PHYSICAL REVIEW B **66**, 125306 (2002)

Dissociation mechanism of methanol on a Si(111)-(7×7) surface studied by scanning tunneling microscopy

Zhao-Xiong Xie,[1,2] Yusuke Uematsu,[1] Xin Lu,[2] and Ken-ichi Tanaka[1,*]
[1]*Advanced Science Research Laboratory, Saitama Institute of Technology, 1690 Fusaiji, Okabe, Saitama, Japan*
[2]*State Key Laboratory for Physical Chemistry of Solid Surfaces;*
Department of Chemistry, Xiamen University, Xiamen 361005, China
(Received 6 March 2002; published 11 September 2002)

Adsorption of methanol on a Si(111)-7×7 surface was studied by means of scanning tunneling microscopy (STM). The STM image of adatoms and the tunneling spectroscopy at the rest atom position suggest that the CH_3OH molecule dissociates on an adatom and rest atom pair by forming Si-OCH_3 and Si-H, respectively. At saturation, half of the adatoms, three adatoms, and all three rest atoms are changed to Si-OCH_3 and Si-H in every half unit cell. When the adatom changes to Si-OCH_3, the Si adatom becomes invisible at the bias potential of 2.0 V. In contrast, Si-OCH_3 and the intact adatom have equal image intensity at 3.0 V, although center adatoms are brighter than corner adatoms. As a result, the saturated surface shows a characteristic uniform pattern at 3.0 V, although half of the adatoms are Si-OCH_3 and the other half are intact Si adatoms. By counting darkened corner and center adatoms at the bias of 2.0 V, the site-dependent kinetics for the adsorption of CH_3OH was established. The sticking probability for the formation of Si-OCH_3 and Si-H was independent of the coverage, and the number of Si-OCH_3 in each half unit cell is consecutively increased in a sequence of 1, 2, and 3 with increasing exposure. These facts indicate that the dissociation of CH_3OH is accomplished via a precursor state in each half unit cell: that is, each half unit cell works independently as if it were a molecule.

DOI: 10.1103/PhysRevB.66.125306 PACS number(s): 68.43.Fg, 68.43.Mn, 68.37.Ef

I. INTRODUCTION

Dissociation of adsorbed molecules on the Si(111)-7×7 surface is a chemical reaction of the molecules with the dangling bonds of Si atoms. Therefore, the reactivity of Si atoms depends markedly on the molecules and the local structure and local electronic configuration of the dangling bond. From this view point, it is interesting to know the site-dependent kinetics and/or dynamics of the adsorption of molecules on the silicon surfaces.

The dangling bond of Si atoms on the Si(111)-7×7 surface has been experimentally as well as theoretically deduced, so the site-dependent adsorption of molecules on the Si(111)-7×7 surface is an interesting subject to investigate the reactivity of Si adatoms in relation to the electronic configuration of dangling bonds. Adsorption of H_2O, NH_3, H_2S, and alcohol on silicon surfaces has been extensively studied experimentally and theoretically.[1–8] The adsorption of methanol and ethanol on Si(111) surfaces was also precisely studied by electron energy loss spectroscopy[9,10] as well as by high-resolution photoemission spectroscopy,[11–14] which suggested the dissociation of methanol and ethanol (*R*OH) on the Si(111)-7×7 surface forming Si-O*R* and Si-H. In this paper, we studied the adsorption of methanol on a Si(111)-7×7 surface by using scanning tunneling microscopy (STM), and it is deduced that the dissociation of CH_3OH is conducted via a precursor-state adsorption in a half unit cell. Interaction of the lone pair electrons of oxygen in CH_3OH with the electron-deficient dangling bond on the Si adatoms might be responsible for the precursor state of adsorption. That is, when a precursor alcohol moves onto an adatom which has adjacent intact rest atom(s), the precursor CH_3OH undergoes dissociation by transferring a proton onto the rest atom and dissociation into Si-OCH_3 and Si-H is established. We show that dissociation of CH_3OH via the precursor state is accomplished within a half unit cell.

