

Site-selective adsorption of C_2H_5OH and NO depending on the local structure or local electron density on the $Si(111)-7\times 7$ surface

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The sticking probability of ethanol (C_2H_5OH) on a $Si(111)-7\times 7$ surface is entirely coverage independent, and the adsorption is suddenly stopped when three adatoms (half of the adatoms) are changed to $Si-OC_2H_5$ in every half unit cell. This $Si(111)-7\times 7$ surface saturated with C_2H_5OH , however, is active for the adsorption of NO . A more surprising fact is that the sticking probability of NO on this surface is equal to that on the virgin $Si(111)-7\times 7$ surface. That is, the sticking probability of C_2H_5OH and NO on a $Si(111)-7\times 7$ surface has no influence of the coverage of Si -adatoms with $Si-OC_2H_5$. From these results, we deduced that the dissociation of NO and C_2H_5OH takes place via the precursor state adsorption. The coverage of adatoms gives no effect on the sticking probability of NO and C_2H_5OH , the adsorption of NO on the faulted halves prefers that on unfaulted halves ($F/U=2.2\sim 2.4$), although no such preference was observed in the adsorption of C_2H_5OH ($F/U=1$). N and O atoms formed by the dissociation of NO migrate over the surface and are finally trapped by Si -adatoms. On the other hand, adsorption of C_2H_5OH occurs by dissociating the precursor state molecule on an adatom-rest atom site, which is the final step of the adsorption. Therefore, the scanning tunneling microscopy image of C_2H_5OH reflects the structure of the sites, while that of NO reflects the electron density of sites. The physical meaning of the sticking probability, preferential adsorption on the faulted or unfaulted halves, and site selectivity of the center to corner adatoms in a half unit cell are discussed.

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I. INTRODUCTION

Sticking probability has been introduced to explain the macroscopic kinetics as the uptake probability of a molecule per collision. The physical meaning of it, however, is not so simple when the adsorption takes place via several steps. Scanning tunneling microscopy (STM) enables us to count the site by site adsorption so that we can separately derive the sticking probability and the selectivity for adsorption sites. To clarify the physical meaning of sticking probability in relation to the local structure and the local electron density of sites, the adsorption on the $Si(111)-7\times 7$ surface is interesting because the array of Si atoms and their electronic state are well established. According to the DAS model (double bond, adatom, and stacking fault), a unit cell is composed of two half unit cells, one has a stacking fault and the other does not. A half unit cell, either faulted or unfaulted, contains nine Si -atoms with a dangling bond, which are three corner Si -adatoms, three center Si -adatoms, and three Si -rest atoms. The dangling bond of the Si -adatom is almost devoid of electrons but that of the Si -rest atom is nearly filled with electrons and the electron density on a corner adatom is slightly higher than that on a center adatom.¹⁻³ It is also known that the local density of state is higher on the faulted half unit cell than the unfaulted half.

If the adsorption does not occur by direct collision of a molecule with an adsorption site, the physical meaning of sticking probability should be discussed in relation to a series of surface processes. The adsorption of H_2O (Refs. 4 and 5) and H_2S (Refs. 6 and 7) on the $Si(111)-7\times 7$ surface is a good example, which occurs preferentially on the faulted halves with higher electron density, but the adsorption prefers on center Si -adatoms to corner Si -adatoms in either

faulted or unfaulted halves although electron density of the corner adatom is higher than that of center adatom. The STM image shows the final state of the adsorption, and as it will be discussed in this paper, the site selectivity decided by the final step depends on the mechanism, either the trapping of a migrating atom or molecule or the dissociation of a migrating precursor or molecule. In the former case, the site selectivity will relate to the electron density of the site, but the selectivity is decisively controlled by the sites structure in the latter case. Taking these facts into account, we have to discuss the physical meaning of the sticking probability.

Adsorption of CH_3OH (Ref. 8) and $(CH_3)_2CHOH$ (Ref. 9) on the $Si(111)-7\times 7$ surface takes place entirely with coverage independent sticking probability, and it was shown that the adsorption occurs exactly equally on the faulted and unfaulted halves but takes a large site selectivity of corner/center=0.25 (1/4) in faulted as well as unfaulted halves. In contrast, the adsorption of NO on the faulted halves prefers 1.9–2.2 times to that on the unfaulted halves, and the site selectivity takes a ratio of corner/center = 1.5–1.8 (opposite to alcohols) in either the faulted or unfaulted halves at 50 °K–120 °K (Ref. 10). To gain insight into the sticking probability and site selectivity, the adsorption of C_2H_5OH and NO and their co-adsorption was performed by the STM.

