Adsorption of Acetonitrile on Si(111)-(7 × 7)

Suklyun Hong,* Kyung-Ah Min, Jinwoo Park, Hanchul Kim, Hironori Mizutani, and Michio Okada*

ABSTRACT: The adsorption of acetonitrile (CH₃CN) on Si(111)-(7 × 7) at a room temperature has been investigated using scanning tunneling microscopy (STM) and first-principles calculations. The site-specific information on adsorption enables us to understand the site-by-site and step-by-step adsorption mechanism. From theoretical simulations, the most stable configuration of CH₃CN on Si(111)-(7 × 7) is found to be a molecularly chemisorbed CH₃CN with the carbon and nitrogen atoms of CN bonded to the rest atom and adatom on the Si surface, respectively. Some chemisorption-induced features in the STM topographic image are assigned based on the theoretical calculations.

1. INTRODUCTION

The technologically most important material, silicon (Si), plays ubiquitous and irreplaceable roles in the development of micro- and optoelectronic devices and so on. Studies on the surface chemistry of silicon have received much attention from the viewpoint of basic science.¹⁻⁵ Many previous reports in this area have focused primarily on the binding of molecules comprising unpolarized C=C or C≡C,⁶⁻¹⁰ five-membered aromatics,¹¹⁻¹⁵ benzene and its derivatives,¹⁴⁻¹⁷ and some other unsaturated cyclic hydrocarbons on pure Si surfaces.¹⁸,¹⁹ These molecules can be adsorbed on Si(100) via [2 + 2] or/and [4 + 2] cycloaddition reactions. Turning our eyes to the polarized molecules, the adsorption behavior of organic molecules with the cyano group (C≡N), for example, the simplest nitrile of acetonitrile (CH₃CN), has been also investigated on Si(100).²⁰⁻²⁴ Several experimental²⁰,²¹ and theoretical²⁰,²²⁻²⁴ studies suggested a [2 + 2] cycloaddition reaction via the C≡N group (di-σ model). The CH₃CN molecule is adsorbed molecularly on Si(100) through the C≡N group in a di-σ configuration, leaving a C≡N functionality on the surface for further reaction and modification.²⁰⁻²⁴

Compared to Si(100), we expect a relatively simpler binding mechanism for molecules adsorbed on Si(111)-(7 × 7), mainly related to the adatom–rest atom pair (electrophilic and nucleophilic) functioning as a diradical. Si(111)-(7 × 7) is formed via the (7 × 7) reconstruction involving a layer-by-layer structure on a base layer with 49 silicon atoms of a (111) surface, which reduces the number of 3-coordinated Si atoms from 49 to 19 in each unit cell (see Figure 1). For a molecule containing unsaturated polarized bonds, interesting chemistry may arise in the attachment because of the functional polarity and the coexistence of electronically nonequivalent dangling bonds (of adatoms and rest atoms) on the polarized Si(111)-(7 × 7). To explore the interaction of the unsaturated polarized functional group with Si(111)-(7 × 7), CH₃CN with a large dipole moment of 3.92 D was selected as a probe of chemical reactivity in the present study.

Figure 1. (a) Top view and (b) side view of the Si(111)-(7 × 7) unit cell. Purple, blue, and red balls represent the adatom, rest atom, and third layer atom, respectively.

Received: March 31, 2020
Accepted: August 25, 2020
Published: September 14, 2020
In recent work, it was reported that a functionalized organic monolayer of acetonitrile can be formed on Si(111)-(7 × 7) via a di-σ binding mechanism (see Figure S1) related to the coupling of one π$_{CN}$ bond with an adatom–rest atom pair by using various experimental techniques and density functional theory (DFT) calculations. Here, we report detailed STM studies and theoretical calculations for elucidating the site-by-site and step-by-step reactivity of CH$_3$CN on Si(111)-(7 × 7). We propose possible configurations of CH$_3$CN on Si(111)-(7 × 7), which can explain some experimental STM images.