II. EXPERIMENT

The STM (JEOL) experiments were performed in an UHV chamber with a base pressure of 2×10^{-8} Pa. A rectangular Si(111) wafer (*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 repeatedly flashed to ca. 1250 °C until a clean well-ordered Si(111)-7×7 surface was obtained. After this, the sample was transferred from the treatment chamber to the STM chamber and cooled down to room temperature (ca 298 K). Methanol was adsorbed on the Si(111)-7×7 surface by exposing the sample to a controlled pressure of CH_3OH in the STM chamber. During the adsorption procedure of methanol, the STM tip was retracted far away from the surface to reduce the adsorption shielding by the tip. The STM image was observed at room temperature by a constant-current mode with an electrochemically etched tungsten tip.

III. RESULTS AND DISCUSSIONS

The STM images shown in Figs. 1(a) and 1(b) represent the same area of a Si(111)-(7×7) surface exposed to methanol at 1×10^{-6} Pa for 50 sec (about 0.4 L) at room temperature, where the images (a) and (b) were obtained at the bias potential of 2.0 and 3.0 V, respectively. A lot of Si adatoms become invisible at the bias of 2.0 V in Fig. 1(a), but basically all adatoms become visible at the bias of 3.0 V in Fig. 1(b), although the contrast is not uniform. A very similar phenomenon was observed in the adsorption of am-

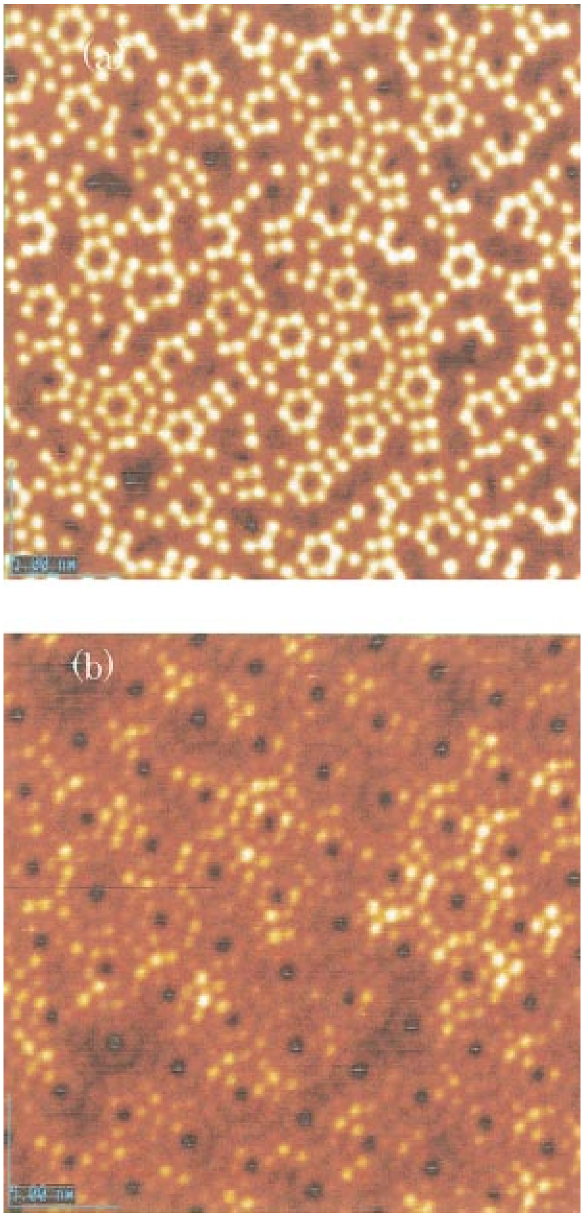

FIG. 1. (Color) STM images of a Si(111) surface (30 nm × 30 nm) exposed to 0.4 L of methanol at room temperature, which were obtained at the bias potentials of 2.0 V (a) and 3.0 V (b) with a tunneling current of 0.2 nA.

monia on the Si(111)-7×7 surface by Wolkow and Avouris.[1] As will be discussed latter, the number of invisible Si adatoms increases in proportion to the exposure, so the adsorption of methanol is responsible for the darkened Si adatoms at the bias of 2.0 V. An interesting fact is that the number of invisible Si adatoms does not exceed three adatoms per half unit cell, even on the surface saturated with methanol after an exposure of 20 L. That is, no more adsorption of methanol takes place even if three adatoms remain intact in every half unit cell. As was mentioned above, when the bias potential is increased to 3.0 V, all adatoms become visible, although the contrast of Si adatoms depends on the coverage. These results indicate that the 7×7 surface is not restructured by the adsorption of methanol, although the low-energy electron diffraction (LEED) pattern may be changed by the adsorption.[10] It is noteworthy that the darkened adatoms at the bias of 2.0 V become a little brighter than the other adatoms at the bias potential of 3.0 V in Fig. 1(b). As a result, the surface saturated with methanol gives a unique STM pattern with uniform intensity at the bias potential of 3.0 V as shown in Fig. 3(b).

