammonia adsorbed non-dissociatively [8], while recent studies including STM [6, 7] and core-level and valence-band PES [9] found the formation of different dissociation fragments, i.e. NH$_2$, NH, N and H, at elevated adsorption temperatures on silicon surfaces. Consensus has been reached that at the adsorption temperature between 200 and 600 K: (1) there are two reaction channels of NH$_3$ on the Si(111)-(7 × 7) surface:

$$NH_3 \rightarrow NH_2 + H \qquad (a)$$

and

$$NH_3 \rightarrow NH + 2H; \qquad (b)$$

(2) the proportion of NH and NH$_2$ species is varied and (3) nitrogen atoms are generated on further annealing to 700 K [4, 9]. However, on the atomic scale, there are still controversies regarding the site-selective reaction of NH$_3$ with different dangling bond (DB) states on Si(111) surfaces, especially those on the rest atoms [10] and the adatoms [11, 12]. Density functional theory (DFT) studies [13] revealed that both the adatom and the rest atom sites can cause the dissociation of NH$_3$, while Stauffer *et al* [11] suggested that the adatom sites are most favorable. On the other hand, a recent DFT theory calculation performed by Kang concluded that NH$_3$ should react with adatoms and dissociate into H atoms adsorbed on adjacent rest atom sites [12]. These controversies lead to several inconclusive models [10–15] related to the adsorption and dissociation process of ammonia on Si(111)-(7 × 7).

To resolve the existing ambiguities and to clarify the surface structural evolution as well as the modification of the

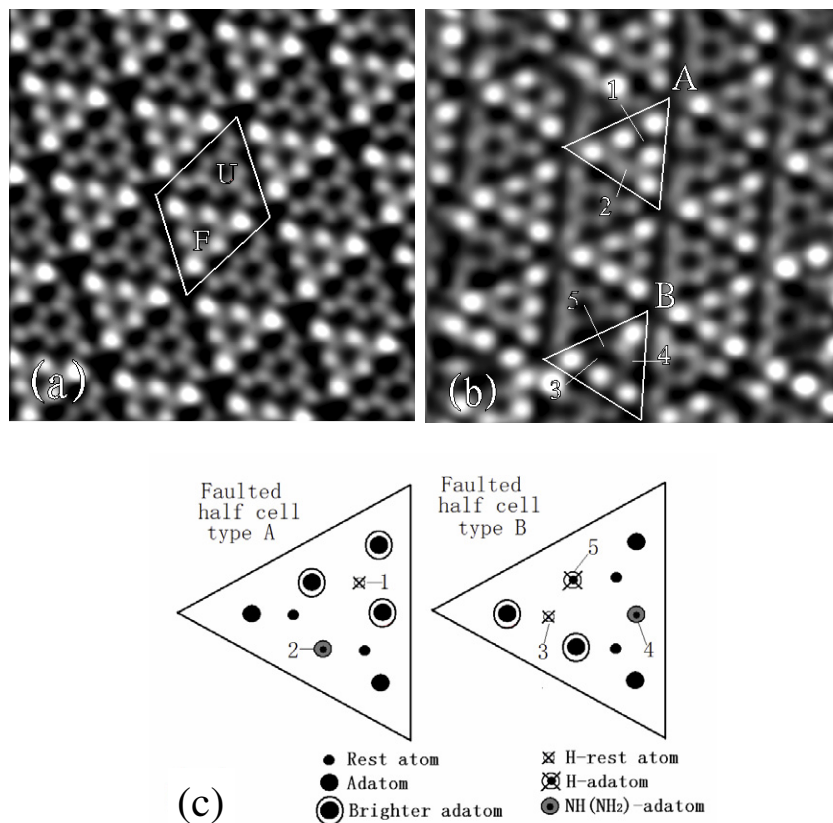[3] Author to whom any correspondence should be addressed.

Figure 1. STM image acquired from (a) clean Si(111)-(7 × 7) surfaces; (b) NH$_3$-reacted Si(111)-(7 × 7) surfaces; two different adsorption structures A and B are marked by triangles. $V_s = -1.3$ V and $I_t = 500$ pA. (c) Adsorption structure model for the NH$_3$/Si(111)-(7 × 7) system. H-rest (adatom) atom represents the rest (adatom) site where H atom adsorbs.

electronic structures due to chemisorbed ammonia species on Si(111), we studied the adsorption process and site-specified local density of states (LDOS) of the NH$_3$/Si(111) by low temperature atomically resolved STM. We found that the reacted surface exhibited two adsorption features resulting from different reaction channels and showed a model for these reactions. In order to understand the reaction process, scanning tunneling spectroscopy (STS) on different sites was recorded after the NH$_3$ adsorption. Moreover, our results revealed that H atoms could not adsorb on the top of the rest atom as expected previously [16–18].