2. EXPERIMENTAL AND COMPUTATIONAL METHODS

The experiments were carried out with a scanning tunneling microscope (UMS-901S, UNISOKU Co.) under ultrahigh vacuum (UHV). The base pressure of the apparatus is below 1 × 10$^{-8}$ Pa. The topographic STM images were taken at ~300 K with a Pt–Ir tip. CH$_3$CN was introduced into the UHV chamber after being freeze–pump–thaw cycles. The purity of the CH$_3$CN gas was checked using a quadrupole mass spectrometer. The Si(111) (P doped n-type, 0.4–0.6 Ω·cm$^{-1}$) sample cut from the wafer was mounted on a well-degassed Mo sample holder after the treatment with methanol in an ultrasonic bath. The sample was cleaned by means of repeated heating to 1473 K under UHV conditions.

To investigate the configuration of acetonitrile on the Si(111)-(7 × 7) surface, we have performed ab initio calculations using the Vienna Ab initio Simulation Package (VASP). For the exchange and correlation interactions of electrons in the generalized gradient approximation (GGA), we employ the Perdew–Burke–Ernzerhof (PBE) functional form. The electron–ion interactions are described by the projector augmented-wave (PAW) method. A plane wave basis set is used with an energy cutoff of 400 eV. For van der Waals (vdW) corrections, Grimme’s DFT-D3 vdW approach is adopted.

The acetonitrile-adsorbed Si(111) surface is modeled by a slab with a Si(111)-(7 × 7) surface supercell which is composed of an adsorbed acetonitrile molecule, seven Si atomic layers (including one adatom layer), and an H passivating layer. The reconstructed Si(111)-(7 × 7) surface adopts the dimer–adatom–stacking fault (DAS) structure. The bottom H atom layer and the two Si atom layers are fixed, and the rest of the Si atom layers and the adsorbed molecules were allowed to relax during the structure optimization. The structure was considered to be in equilibrium when the Hellman–Feynman force is smaller than 0.02 eV/Å. For the Brillouin-zone integration, we use a 3 × 3 × 1 grid in the Monkhorst–Pack special point scheme. A Gaussian broadening with a width of 0.02 eV was used to accelerate the convergence in the k-point sum. With the use of the self-consistent Kohn–Sham eigenvalues and wavefunctions, the constant-current STM images are simulated within the Tersoff–Hamann scheme. The tunneling current $I(r, ±V)$ is proportional to the energy-integrated local density of states (LDOS)

$$I(r, ±V) \propto \sum_{nk} \int_{E_{F}}^{E} I(E) \delta(E - E_{nk}) dE$$

where $+V$ and $-V$ represent the sample bias voltages for empty-state and filled-state measurements, respectively. To create simulated STM images, we adopted the p4vasp software package.

3. RESULTS AND DISCUSSION

Figure 2 shows the CH$_3$CN-exposure dependence of filled-state STM topographic images on Si(111). Both doses of CH$_3$CN and STM measurements were carried out at ~300 K. The filled-state STM images in Figure 2 were taken in a constant-current mode at negative sample bias. The density of adatom defects was low on our routinely prepared clean surface, as shown in Figure 2a. With counting more than 10$^4$ adatoms, the defect density is estimated to be below 0.3% of surface adatoms. Figure 2b–d shows three typical filled-state STM topographs taken after the exposure of the surface to 1.0, 3.0, and 7.0 L (1 L = 1.33 × 10$^{-4}$ Pa·s) of CH$_3$CN. Compared with the clean surface, the (7 × 7) reconstruction still survived after the acetonitrile exposure. The appearance of darkened adatom sites, whose number increases with increasing CH$_3$CN exposure, can be related to the adsorption of CH$_3$CN. Recently, a large influence of nonlocal manipulation events is reported on the molecules on the Si(111)-(7 × 7) surface. Under the present experimental conditions, there are no signs of such nonlocal effects in the obtained STM topographic images during several scans.