The dangling bond on the rest Si atom, nearly filled with an electron pair, is difficult to see in the ordinary STM image. However, the tunneling spectroscopy (I-V curve) at the rest-atom position may reflect the density of states of the dangling bond, which will be changed by forming Si-H. As will be discussed below, all rest atoms are changed to Si-H when the surface is saturated with adsorption of methanol.

The triangles drawn in the STM images of Figs. 2(a) and 2(c) are the half unit cells containing one, two, and three darkened Si adatoms, and (d), (e), and (f) are the corresponding I-V spectra obtained at the rest-atom position adjacent to the darkened adatoms, where the STM images were attained at 2.0 V. Figure 2(b) is the same area of (a) obtained at 3.0 V. It is known that the tunneling spectrum of the Si rest atom on the clean Si(111)-7×7 surface has a characteristic peak at −0.8 V below the Fermi level which is assigned to the dangling bond.[1,2] Dissociation of methanol forming Si-OCH_3 and Si-H on the Si(111)-7×7 surface was proposed by using high-resolution electron energy loss spectroscopy (HREELS),[9,10] photoemission, and desorption spectra.[18–21] The dissociation of NH_3 was supposed to provide Si-H on the Si adatom and NH_2 on the Si rest atom, but it is undetermined if the dissociation of CH_3OH forms Si-H on the Si adatom and Si-OCH_3 on the Si rest atom. In our experiment, we concluded the opposite dissociation, Si-OCH_3 on the Si adatom and Si-H on the Si rest atom, by measuring the site-dependent I-V spectra at the rest-atom positions adjacent to the darkened Si adatoms. As shown in Fig. 2(d), a small hump appeared at −0.8 V marked by the arrow on curves 2 and 3, which reflects the dangling bond on the rest atom. However, no such characteristic hump was seen on the curve 1 attained at the position of the rest atom 1 shown in the triangular model, which proves that the rest atom 1 contributes to the dissociation of CH_3OH molecules and it changes to Si-H. As will be shown below, the dissociation of CH_3OH takes place via a precursor state and the dissociation is brought about by a pair of Si adatom and Si rest atom in the half unit cell. When the two Si adatoms become invisible in the half unit cell as shown in (b), spectrum 1 and spectrum 2 attained on the two rest atoms have no characteristic hump at −0.8 V as shown in Fig. 2(e), but it is recognized on spectrum 3. This result proves that Si-H is formed at Si rest atom 1 and Si rest atom 2. The two Si-H rest atoms in Fig. 2(b) are surrounded by three center adatoms and two corner adatoms. By careful observation, it is seen that the two center adatoms are brighter than the other Si adatoms, and we can identify the Si rest atoms which were changed to Si-H by measuring the I-V spectrum. When the three rest atoms are fully occupied with H, the three I-V spectra show no dangling bond feature as shown in Fig. 2(f) and the topographic image shows three center adatoms with equal intensity. Consequently, when the surface is saturated, the STM image at the