A. Experimental

The STM experiments were performed using an ultrahigh vacuum (UHV) STM (JEOL) in a chamber with a base pressure lower than 2×10^{-8} Pa. A rectangular $Si(111)$ wafer ($2\times 7\times 0.3$ mm³; n -type, ~ 0.1 Ω cm) was degassed at about 450 °C in the treatment chamber by direct current through

the sample. The degassed sample was flashed to ca. 1250 °C until a clean well-ordered Si(111)- 7×7 surface was obtained. Then the sample was transferred from the treatment chamber to the STM chamber and cooled down to room temperature (ca. 298 K). The Si(111)- 7×7 surface was exposed to C_2H_5OH at room temperature, and the saturation was confirmed by STM. After that, adsorption of NO was performed at room temperature in the STM chamber.

The exposure of NO was controlled by adjusting the exposing time at a pressure below 2×10^{-8} Pa. During adsorption of NO or ethanol, the STM tip was retracted far away from the surface to reduce shielding of the adsorption by the tip. The STM image was observed by using an electrochemically etched tungsten tip at room temperature by a constant-current mode.

B. Results

Figures 1(a) and 1(b) are the STM image of the Si(111)- 7×7 surface of 12% and 48% of adatom coverage obtained by exposure to C_2H_5OH at room temperature, where the darkened Si-adatoms are the Si- OC_2H_5 formed by dissociation of C_2H_5OH . As shown in Fig. 2, the adsorption is linearly increased with exposure and is suddenly stopped when the coverage of the adatoms is attained at 50%, which is very similar to that of CH_3OH reported in a previous paper.⁸ The slope of C_2H_5OH is almost equal to that of CH_3OH , which means the sticking probability of C_2H_5OH is 1.2 times of that of CH_3OH , because the collision frequency depends on the reciprocal square root of the mass ratio (46/32). The coverage independent sticking probability is well explained by the dissociation of the precursor state molecule on the Si-adatom Si-rest atom pair sites and the sticking probability reflects the formation probability of the precursor state per collision as discussed in previous papers.^{8,9} As a half unit cell has six Si-adatoms and three Si-rest atoms, half of the Si-adatoms (three Si-adatoms) can contribute to the dissociation of precursor molecule by making a pair with an adjacent rest atom. On the other hand, a clear site selectivity of center/corner=4 is observed at low coverage as shown in Fig. 3(a). From these results, we can conclude that the dissociation by direct collision of an alcohol molecule with adsorption sites is very rare. Dissociation of alcohols is little influenced by the local electron density of the site but is decisively controlled by the local structure of the site, that is, the number of the rest atoms adjacent to a Si-adatom is responsible for the dissociation probability.¹¹

NO molecules are known to dissociate on the Si(111)- 7×7 surface at room temperature, and the STM image of Si-adatoms becomes dark by bonding with N and O. Figure 4(a) is a Si(111)- 7×7 surface having 29% darkened adatoms in the faulted halves and 12% in the unfaulted halves, and Fig. 4(b) is a surface having 66% darkened adatoms in the faulted halves and 29% in the unfaulted halves. When the surface is saturated by the adsorption of NO, all Si-adatoms (three corner and three center adatoms in a half unit cell) of the faulted as well as unfaulted halves will be darkened. If this expectation is correct, NO can adsorb on the ethanol saturated Si(111)- 7×7 surface, because half of the Si-