A statistical counting of darkened dangling bond sites enables us to gain insights into the spatial selectivity for acetonitrile adsorption. Figure 3 shows the CH$_3$CN-uptake curves determined from the STM images at room temperature. By counting more than 10$^4$ adatoms for each exposure, the uptake curves were produced. The dose of 20 L is enough to reach the saturation coverage. It is clear that CH$_3$CN prefers to adsorb on the faulted half of the unit cells for all exposures. The stacking fault increases the LDOS, and as a result, the density of adatom defects was low on our routinely prepared clean surface. In contrast, the stacking fault defect density is estimated to be below 0.3% of surface adatoms. Figure 2b–d shows three typical filled-state STM topographs taken after the exposure of the surface to 1.0, 3.0, and 7.0 L of CH$_3$CN. Compared with the clean surface, the (7 × 7) reconstruction still survived after the acetonitrile exposure. The appearance of darkened adatom sites, whose number increases with increasing CH$_3$CN exposure, can be related to the adsorption of CH$_3$CN. Recently, a large influence of nonlocal manipulation events is reported on the molecules on the Si(111)-(7 × 7) surface. Under the present experimental conditions, there are no signs of such nonlocal effects in the obtained STM topographic images during several scans.
related species, compared to 39% in the unfaulted half as shown in Figure 3. The saturation coverage agrees exactly with the previously reported value of 42%.\textsuperscript{28} The LDOS is slightly higher on the faulted halves than on the unfaulted halves. Thus, the higher reactivity of the faulted halves may be attributed to the higher LDOS. As the Si(111)-(7 × 7) surface contains 3.2 × 10\(^{13}\) half unit cells per cm\(^2\) and the collision of acetonitrile is about 2.8 × 10\(^{14}\) per cm\(^2\) for 1 L (Torr·sec), about 9 collisions for 1 L occurs on each half unit cell. Thus, the present data in Figure 3 suggest the average initial sticking probability of 0.05 (0.07 for unfaulted half and 0.03 for faulted half). This small value of sticking probability suggests that the activation barrier between a precursor state and the chemisorbed states may be high enough that the desorption from the precursor state may be dominant at room temperature. Here, the precursor state is a mobile physisorbed state because of the dispersion force and finds the possible ways into the molecularly chemisorbed state or the desorption. Low-temperature exposure enhances the sticking probability as it can be seen in the data in ref 28. In addition, although corner holes and dimers are possible reaction sites, the reactivity may be underestimated because of their invisibility in the present experiments.

As exhibited in Figure 4, the center adatoms are more preferable for chemisorption than the corner adatoms in both faulted and unfaulted halves with a ratio of 4 to 2. This selectivity can be understood by the local conformation if we assume each molecule binding with a neighboring adatom and rest atom pair. There are two available adjacent rest atoms for each center adatom, while only one for each corner adatom. Therefore, we expect the higher reactivity for center adatoms. In addition, each corner adatom has two neighboring Si dimers, while a center adatom has one, possibly inducing a larger steric strain during the acetonitrile chemisorption on corner adatoms. Furthermore, the dangling bond on the adatom is almost empty, while that on the rest atoms is filled with electrons.\textsuperscript{44} Moreover, the corner adatoms are known to have slightly higher LDOS than the center adatoms. Such an LDOS can also contribute to the site selectivity of the highly polarized acetonitrile molecule.

In the case of adsorption of CH\(_3\)CN, the precursor state for adsorption is more stabilized in the faulted halves than in the unfaulted halves at room temperature. The STM image is considered to reflect the site-by-site adsorption probability of the precursor. Thus, it is clear that site selectivity, center/corner ratio, depends on the occupied adatoms in each half unit cell. The center/corner ratio is 4 for the adsorption on a pristine surface as shown in Figure 4, but it is monotonously lowered to 2 as the exposure (coverage) increases.