2. Experiments

The experiment was carried out in an ultra-high vacuum (base pressure $< 1 \times 10^{-10}$ Torr) system equipped with a low temperature STM (USM-1300s, Unisoku). The Si(111) samples, cut from an n-type Si(111) wafer with a resistivity of 0.005 Ω cm, were degassed for at least 10 h in advance. The Si(111)-(7 × 7) reconstruction was obtained by rapidly flashing up to about 1500 K, as monitored by an optical pyrometer. After that, the sample was cooled down to about 550 K and exposed to NH$_3$ gas (purity of 99.999%). During NH$_3$ exposure, the pressure was maintained at 3×10^{-9} Torr by a leak valve. Finally, the sample was transferred to the STM head in a liquid-nitrogen cryostat. All STM images were obtained

with electrochemically etched tungsten tips at about 78 K. The dI/dV curves were measured using a lock-in amplifier (SR850 Stanford) with a modulation voltage of 30 mV.

3. Results and discussion

3.1. Adsorption structure

The NH$_3$-reacted surface was obtained by exposing a clean Si(111)-(7 × 7) surface to a small amount of NH$_3$, ~0.03 L (1 langmuir = 10^{-6} Torr s). Figure 1 shows the filled-state STM images acquired from the clean and reacted surfaces at about 78 K[4]. Figure 1(a) corresponds to the image of the clean surface where the atoms in the faulted half-unit cell (HUC) are brighter than those in the unfaulted one. According to the dimer-adatom-stacking (DAS) fault model [19], 12 bright spots correspond to the adatoms and 6 gray regions between adatom sites are rest atoms. After dosing NH$_3$, Si(111)-(7 × 7) unit cells transformed into two types, A and B (see figure 1(b)). In both cases some rest atoms are invisible and the adatoms show different brightness which is indicative of the different heights. The reacted sites show depressed electronic density and most of them are located in the faulted HUC[5] since it is

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[4] The empty state images of the reacted surfaces have no difference from the clean ones, so here we do not show them.
[5] There is little adsorption in unfaulted HUC at low NH$_3$ exposure, so we do not discuss it here.

more reactive towards NH_3 dissociation than unfaulted HUC as reported previously [10, 15]. In type A marked by a triangle in figure 1(b), one center adatom (labeled as 2) lowers the height. In contrast, one of the center adatoms (labeled as 5) in type B is invisible and the other (labeled as 4) lowers its height compared with that on clean surfaces. In both typical adsorption features, we find the vanishing of a rest atom (labeled as 1 and 3) with the increasing heights of some neighboring adatoms.

Based on the above experimental facts, an adsorption model is proposed as shown in figure 1(c) to explain those observed images. For type A in figure 1(b), we suggest it originated from the channel (a): $NH_3 \rightarrow NH_2 + H$. H atoms derived from NH_3 decomposition passivate the rest atom as discussed later (labeled as 1) and reduce the local density of states (LDOS) significantly, resulting in the vanishing of the rest atom in the STM image. This can be inferred by three tripod-shaped and bright spots which are caused by charge transfer from the rest atom to neighboring adatoms [17, 18]. Meanwhile, the NH_2 fragment adsorbs on the center adatom (labeled as 2) and thereby decreases its height in the STM image. For type B in figure 1(b), a rest atom (labeled as 3) is invisible and a center adatom (labeled as 4) becomes dark, similar to the case in type A. However, the atom labeled as 5 near the H-rest atom (labeled as 3) looks like a missing adatom. This is the result of the reaction channel (b): $NH_3 \rightarrow NH + 2H$ that the second H atom adsorbs on this site and the NH adsorbs on the same center adatom (labeled as 4) as NH_2 adsorption in type A. On the basis of the above discussion, it can be speculated that the rest atom is the stable H adsorption site on the Si(111) surfaces [17, 18, 20, 21]. The species such as NH_2, NH and the other H in the channel (b) are found to adsorb preferentially on the adatoms. In addition, NH and NH_2 mainly react with the center adatoms rather than the corner adatoms, implying the adsorption energies for the center adatoms are higher than those for corner adatoms [6].