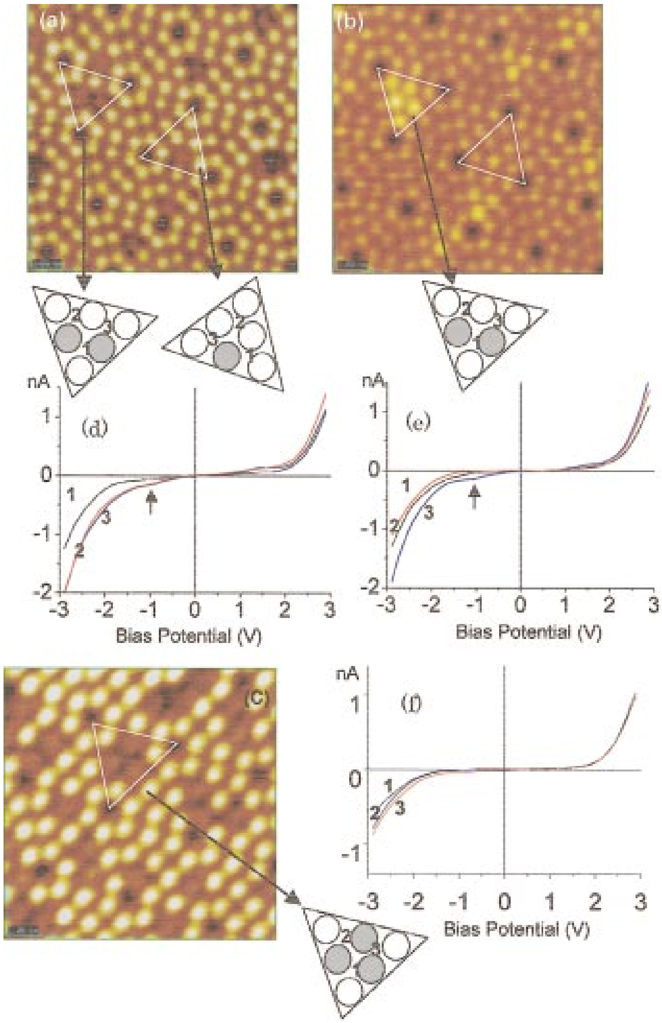

FIG. 2. (Color) Topographic STM image of the surfaces having one and two darkened adatoms in a half unit cell (a) and three darkened adatoms in a half unit cell (c). Images (a) and (c) were obtained at 2.0 V but (b) was attained at 3.0 V for the same area to (a). The image of (a) and (b) corresponds to the surface exposed to 0.1 L of methanol at room temperature and that of (c) is the surface exposed to 0.2 L. Tunneling spectra (I-V curves) of (d), (e), and (f) were obtained at the specified rest-atom positions numbered in the triangular model. A hump indicated with arrows at -0.8 V is a state for the dangling bond on rest atoms.

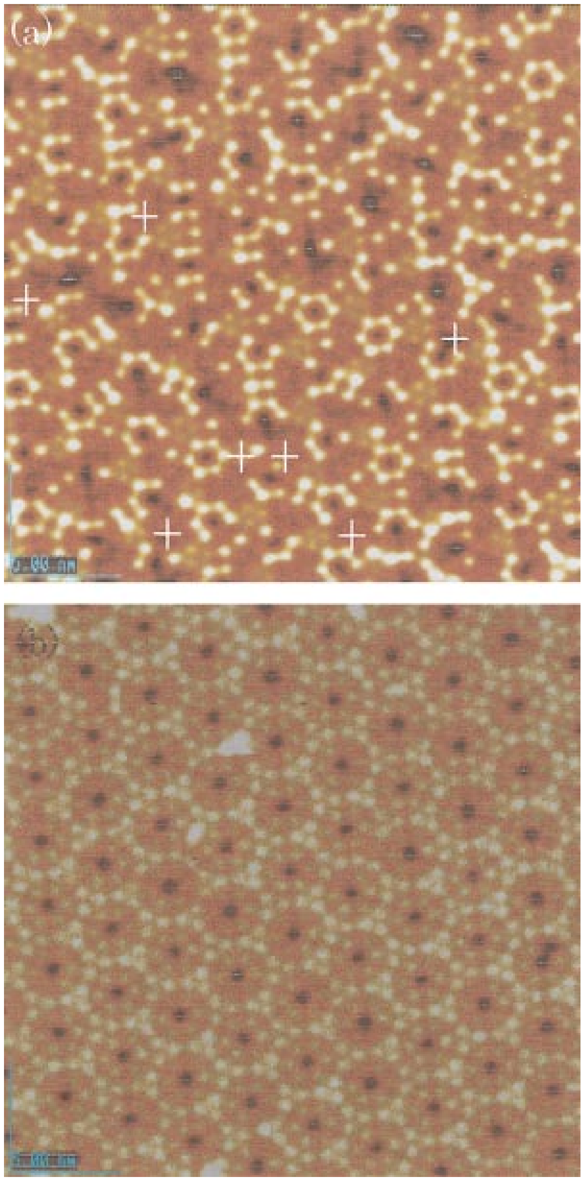

FIG. 3. (Color) Si(111)-7×7 surface exposed to 20 L of methanol. The STM images were attained at the bias potentials of 2.0 V (a) and 3.0 V (b). Three Si adatoms in every half unit cells are invisible at 2.0 V in (a), but all adatoms becomes visible at 3.0 V in (b). The center adatoms are brighter than the corner adatoms at 3.0 V in the (b).