Figure 5 shows the bias dependence of the STM images for the 3L-CH\(_3\)CN-exposed Si(111), obtained in the same area. The darkened adatom sites observed in the filled-state image at the negative sample bias in Figure 2c can be classified into four types. One is the adatom A (red arrows) that appears like the nonreacted adatoms in the empty-state image at a sample bias of +1.7 V and then becomes darkened at the sample bias of +1.0 V and again as bright as the nonreacted adatoms in the filled-state image at a sample bias of −3.0 V. The second is the adatom B (cyan arrows) that appears somewhat like the adatom A in the empty-state image at a sample bias of +1.7 and +1.0 V and remains dark in the filled-state image even at the sample bias of −3.0 V. The third is the adatom C (blue arrows) that remains slightly dark at all sample biases but is accompanied with a bright spot between the adatom and its two nearest neighbor adatoms (not on the rest atom) especially at the sample bias of −3.0 V. The population of adatoms A, B, and C is about 25, 56, and 13% of total reacted adatoms in our STM images for the 3L-CH\(_3\)CN-exposed Si(111), respectively, determined from counting more than 10\(^4\) adatoms. On the other hand, the fourth type denoted as D is recognized in the STM images shown in Figure 5. Note that careful examination of the STM images suggests that a pair of the type-A and type-B adatom appears most frequently in a half unit cell, as indicated by A and B in Figure 5. One of the reacted adatoms is bright (type-A adatom) and the other is darker (type-B adatom) in the filled-state image at the sample bias of −3 V. The pair of type-B adatoms in a half unit cell is rarely observed, and the population is 10% relative to a pair of type-A and type-B adatoms. No pair of type-A adatoms was observed.

Figure 6 shows the STM images after annealing of the 5 L CH\(_3\)CN-dosed Si(111) prepared at ∼300 K. After annealing at 873 K,\textsuperscript{43} we measured the bias dependence of the STM images in the same area. In the filled-state image, many bright protrusions at adatoms which disappear in the empty-state image are clearly observed. These protrusions may correspond to the dissociated-species (possibly CH\(_2\)CN or further dissociated species) adsorbed adatoms produced in the
dissociation of CH$_3$CN. It should be noted that on Si(100), after annealing to 550 K, the decomposition of CH$_3$CN was observed by HREELS. Similar bright adatom spots expected for the dissociated species can be seen in our STM images for exposures at $\sim$300 K, as shown in the inset of Figure 6b, although the population is very small (see also ref 30).

The dissociation into H and CH$_2$CN can be very probable. If the adsorption geometry is limited only to the most stable AD-N-C-RA configuration (see Figure 7a and Table 1), the maximum reacted adatom in a half unit cell is expected to be three. However, the number of the half unit cells containing more than 4 reacted adatoms increases with exposures and reaches 10% of the reacted half unit cells at 5 L. The rate of 10% for the half unit cells with more than 4 reacted adatoms is larger than expected from the pre-existing defects. The result can be explained by the dissociation of CH$_3$CN, possibly into H and CH$_2$CN, as reported for the higher exposure of 40 L by Bournel et al.

Comparing the direct distance between two Si atoms of the clean surface and the typical bond length in a free CH$_3$CN suggests that CH$_3$CN is possibly di-$\sigma$ bonded to a pair of adatom and rest atom. We performed first-principles calculations to determine the stable configuration of CH$_3$CN on Si(111). Three types of adsorbed molecules are considered on Si(111). Considering the most probable di-$\sigma$ bonding of the cyano group to an adjacent adatom–rest atom pair, the first two configurations (AD-N-C-RA and RA-N-C-AD; see Figure 7a,b) can be possible. In the AD-N-C-RA configuration, the C and N atoms of CN are bonded to the rest atom and the adatom of the Si surface, respectively, while in the RA-N-C-AD configuration, the N and C atoms of CN are bonded to the rest atom and the adatom of the Si surface, respectively. The RA-N-C-AD configuration may be expected to be unfavorable.

![Figure 5](image_url)

**Figure 5.** Bias dependence of constant-current STM images for 3L-CH$_3$CN-exposed Si(111)-(7 × 7) at room temperature, which were obtained for the empty states (the sample biases of +1.7 and +1.0 V) and the filled states (the sample biases of −1.0 and −3.0 V) with a tunneling current of 0.25 nA. Type-A, -B, and -C adatoms (see text) are indicated by red, cyan, and blue arrows, respectively, while the type-D configuration is represented by a red triangle.