Regarding both type A and B, two possibilities of reaction pathways should be taken into account: (1) an incoming NH_3 molecule adsorbs on the rest atom and dissociates into NH_2 bonding to the adjacent adatom; (2) an incoming NH_3 adsorbs on the adatom and dissociates into 2H bonding to the adatom and adjacent rest atom, respectively. According to the theoretical calculation [12], the rest atom of the Si(111)-(7×7) surface is overcharged and expected to be repulsive to NH_3 which is in a closed-shell electronic configuration, while the adatoms with partially filled states can react with NH_3. Therefore an electron-rich NH_3 molecule selectively adsorbs on the adatoms and after that dissociates into $NH_2 + H$ or $NH + 2H$. The obtained H atoms will react with the rest atoms or the center adatoms. Our experiments testify to the theoretical results [12] and indicate that the second reaction pathway is possible. Meanwhile, we find no change of adsorption structure after the same area is scanned at different biases, implying that both adsorption features A and B are stable.

The rest atom and adatoms involved in the NH_3 dissociation reaction are not adjacent, which is inconsistent with the theoretical analysis [12]. There is a possibility for this discrepancy: the electron structure of the adjacent rest atom
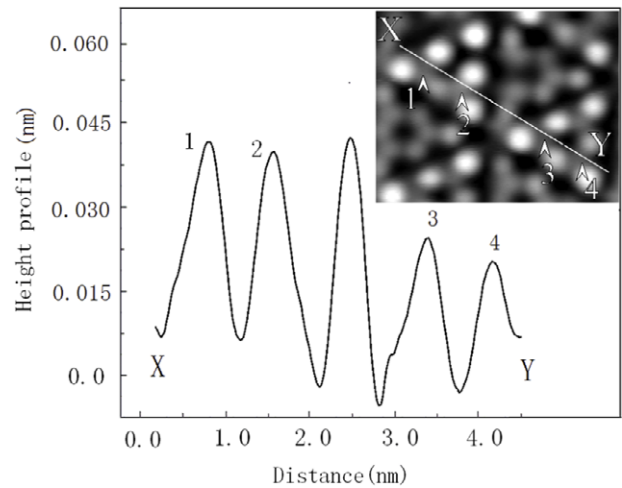

Figure 2. Image height profiles along four rest atom sites in reacted and clean Si(111)-(7×7) subunit cells. The height change of the rest atom sites between two different subunit cells can be clearly viewed. The small difference between peaks 1 and 2 in the reacted subunit cell and the difference between peaks 3 and 4 in the clean subunit cell come from the image slope. The inset shows the STM image where the profile is obtained along the line.

site might be affected by the NH_2 (NH) bonding to the center adatom (labeled as 2 and 4). This possibility is confirmed by the image height profile along the four rest atoms in figure 2. By analyzing the height profile of these rest atoms, one finds that, after NH_3 exposure, the electron density of the rest atoms on reacted surfaces becomes higher than that on the clean surfaces as seen in figure 2. Thus it is concluded that NH or NH_2 adsorbing upon center adatoms influences the electronic properties of the nearest-neighbor rest atom. There is charge transfer from the center adatom back to the nearest rest atoms. However, owing to the charge repulsive feature of the H atoms adsorbing on the rest atom sites, the charge should transfer to the neighboring adatom. Therefore a competition between the above two pathways exists. As a result, the second nearest-neighbor rest atom site (labeled as 1 and 3 in figure 1(b)) with low LDOS becomes more reactive towards H atom adsorption. On the other hand, the temperature of the sample is higher than room temperature after flashing (at about 550 K, measured by thermocouple). H atoms can get enough thermal energy to overcome the diffusion barrier and arrive at the second-nearest-neighbor rest atom sites, while it could not cross the dimer row to the neighboring HUC [16, 18].

3.2. Evolution of LDOS

As discussed above, ammonia passivates the surface DBs and thereby modifies the surface electronic properties dramatically. To further confirm this point and clarify the effect of different adsorbed fragments on the surface states, we examined the changes of the LDOS by means of atomically resolved STS.