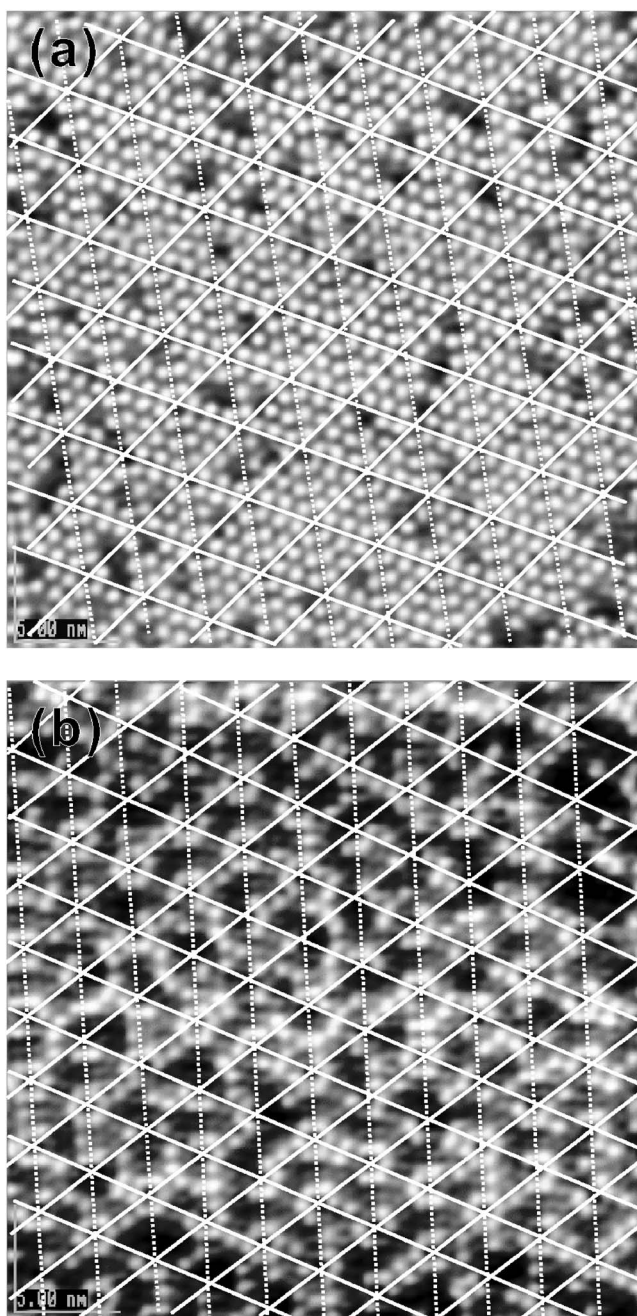


FIG. 1. STM image of C_2H_5OH adsorbed Si(111)- 7×7 surface. (a) 12% of adatom coverage attained by exposing for 10×10^{-6} Pa s. (b) Saturated adsorption (48%) attained by exposing for 60×10^{-6} Pa s.

adatoms (three Si-adatoms) are intact in every half unit cell on this surface. Therefore, we can evaluate the adsorption of NO by counting the darkened adatoms which are more than three in half unit cells.

The darkened adatoms in a half unit cell are described by (m,n) notation, where “ m ” is the darkened center adatoms and “ n ” is the darkened corner adatoms. The $(m+n)$ changes from 0 to 6, where 0 corresponds to a virgin half unit cell and 6 corresponds to the saturated half unit cell. The (m,n) values of Figs. 4(a) and 4(b) are counted for the all half unit cells and are summarized in Table I (A) and (B). It is known

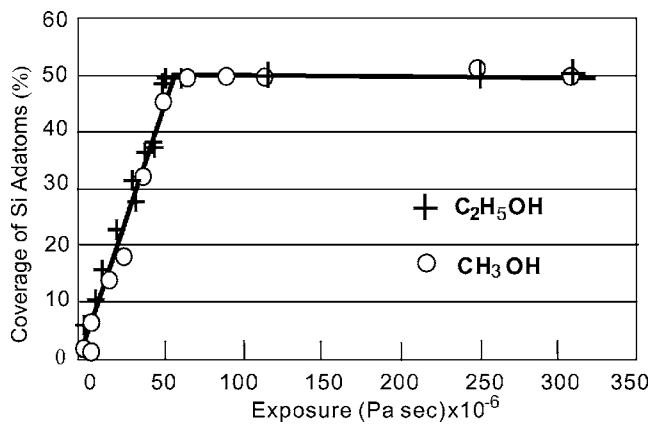


FIG. 2. Increase of adatom coverage with exposure of CH₃OH and C₂H₅OH at room temperature. Slope indicates coverage independent sticking probability.

that the value of faulted/unfaulted (F/U) takes 2.4 and 2.2 on the two surfaces with different coverage, and this ratio is established in a wide coverage range as shown in Fig. 5(a).