![Figure 6](image_url)

**Figure 6.** Bias dependence of constant-current STM images for the CH$_3$CN exposed Si(111)-(7 × 7), which were obtained at the sample bias of (a) +1.5 (empty state) and (b) −1.5 V (filled state) with a tunneling current of 0.25 nA at room temperature. The surface was obtained after the annealing at 600 °C of 5L-CH$_3$CN exposed Si(111)-(7 × 7) at room temperature. The spot “A” in (a) indicates the same half unit cell. The inset in (b) shows the constant current topograph images for the 3L-CH$_3$CN exposed Si(111)-(7 × 7) at room temperature, which were obtained at the sample bias of −1.7 V (filled state) with a tunneling current of 0.25 nA.

![Table 1](image_url)

**Table 1.** Adsorption Energies ($E_{\text{ads}}$), in Units of eV, for Four Types of Adsorbed CH$_3$CN Molecules on Si(111)-(7 × 7)

| configuration         | $E_{\text{ads}}$ [present work] | $E_{\text{ads}}$ (Tao et al.) |
|------------------------|----------------------------------|-------------------------------|
| AD-N-C-RA              | 2.18 1.59 0.59 1.06              |                               |
| RA-N-C-AD              | 1.59 1.27 0.32 1.19              |                               |
| AD-N                   | 0.58 0.42 0.16 0.79              |                               |
| H-dissociated AD-N-C-RA| 1.70 0.54 1.16                   |                               |

![Figure 7](image_url)

**Figure 7.** Schematic models (top and views) of CH$_3$CN adsorbed on Si(111)-(7 × 7): (a) AD-N-C-RA, (b) RA-N-C-AD, (c) AD-N, and (d) C–H dissociated AD-N-C-RA. Adatoms are represented by purple balls, while Si, N, C, and H atoms are represented by yellow, blue, grey, and white balls, respectively.
from the polarization of C≡N group and the higher electron density of the rest atom, although this configuration is expected to reduce greater steric repulsions from the methyl group. The AD-N configuration is that only N atom of CN is bonded to the adatom of the Si surface (Figure 7c). To determine the stability of these configurations, we calculate the adsorption energies of acetonitrile on Si(111)-(7 × 7), which are shown in Table 1. The adsorption energy (E_{ads}) is defined by

\[
E_{ads} = - \left[ E_{\text{acetonitrile}/\text{Si}(111)-(7\times7)} - E_{\text{Si}(111)-(7\times7)} \right]
\]

where \( E_{\text{acetonitrile}/\text{Si}(111)-(7\times7)} \) and \( E_{\text{acetonitrile}} \) are total energies of the acetonitrile on the Si(111)-(7 × 7) surface, the clean Si(111)-(7 × 7) surface, and the acetonitrile molecule, respectively. As shown in Table 1, the AD-N-C-RA structure is the most stable, while RA-N-C-AD and AD-N structures are higher in energy by about 0.59 and 1.60 eV than AD-N-C-RA, respectively. This result agrees with the conclusion from the X-ray absorption experiments.29 On the other hand, our most stable structure does not agree with one proposed theoretically by Tao et al.28 where the most stable structure was found to be RA-N-C-AD. The reason for the difference may be that the calculation using a cluster model does not accommodate the strains by adsorption.29 Another structure considered here (see Figure 7d) comes from the breakage of a C–H bond of CH₃CN, that is, the dissociation into H and CH₂CN; this structure is similar to the AD-N-C-RA configuration except for the dissociated H bonded to a neighboring adatom. Using the optimized geometries of the three configurations mentioned above, we simulate theoretical STM images for comparison with experimental ones. Simulated images are shown in Figure 8 for using the configurations on faulted half cells. Experimental STM images for the type-C adatoms in Figure 5 are very close to simulated STM images obtained from the AD-N-C-RA configuration on the faulted half. Note that for STM simulations, we use only the configurations on faulted half cells because both configurations on faulted and un faulted half cells give almost the same simulation results. The simulated empty and filled states are shown in Figure 8 for the most stable AD-N-C-RA configuration, which can explain experimental STM images for the type-C adatoms shown in Figure 5. Moreover, the RA-N-C-AD configuration gives similar simulated STM images (not shown here) for type-C adatoms. However, because the RA-N-C-AD structure is higher in energy by about 0.59 (or 0.32) eV than the AD-N-C-RA structure on the faulted (or un faulted) half, its possibilities are, if any, relatively low. As a result, we conclude that the bias dependence of the type-C configuration shown in Figure 5 can be explained by the simulated STM image of the most stable AD-N-C-RA structure.