bias of 3.0 V represents a unique pattern with uniform intensity such as shown in Fig. 3(b). In contrast, the STM image at the bias potential of 2.0 V has three darkened adatoms in every half unit cell when the surface is saturated with methanol.

Figures 3(a) and 3(b) reflect the empty-state image of a saturated surface prepared by exposing to 20 L of methanol (2660×10^{-6} Pa sec), where (a) and (b) are images obtained at bias potentials of 2.0 and 3.0 V, respectively. The darkened site in image (a) corresponds to Si-OCH$_3$, and the bright site reflects the intact Si adatoms persisting in the half unit cells. By counting darkened adatoms, the coverage of adatoms (the fraction of darkened Si adatoms) increases linearly with exposure until the coverage reaches 0.5 with respect to the total Si adatoms (center+corner adatoms) as shown in Fig. 4(a). It is clear that the dissociation probability of methanol is constant until half of the adatoms are occupied by methoxy (i-OCH$_3$) groups ($q=0.5$). As the Si(111)-7×7 surface contains 3.2×10^{13} half unit cells per cm^2 and the collision of methanol is about 0.75×10^{15} per cm^2 for 1 L (Torr sec), each half unit cell takes about 23 collisions for 1 L, that is, 11–12 collisions for 0.5 L (saturation occurs for 0.49–0.51 L). Taking into account the fact that the dissociation probability is independent of the coverage as shown in Fig. 4(a), the dissociation of methanol molecule occurs every four collisions, because three Si adatoms per half unit cell undergo a reaction at the saturation. Adsorption of methanol molecule as a pre-

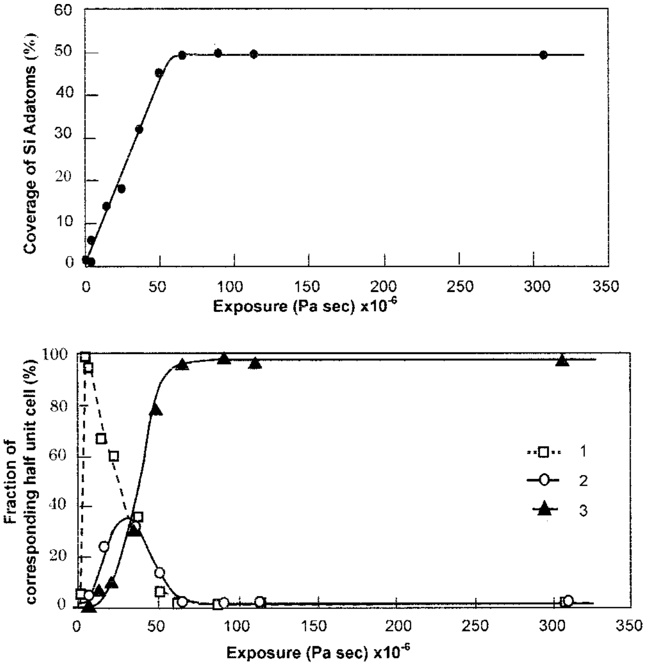

FIG. 4. Site-resolved kinetics in adsorption of CH_3OH on Si(111)-7×7 surface. (a) Fraction of darkened adatoms linearly increases with exposure. (b) Fraction of the half unit cells having one, two, and three darkened adatoms changes consecutively with exposure.

cursor state on the surface might depend on the colliding orientation of the molecule. A coverage-independent sticking probability has been explained by the mechanism of adsorption via a precursor state as deduced by Kisliuk.[22] If we apply this model, the apparent sticking probability (S) is expressed by the equation $S=S_0[1+\{\theta/(0.5-\theta)\}\alpha]^{-1}$, where S_0 is the sticking probability of the gas-phase molecules on the surface at $\theta=0$ and α is the desorption probability of the precursor molecules without final adsorption. The result of Fig. 4(a) shows that α is very small: that is, most precursor state molecules undergo rapid dissociation on an adatom rest-atom pair within a half unit cell. By counting a total of 146 half unit cells in Fig. 3(a), which was obtained by exposing to 20 L of methanol, three adatoms are darkened in 139 half unit cells, but no half unit cells with one or two darkened adatoms are found. Exceptionally, 7 half unit cells marked with crosses in Fig. 3(a) have 4 darkened adatoms, which may contain impurities.