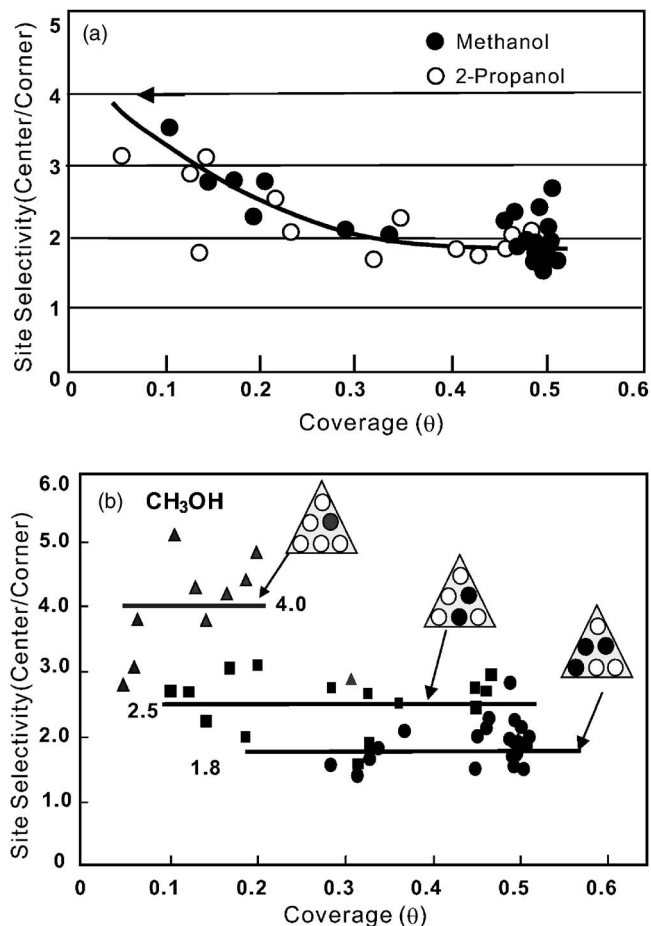


FIG. 3. (a) Overall site selectivity (center/corner) of CH₃OH and (CH₃)₂CHOH decreases monotonously as increasing the coverage. (b) The center/corner ratio obtained for the half unit cell with individual each (m+n)=1, 2, and 3. The lines of 4.0, 2.5, and 1.8 are the calculated center/corner ratio for the half unit cells with (m+n)=1, 2, and 3.

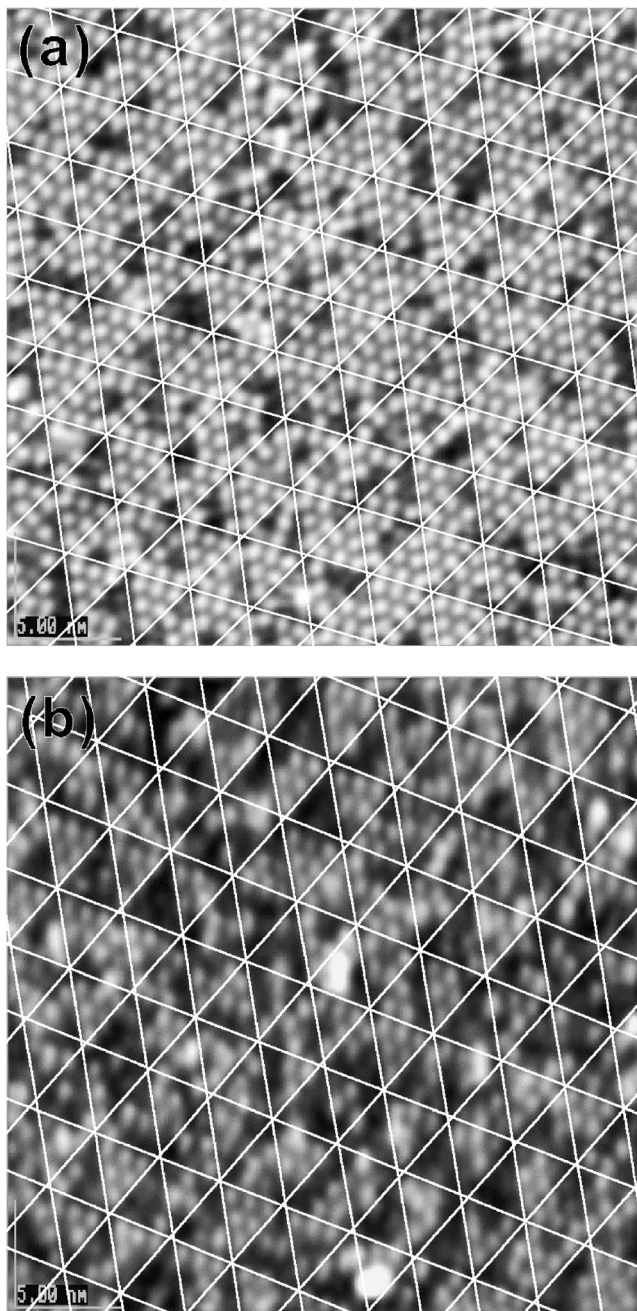


FIG. 4. STM image of the Si(111)-7 × 7 surface exposed to NO. (a) Exposed for 1 × 10⁻⁶ Pa × 40 s. Coverage of faulted and unfaulted halves is 29% and 12%, respectively, and the total adatom coverage is 20%. (b) Exposing for 2 × 10⁻⁶ Pa × 150 s. The coverage of faulted and unfaulted halves is 66% and 29%, respectively, and the total coverage is 48%.