However, type-A and type-B configurations showing the larger population compared to the type-C configuration cannot be explained by the remaining structures such as the RA-N-C-AD or AD-N structure. It is mainly because the adsorbed molecules attached to adatoms or rest atoms on the surface do not reproduce dark protrusions in Figure 5. It is well known that hydrogen passivation of dangling bonds usually gives dark protrusions in the STM images. Because the hydrogen dissociation may occur in the CH₃CN molecule, the H-dissociated AD-N-C-RA structure is considered, where the detachment of H from the AD-N-C-RA configuration occurs, and then, the dissociated hydrogen is attached to the nearest adatom. Calculations show that the H-dissociated AD-N-C-RA structure is quite stable; among several local minima depending on the location of dissociated H, the most stable dissociated structure is less stable by 0.48 eV/molecule than the most stable AD-N-C-RA configuration. Using this optimized structure for the C–H dissociated AD-N-C-RA configuration, we obtain the corresponding theoretical STM images shown in Figure 8b, which may explain the bias dependence of the type-D configuration in Figure 5.

For the type-A and/or type-B configurations, we first speculate that these configurations might be explained by the adsorption of hydrogen atoms at the adatom sites of the Si(111)-(7 × 7) surface because the H adsorption can partly explain dark protrusions found in type-A and/or type-B configurations. However, the experimental observation implies that there should not be many H atoms on the surface, so we exclude the possibility of the presence of abundant H atoms. Thus, we cannot provide proper model structures to explain the type-A and/or type-B configurations among the configurations considered in this paper. It is speculated that the type-A and/or type-B configurations may be related to the further dissociated atomic and molecular species, or complicated combinations of two CH₃CN molecules.

4. CONCLUSIONS

In summary, the covalent binding and structure of acetonitrile on Si(111)-(7 × 7) at a room temperature have been investigated using STM and first-principles calculations. Theoretical simulations reveal that the most stable configuration of CH₃CN on Si(111)-(7 × 7) is the AD-N-C-RA configuration.
configuration having a molecularly chemisorbed CH$_3$CN with the C and N atoms of CN bonded to the rest atom and adatom of the Si surface, respectively. Dissociative adsorption occurs partially at ~300 K. Comparison of experimental and theoretical STM images shows that some experimental STM images can be explained by theoretical model configurations. However, because we cannot assign proper model structures to all the experimentally observed features, the exact identification of these features remains as a future study.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01445.

Schematic representation of di-$\sigma$ bonds of CH$_3$CN on Si(111), top and side views of the unit cell of RA-N-C-AD structure, and coordinates of the RA-N-C-AD structure (PDF)

### AUTHOR INFORMATION

**Corresponding Authors**

Suklyun Hong — Department of Physics, Graphene Research Institute and GRI-TPC International Research Center, Sejong University, Seoul 05006, Korea; orcid.org/0000-0001-6504-9209; Email: hong@sejong.ac.kr

Michio Okada — Institute of Radiation Sciences and Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan; Email: okada@chem.sci.osaka-u.ac.jp

**Authors**

Kyung-Ah Min — Department of Physics, Graphene Research Institute and GRI-TPC International Research Center, Sejong University, Seoul 05006, Korea

Jinwoo Park — Department of Physics, Graphene Research Institute and GRI-TPC International Research Center, Sejong University, Seoul 05006, Korea

Hanchul Kim — Department of Physics, Sookmyung Women’s University, Seoul 04310, Korea

Hironori Mizutani — Institute of Radiation Sciences and Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.0c01445

### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This research was supported by the Global Research and Development Center Program (2018K1A4A3A01064272) through the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT, and the Priority Research Center Program (2010-0020207) through the NRF funded by the Ministry of Education, and computational data were transferred through a high-speed network provided by the Korea Research Environment Open NETwork (KREONET). We gratefully acknowledge MEXT for a Grant-in-Aid for Scientific Research (nos. JP15KT0062, JP17550011, JP20350005, JP22655005, JP25620013, and JP26248006). This work was also financially supported by The Sumitomo Foundation, The Murata Science Foundation, and Shin-etsu Chemical Co., Ltd., Japan.