The STS shown in figure 3 was recorded with the bias voltage from −1.5 to +1.5 V for corner adatom, center adatom and rest atom on the clean and NH_3 reacted surfaces, respectively. There are three peaks around ±0.3
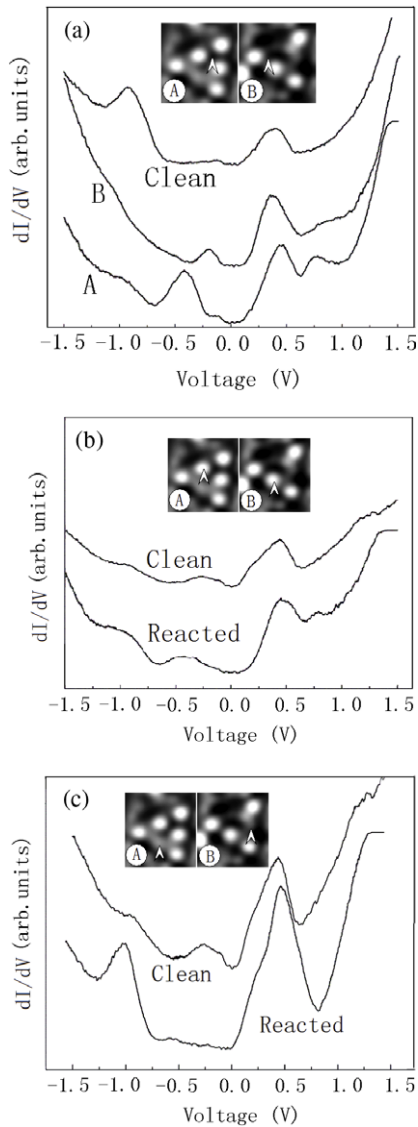
Figure 3. (a) dI/dV−V curves taken on rest atom sites. The upper curve is obtained from the rest atom on the clean surface. The bottom two curves were acquired from types B and A of the adsorption structures after dosing NH₃, respectively. The insets show the positions for STS measurements indicated by arrows. (b) Evolution of the LDOS at the brighter center adatom site near the H-rest atom. (c) STS acquired on the NH (NH₂)-reacted adatoms in both adsorption structures A and B highlighted by arrows.

and −0.8 V in the STS acquired from the rest atom of the clean surface (figure 3(a)), which correspond to the emission from the neighboring adatom and the rest atom states, respectively [17, 22]. However, after NH₃ exposure the peak intensity at −0.8 V reduced significantly; meanwhile a new peak appears at ∼ + 0.8 V in both adsorption types. Moreover, the occupied state of the adatom around −0.3 V shifts away from the Fermi level with the increasing intensity. It is further evidence for charge transfer from the rest atom to adatom sites. Here the new peak at +0.8 V is assigned to the adsorption of an H atom on the rest atom, mainly based on the fact that the transformation of the surface states depends on the adsorption of dissociated species H or NH₂

(NH). In fact, we found no evidence of the peak at about +0.8 V on the NH₂ (NH)-center adatom sites, as discussed later. Therefore it is suggested that this new state results from the H adsorption on the rest atom site. A possible explanation of this new feature is that the H atom repulses the charge of the rest atom sites and an unoccupied state at about +0.8 V on this site can be formed after H adsorption. For the precise interpretation, it is necessary to combine with data from theoretical calculation and other techniques, for example, photoemission spectroscopy. As for the shift of the −0.3 V peak on the adatoms, it is attributed to the increased charge density in the adatom states [17, 23]. In the adsorption type B, the amount of energy shift is less than that of type A (figure 3(a)) as explained by Wolkow *et al* considering the DAS model [23].

The evolution of LDOS at the brighter center adatom site (marked by an arrow in the inset) near the H-rest atom is also studied as shown in figure 3(b). However, there is little difference in the LDOS of the sites in both types A and B because of the charge transferring from the neighboring rest atom. The curve features from clean and reacted surfaces are almost the same except for the component caused by an H-rest atom at +0.8 V and the energy shift of the peak at −0.3 V which are similar to the case in figure 3(a).