When the coverage is moderate, half unit cells have darkened Si adatoms of zero to three as shown in Fig. 1. The fraction of half unit cells having one, two, and three darkened adatoms changes consecutively with exposure, and it is obvious that the fraction consecutively changes with coverage as shown in Fig. 4(b). This result strongly indicates that the adsorption is brought about independently in each half unit cell: that is, the precursor state is localized in each half unit cell and undergoes rapid dissociation within the half unit cell. It is worth noting that the center adatoms are 4 times more reactive than corner adatoms.

It is known that the three center adatoms of a half unit cell in Fig. 2(b) are not uniform, but their intensity becomes uniform when the surface is saturated with the adsorption of methanol as shown in Fig. 3(b). Provided that the dissociation of CH_3OH occurs on an adatom and a rest-atom pair in a half unit cell, all the rest atoms are changed to Si-H when half of the Si adatoms are changed to Si-OCH_3. Taking these facts into account, the STM image with uniform intensity at the bias of 3.0 V may reflect the empty state of adatoms influenced by Si-H rest atoms.

According to the DAS model (dimer adatom and stacking fault) for the Si(111)-(7×7) surface,[15] a unit cell has 19 dangling bonds, 6 on the rest atoms, 12 on the adatoms, and 1 on the atom at the bottom of the corner hole: that is, a unit cell contains in total 19 electrons in the dangling bonds. By comparing the STS on the specific sites[1] with the photoemission and inverse photoemission spectra, Himpsel[23] deduced that the dangling bond on the rest atom is filled with lone pair electrons, but the dangling bond on the adatoms is almost empty. Calculation supported this experimental result: that is, the dangling bonds on the rest atoms and on the corner hole atom are filled, and the 12 Si adatoms have 5 partially occupied and 7 empty dangling bonds.[16] We found that the adsorption of NO makes a bond with all 12 Si adatoms on a Si(111)-7×7 surface, but no adsorption of N_2O occurs on the surface at room temperature.[17] In contrast, half of the Si adatoms contribute to the dissociation of CH_3OH in cooperation with Si rest atoms, which is brought about equally on the faulted and unfaulted halves. As a result, the three intact Si adatoms persisting per half unit cell have no ability to dissociate CH_3OH because they have no adjacent Si rest atom. We can deduced that precursor methanol may be localized in each half unit cell by interacting with the dangling bond of Si adatoms, and it undergoes dissociation into Si-OCH_3 and Si-H with little desorption.

The STM images in Figs. 1(b) and 3(b) reflect the empty state at 3.0 V, where the center adatoms are seen to be brighter than the corner adatoms when the rest atoms are adjacent to the Si-H center adatoms. On the saturated surface, the center adatoms, which are either intact Si or Si-OCH_3, are necessarily adjacent to two Si-H rest atoms, while the Si corner adatoms, either intact Si or Si-OCH_3, are adjacent to one Si-H rest atom, which may be responsible for the image of the saturated surface shown in Fig. 3(b). As was mentioned above, the ratio of darkened corner to darkened center adatoms caused by adsorption of CH_3OH was 1:4 at low coverage, which suggests that the electron density of the dangling bond of the center adatoms may be lower than that of the corner adatoms.

From the Si $2p$ core-level photoemission spectrum after methanol adsorption on the Si(111)-(7×7) surface,[11–13,18] it was shown that the $S2$ surface state related to the rest atoms was quickly quenched upon low coverage adsorption, whereas the $S1$ surface state partially related to the adatoms was quenched only subsequently at much higher coverage. From these results, Piancastelli and co-workers[18,24] deduced that the reactivity of the Si rest atom is higher than that of the adatoms towards methanol and the methoxy species are preferentially formed on the rest atom. It should be pointed out that there are twice as many adatoms as rest atoms so that the dangling bonds on the rest atoms appear to quench more quickly compared to those on the adatoms when the experiment is performed at rather high coverage, but it does not mean that rest atoms are the first reaction sites on the Si(111)-7×7 surface. In this paper, we deduced that the precursor state localized in a half unit cell undergoes dissociation on an adatom and rest-atom pair to form Si-OCH_3 and Si-H, respectively.