From the fact that F/U=2.2 at 50 °K, 1.9 at 120 °K, and 2.0 at room temperature (Table II), we can conclude that the preferential adsorption on faulted halves (F/U > 1) is temperature independent. On the other hand, site selectivity ($\Sigma m / \Sigma n$ or $\Sigma n / \Sigma m$) depends on temperature, the value of $\Sigma n / \Sigma m$ is 1.0 at room temperature (Table I) in the faulted and unfaulted halves but it is 1.5 ~ 1.8 at 50 °K ~ 120 °K.¹⁰ It has been proposed that N and O atoms formed by the dissociation of NO migrates a long distance to dissipate their

TABLE I. Darkened adatoms in faulted (*F*) and unfaulted (*U*) halves formed by adsorption of NO. “*m*” and “*n*” are the number of darkened center adatoms and darkened corner adatoms, respectively. (A): Exposed to NO for 1×10^{-6} Pa \times 40 s. The 88 faulted and 89 unfaulted half unit cells were counted. (B): Exposed to NO for 2×10^{-6} Pa \times 150 s. The 67 faulted and 68 unfaulted halves were counted.

A																	
	0		1		2		3		4		5		6		Total		
(<i>m,n</i>)	(0,0)	(1,0)	(0,1)	(2,0)	(1,1)	(0,2)	(3,0)	(2,1)	(1,2)	(0,3)	(3,1)	(2,2)	(1,3)	(3,2)	(2,3)	(3,3)	($\Sigma m/\Sigma n$)
F	14	10	13	6	19	6	1	4	7	0	1	5	1	1	0	0	76/78
U	50	9	12	2	9	1	0	4	2	0	0	0	0	0	0	0	32/31
	64	19	25	8	28	7	1	8	9	0	1	5	1	1	0	0	108/109

Coverage of faulted halves=29%, and unfaulted halves=12%, Total coverage=20%. F/U=2.4, Center/Corner=0.99.

B																	
	0		1		2		3		4		5		6		Total		
(<i>m,n</i>)	(0,0)	(1,0)	(0,1)	(2,0)	(1,1)	(0,2)	(3,0)	(2,1)	(1,2)	(0,3)	(3,1)	(2,2)	(1,3)	(3,2)	(2,3)	(3,3)	($\Sigma m/\Sigma n$)
F	0	0	0	1	8	0	0	8	10	3	1	13	1	6	3	13	128/137
U	10	13	8	2	13	3	1	3	6	2	0	6	0	0	1	0	57/63
	10	13	8	3	21	3	1	11	16	5	1	9	1	6	4	13	185/200

Coverage of faulted halves=66%, and unfaulted halves=29%, Total coverage=48%. F/U=2.2, Center/Corner=0.93.

kinetic energy because few darkened pairs are observed by the STM.¹⁰

We can see also few darkened pairs In our STM image attained at a bias potential of 2.0 V as shown in Fig. 6(a), but the distribution of darkened dots may not be random. When the bias potential was changed from 2.0 to 3.0 V, about half of the darkened adatoms became bright, and the dark and bright dots may locate in a short distance as temporarily shown by a couple of solid and broken arrows in Fig. 6(b). However, it is difficult to identify either N or O bonded Si-adatoms are bright dots at 3.0 V.

Adsorption of NO on the faulted halves is preferential in a wide temperature range (Table II), but the sticking probability on the faulted and unfaulted halves changes simultaneously at a certain exposure as shown in Fig. 5(a), where the coverage is quite different between the faulted and unfaulted halves. This phenomenon strongly indicates that the adsorption is controlled by the formation of a common precursor, that is, the N and O atoms are provided by the dissociation of a common precursor. It is not clear if the dissociation of precursor NO occurs by unimolecular or bimolecular mechanism on the surface, but the dissipation of kinetic energy of N and O may be more efficient on the unfaulted halves with higher electron density so that the adsorption on the faulted halves is preferential.

To gain insight into the dissociation of the NO precursor, the adsorption of NO on a virgin Si(111)- 7×7 surface was compared to that on a C₂H₅OH saturated Si(111)- 7×7 surface. As cited above, three Si-adatoms are changed to Si-OC₂H₅ in the whole half unit cells on the C₂H₅OH saturated Si(111)- 7×7 surface. Therefore, the darkened fourth, fifth, and sixth adatoms in a half unit cell are the adsorption of N and/or O atoms. The adsorption of NO obtained this way is plotted with crosses in Fig. 5(b), which is in good agreement with the adsorption of NO on the virgin Si(111)- 7×7 surface (open circles). This result proves that

the sticking probability of NO has little influence from the occupation of Si-adatoms and Si-rest atoms. This is an interesting common feature of the precursor state as it will be discussed below.