The ammonia-adsorption-derived fragments NH₂ (NH) are another focus in this work. During the STS measurements in figure 3(c), the tip was positioned upon another center adatom in both adsorption structures (labeled as 2 and 4 in figure 1(b)). We found no peak around +0.8 V from the NH₂ (NH)-center adatom as in the case in figure 3(a). The peak at −0.3 V diminishes as the DBs on the adatom are passivated by NH₂ (NH) species. Meanwhile, the peak at −0.8 V arising from the neighboring rest atom shows the increasing intensity, indicative of the charge transfer from the adatom back to the rest atom which has been verified by the height profile measurement in figure 2. It is interesting that the LDOS difference between both adsorption types on the center adatom site is very small. This fact indicates that the similar fragments NH₂ and NH react with these sites. Previous reports pointed out that the origin of the similar dI/dV curves in both types may be the result of the same structure as the adatom–NH-backbone [9, 11, 13], where NH₂ dissociated into H and NH and the NH bonded with the backbone atom. However, this mechanism can be ruled out in our experiments due to the fact that we do not observe a trace of the additional H atom released during this process in type A. Moreover, the formation of the adatom–NH-backbone structure suggests that only one adsorption feature resulting from NH + 2H should be observed on the reacted surface, inconsistent with our results.

3.3. Adsorption site of H atom

Surface reactions are usually accompanied by charge transfer and thereby result in the height transformation in STM images. In figure 1(b), the height of the rest atom and its neighboring adatoms changed dramatically after NH₃ exposure and the position of the H adsorption can be evaluated by these variations. As shown in figure 4(a), the triangle consisting
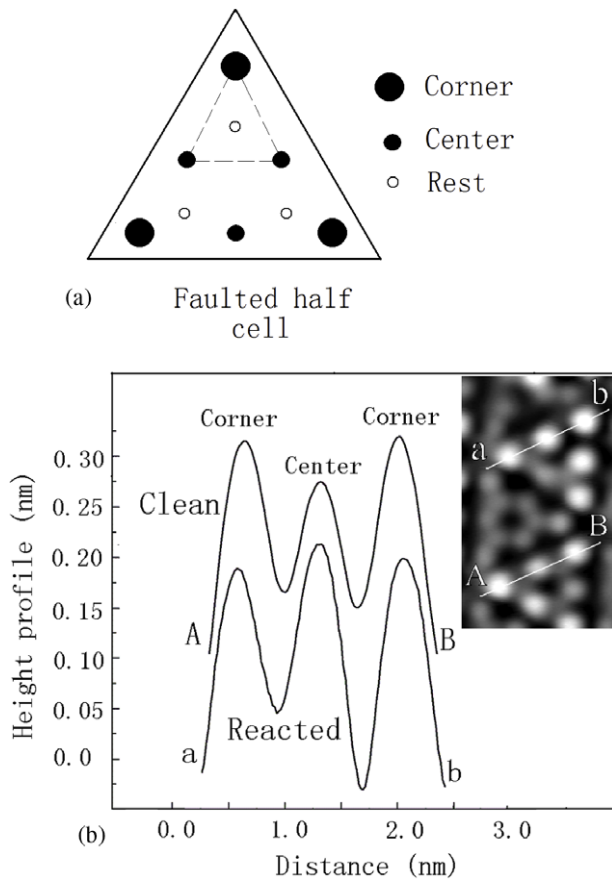
Figure 4. (a) Adsorption site for H atom. (b) Height profiles along two corner adatoms and one center adatom in reacted and clean subunit cells. The center adatom is higher than the corner adatom after NH_3 exposure. The inset shows the STM image where the profile is obtained along the lines.

of a corner and two center adatoms is not fully symmetrical, since the center and corner adatoms are not electronically equivalent and shows a height difference of about 0.05 nm [17]. Therefore, during the adsorption of an H atom there is a nonequivalent charge transfer to the neighboring adatoms, resulting in the different variation of the LDOS and thereby of the height in the line profile of figure 4(b). The interaction among H and the three neighboring adatoms will cause the H atom to shift a little bit away from the top of the rest atom site. Our analysis does not support the previous conclusion that H adsorbs on the top of the rest atom due to the symmetry of the atomic structure [16–18]. As for the exact position of H, relevant theoretical calculations are needed.

4. Conclusions

The initial stage of the NH_3 adsorption on Si(111)-(7 × 7) was investigated using low temperature STM. It is helpful for us to understand the initial stage of NH_3 adsorption on Si(111), which is important for the production of silicon nitride (Si_3N_4) film in the microelectronics industry. We found two types of adsorption features resulting from different reaction channels. The adsorption of H and NH_2 (NH) caused the charge transfer between the rest atom and adatom sites. LDOS evolution of these sites on the clean and reacted surfaces illustrated the effect of the NH_3 reaction on Si(111) surface states. A new state at about +0.8 V was observed which is associated with the H adsorption site. Our results suggested that the H adsorption position could shift away from the top of the rest atom.

Acknowledgment

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