ACKNOWLEDGMENTS

This work was performed by the support of High-Tech Research Center of Saitama Institute of Technology, and one of the authors (Z.X.X.) thanks Saitama Institute of Technology for financial support during his stay in Japan. The authors appreciate the valuable comments of Professor X. Xu of Xiamen University.

---

*Author to whom all correspondence should be addressed.

[1] R. Wolkow and Ph. Avouris, Phys. Rev. Lett. **60**, 1049 (1988).

[2] Ph. Avouris and R. Wolkow, Phys. Rev. B **39**, 5091 (1989).

[3] M. A. Rezaei, B. C. Stipe, and W. Ho, J. Chem. Phys. **109**, 6075 (1998).

[4] M. A. Rezaei, B. C. Stipe, and W. Ho, J. Phys. Chem. B **102**, 10 947 (1998).

[5] Ph. Avouris, J. Phys. Chem. **104**, 2246 (1990).

[6] C. Poncey, F. Rochet, G. Dufour, H. Roulet, F. Sirotti, and G. Panaccione, Surf. Sci. **338**, 143 (1995).

[7] H. Ezzehar, L. Stauffer, J. Leconte, and C. Minot, Surf. Sci. **388**, 220 (1997).

[8] X. Lu, Q. Zhang, and M. C. Lin, Phys. Chem. Chem. Phys. **3**, 2156 (2001).

[9] K. Edamoto, Y. Kubota, M. Onchi, and M. Nishijima, Surf. Sci. **146**, L533 (1984).

[10] A. Stroscio, S. R. Bare, and W. Ho, Surf. Sci. **154**, 35 (1985).

[11] M. Carbone, M. N. Piancastelli, M. P. Casaletto, R. Zanoni, M. J. Besnard-Ramage, G. Comtet, G. Dujardin, and L. Heller, Surf. Sci. **419**, 114 (1999).

[12] M. P. Casaletto, R. Zanoni, M. Carbone, M. N. Piancastelli, L. Aballe, K. Weiss, and K. Horn, Surf. Sci. **447**, 237 (2000).

[13] M. Carbone, M. N. Piancastelli, R. Zanoni, G. Comtet, G. Dujardin, and L. Heller, Surf. Sci. **370**, L179 (1997).

[14] M. Carbone, R. Zanoni, M. N. Piancastelli, G. Comtet, G. Dujardin, and L. Heller, Surf. Sci. **352–354**, 391 (1996).

[15] K. Takayanagi, Y. Tanishiro, M. Takahashi, and S. Takahashi, J. Vac. Sci. Technol. A **3**, 1502 (1985).

[16] L. Stauffer, S. Van, D. Bolmont, J. J. Koulmann, and C. Minot, Solid State Commun. **85**, 935 (1993).

[17] K. Tanaka *et al.* (unpublished).

[18] M. Carbone, M. N. Piancastelli, J. J. Paggel, Chr. Weindel, and K. Horn, Surf. Sci. **412/413**, 441 (1998).

[19] J. Eng, Jr., K. Raghavachari, L. M. Struck, Y. J. Chabal, B. E. Bent, G. W. Flynn, S. B. Christman, E. E. Chaban, G. P. Williams, K. Rademacher, and S. Mantl, J. Chem. Phys. **106**, 9889 (1997).

[20] J. A. Glass, Jr., E. A. Wovchko, and J. T. Yates, Jr., Surf. Sci. **338**, 125 (1995).

[21] N. Y. Kim and P. E. Laibinis, J. Am. Chem. Soc. **119**, 2297 (1997).

[22] P. Kisliuk, J. Phys. Chem. **3**, 95 (1957); **5**, 78 (1958).

[23] F. J. Himpsel, Surf. Sci. Rep. **12**, 1 (1990).

[24] M. N. Piancastelli, J. J. Paggel, Chr. Weindel, M. Hasselblatt, and K. Horn, Phys. Rev. B **56**, 12 737 (1997).