C. Discussion

To understand the adsorption process relating to the electronic and/or the atomic structure of the surface, the adsorption of H₂O (Refs. 4 and 5), H₂S (Refs. 6 and 7), NH₃ (Refs. 2, 3, and 12), CH₃OH (Refs. 8 and 13), 2-propanol (Ref. 9) and NO (Refs. 10 and 14) on a Si(111)- 7×7 surface has been studied by numerous researchers, but the results were complex depending on the molecules. Therefore, the physical meaning of the sticking probability and site selectivity in the adsorption are still controversial. On the other hand, the adsorption mechanism of CH₃OH and (CH₃)₂CHOH on Si(111)- 7×7 surfaces has been clarified in the atomic level by the STM,^{8,9,13} in which the physical meaning of the sticking probability is more clarified in relation to the site selectivity.

The sticking probability does not necessarily reflect the final step although the STM image represents the final state of the adsorption. Figure 5(a) shows that the sticking probability (slope) of NO simultaneously changes at an exposure of ca. 70×10^{-6} Pa s on the faulted and unfaulted halves although the coverage of these two halves is quite different. This phenomenon proves that N and O atoms are provided by dissociation of the common precursor, but the dissipation of the kinetic energy occurs more efficiently on the faulted halves. As it was mentioned above, preferential adsorption of NO on the faulted halves is temperature independent, F/U = 2.2~2.4 at room temperature and F/U = 1.9~2.2 at 50~120 K, but the site selectivity (corner/center) depends on temperature, that is, corner/center ($\Sigma n/\Sigma m$) = 1.0 at room temperature but it is 1.5~1.8 at 50~120 K (Ref. 10) as

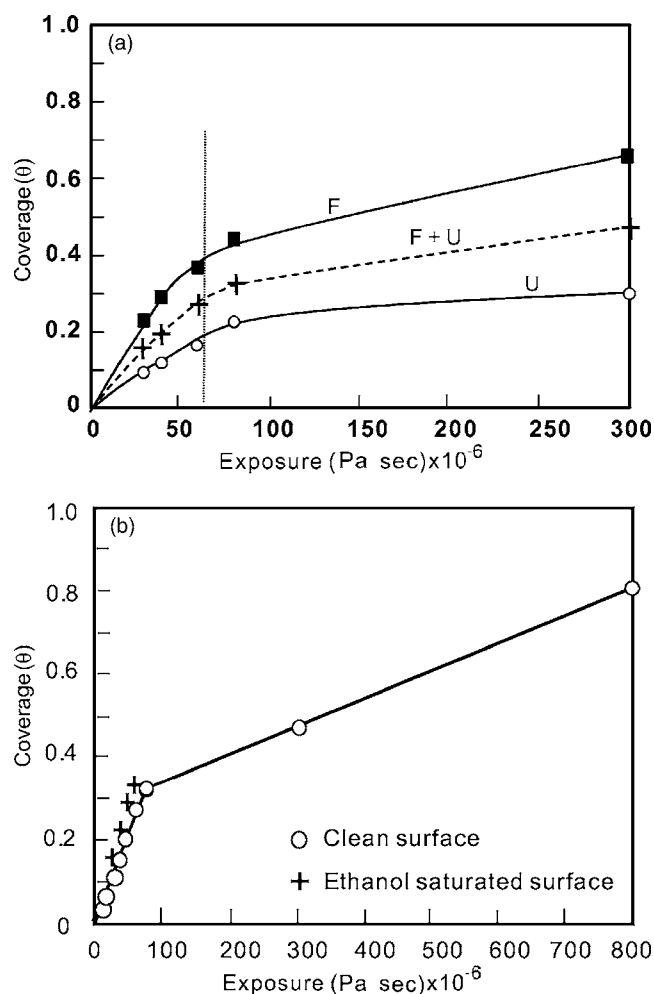


FIG. 5. (a) Coverage of adsorbed adatoms on faulted (F) and unfaulted (U) halves. Sticking probability is simultaneously changed on faulted and unfaulted halves at ca. 70×10^{-6} Pa s exposure. (b) Sticking probability of NO on a virgin Si(111)- 7×7 surface is equal to that on a C₂H₅OH saturated Si(111)- 7×7 surface.

shown in Table II. Two types of selectivity have to be considered on the Si(111)- 7×7 surface, one is the preferential adsorption on the faulted or unfaulted halves ($F/U \geq 1$) and the other is the temperature dependent site selectivity (corner/center) in a half unit cell. We speculate that the trapping probability of N and/or O atoms dissipated the kinetic

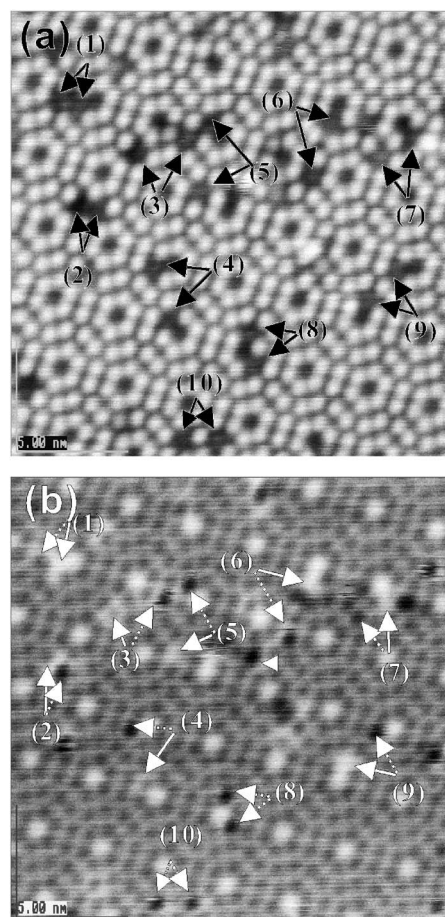


FIG. 6. STM image of the Si(111)- 7×7 surface exposed to NO for 10×10^{-6} Pa 30 s. (a) and (b) are the same area (20×20 nm²) attained at the bias potential of 2.0 V and 3.0 V. Some dark dots at 2.0 V change to bright dots by raising the bias potential from 2.0 V to 3.0 V as indicated with broken arrows

energy in a half unit cell will be higher on the corner adatoms with higher electron density at low temperatures but it is smeared at room temperature (corner/center=1.8 at 50 °K, 1.5~1.6 at 120 °K, and 1.0 at ca. 300 °K) as shown in Table II.

Contrary to the trapping of an N or O atom with a Si-adatom in a half unit cell, the adsorption of alcohols occurs equally on the faulted and unfaulted halves ($U/F=1.0$), but

TABLE II. Selectivity in adsorption of alcohols, NO and H₂S on Si(111)- 7×7 surface.

	Temperature	F/U	Corner/Center (n/m)	References
CH ₃ OH	room temperature	1	0.25 (1/4)	8
C ₂ H ₅ OH	room temperature	1	0.25	This work
(CH ₃) ₂ CHOH	room temperature	1	0.25	9
NO	room temperature	2	1.0	This work
NO	50 °K	2.2	1.8	10
	120 °K	1.9	1.5~1.6	10
H ₂ S	50 °K	96/4	0/100	6 and 7
	room temperature		0.5	6 and 7

the dissociation of CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and $(\text{CH}_3)_2\text{CHOH}$ depends on the local structure of adatom-rest atom pair site, that is, the site selectivity is corner/center=1/4 in faulted and unfaulted halves. It should be pointed out that the change of the site selectivity from 4 to 1.8 with the coverage in Fig. 3(a) is well explained by the pair site structures changing with the coverage.¹¹ We have to refer to the adsorption of H_2S (Refs. 6 and 7) and H_2O (Refs. 4 and 5), of which adsorption on the faulted halves prefers a low temperature although alcohols adsorb equally on the faulted and unfaulted halves, which may indicate that trapping probability of both atoms as well as molecules may be higher on the faulted halves with higher electron density compared to unfaulted halves at low temperature. The site selectivity in the adsorption of H_2S and H_2O , however, is similar to that of alcohol, that is, the dissociation on the center adatoms is preferential.

Accordingly, we could conclude that the adsorption of atoms and molecules prefers on the faulted halves to unfaulted halves, and the final trapping probability of the Si-adatoms in the half unit cell corresponds to the site selectivity. When the final step is given by the trapping of migrating atoms or molecules, competitive trapping by the corner or center adatoms in a half unit cell will be corner/center ≥ 1 although it depends on the temperature. In contrast, when the final step is given by the dissociation of molecule or precursor, the STM pattern reflects the structures requires for the dissociation. As shown in Fig. 3(a), the dissociation probability is 4/1 on the center adatom to the corner adatom on the virgin surface, but the ratio decreases monotonously from 4 to 1.8 as the coverage increases. If we derive the center/corner for the half unit cell having the same number of darkened adatoms, $(m+n)=1, 2,$ and 3 , the ratio of the center/corner takes individual constant values as shown in Fig. 3(b). This fact indicates that the site selectivity (center/corner) depends on the structure of adatom-rest pair sites, and the center/corner lowering with the coverage reflects the change of the distribution of the structures of the adatom-rest atom pair sites in a half unit cell as increasing the coverage. The relative dissociation probability of the precursor state alcohol is in a ratio of 1:1/4:0 depending on the number of adjacent rest atoms of 2, 1, and 0 to a Si-adatom. By using this ratio obtained by the experiment, the site selectivity is simulated for the half unit cells of $m=1, 2,$ and 3 . The simulated selectivity is in good agreement with the experimental values as indicated in Fig. 3(b) with lines of 4.0, 2.5, and 1.8 (Ref. 11).

To gain insight into the dissociation of the NO precursor on $\text{Si}(111)\text{-}7\times 7$, NO was adsorbed on a $\text{C}_2\text{H}_5\text{OH}$ saturated $\text{Si}(111)\text{-}7\times 7$ surface. Half of the Si-adatoms (three) and all of the Si-rest atoms are changed to $\text{Si-OC}_2\text{H}_5$ and Si-H in whole half unit cells, so three intact Si-adatoms still remain in every half unit cell on this surface although no intact rest atoms remain. How these three Si-adatoms contribute to the formation and dissociation of precursor state NO and to bonding with N and O atoms.

The most interesting fact is that the sticking probability of NO on a $\text{C}_2\text{H}_5\text{OH}$ saturated $\text{Si}(111)\text{-}7\times 7$ surface (crosses) is almost equal to that on the virgin surface (open circles) as shown in Fig. 5(b), that is, the occupation of Si-adatoms with

OC_2H_5 gives no effect on the formation of precursor state NO. We could say that this phenomenon is analogous to the coverage independent sticking probability of CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, and $(\text{CH}_3)_2\text{CHOH}$ on the $\text{Si}(111)\text{-}7\times 7$ surface observed in Fig. 2, that is, the formation of the precursor state, either alcohol or NO, has no effect of the coverage of adsorption sites. Despite such an analogous feature on the formation of the precursor state of NO and alcohols, the adsorption of NO on the faulted halves is preferential at room temperature ($F/U=2.2\sim 2.4$) as well as at low temperature ($F/U=1.9\sim 2.2$), but alcohol shows no such preference ($F/U=1$) at room temperature. The site selectivity (corner/center) of NO, however, is opposite to that of alcohol. We speculate that sticking probability is a formation probability of the precursor state by collision of the molecules. On the other hand, the preferential adsorption of NO on the faulted halves reflects the finally trapped population of N and/or O atoms. In the case of alcohol, the sticking probability is also a formation probability of the precursor state by collision of the molecules, but the final step is the dissociation of the precursor state molecules. Therefore, the feature of the STM image is entirely different between NO and alcohols although they have a common feature of the adsorption via precursor state. The adsorption of H_2S (Refs. 6 and 7), NH_3 (Refs. 2, 3, and 12), and H_2O (Refs. 4 and 5) may also take place by dissociation of the molecules at the final step, so that the site selectivity is very similar to that of CH_3OH (Ref. 8) and $(\text{CH}_3)_2\text{CHOH}$ (Ref. 9).

Finally, we wish to emphasize that the dissociation probability of the molecules by direct collision with an active site is very low although it has been tacitly assumed to explain the adsorption kinetics and catalysis. As discussed in this paper, effective collision of molecules depends on the formation of a dynamic precursor state. In this respect, the precursor state proposed in this paper is entirely different from such a precursor state model proposed in the absorption of vinyl bromidethe on a $\text{Si}(100)\text{-}4\times 2$ surface at a very low temperature.¹⁵ Considering the fact that the real precursor discussed in this paper is in a dynamic state on the surface, the frozen state vinyl bromide on the $\text{Si}(100)\text{-}4\times 2$ surface might be a critical state on an adsorption site. An isolated single Sn atom in a half unit cell on the $\text{Si}(111)\text{-}7\times 7$ surface might be a similar indecisive dynamic state, that is moving in a half unit cell but suddenly forms a Sn_2 dimer by passing the Si-dimer wall when another Sn atom comes into a neighboring cell.¹⁶ Therefore, we could say that the dissociation or the reaction at specific sites requires two-dimensional transportation of a molecule or intermediate on the surface, and it will be indispensable to understand the activity and/or the selectivity of heterogeneous catalysis.

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