### REFERENCES

1. Maboudian, R. Surface processes in MEMS technology. Surf. Sci. Rep. 1998, 30, 207–269.
2. Yates, J. T. A. New Opportunity in Silicon-Based Microelectronics. Science 1998, 279, 335–336.
3. Wolkow, R. A. Controlled Molecular Adsorption on Silicon: Laying a Foundation for Molecular Devices. Rev. Phys. Chem. 1999, 50, 413–441.
4. Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenleaf, C. M.; Russell, J. N. Cycloaddition Chemistry of Organic Molecules with Semiconductor Surfaces. Acc. Chem. Res. 2000, 33, 617–624.
5. Filler, M. A.; Bent, S. F. The surface as molecular reagent: organic chemistry at the semiconductor interface. Prog. Surf. Sci. 2003, 73, 1–56.
6. Teplyakov, A. V.; Kong, M. J.; Bent, S. F. Vibrational Spectroscopic Studies of Diels–Alder Reactions with the Si(100)-2×1 Surface as a Dienophile. J. Am. Chem. Soc. 1997, 119, 11100–11101.
7. Liu, H.; Hamers, R. J. Stereoselectivity in Molecule–Surface Reactions: Adsorption of Ethylene on the Silicon(001) Surface. J. Am. Chem. Soc. 1997, 119, 7593–7594.
8. Rochet, F.; Dufour, G.; Prieto, P.; Sirotti, F.; Stedile, F. C. Electronic structure of acetylene on Si(111)-7×7: X-ray photoelectron and x-ray absorption spectroscopy. Phys. Rev. B: Condens. Matter Mater. Phys. 1998, 57, 6738–6748.
9. Hamaguchi, K.; Machida, S.; Mukai, K.; Yamashita, Y.; Yoshinobu, J. Adsorption state of 1,4-cyclohexadiene on Si(100) (2×1). Phys. Rev. B: Condens. Matter Mater. Phys. 2000, 62, 7576–7580.
10. Pecher, J.; Mette, G.; Dürr, M.; Tonner, R. Site-Specific Reactivity of Ethylene at Distorted Dangling-Bond Configurations on Si(001). ChemPhysChem 2017, 18, 357–365.
11. Qiao, M. H.; Tao, F.; Cao, Y.; Li, Z. H.; Dai, W. L.; Deng, J. F.; Xu, G. Q. Cycloaddition reaction of furan with Si(100)-2×1 Surface. J. Chem. Phys. 2001, 114, 2766–2774.
12. Lee, H.-K.; Park, J.; Kim, K.-J.; Kim, H.-D.; Lee, I.-J.; Shin, H.-J.; Kim, B.; Yu, B. D.; Hong, S.; Chung, J. W. Enhanced Deselenizumation of Selenophene Molecules Adsorbed on Si(100)-2×1 Surface. J. Phys. Chem. C 2011, 115, 17856–17860.
13. Park, J.; Lee, H.-K.; Soon, A.; Yu, B. D.; Hong, S. Thermally Induced Desulfurization: Structural Transformation of Thiophene on the Si(100) Surface. J. Phys. Chem. C 2013, 117, 11731–11737.
14. Taguchi, Y.; Fujisawa, M.; Takaoka, T.; Okada, T.; Nishijima, M. Adsorbed state of benzene on the Si(100) surface: Thermal desorption and electron energy loss spectroscopy studies. J. Chem. Phys. 1991, 95, 6870–6876.
15. Schwartz, M. P.; Ellison, M. D.; Coulter, S. K.; Hovis, J. S.; Hamers, R. J. Interaction of π-Conjugated Organic Molecules with π-Bonded Semiconductor Surfaces: Structure, Selectivity, and Mechanistic Implications. J. Am. Chem. Soc. 2000, 122, 8529–8538.
16. Guo, S. Y.; Timm, M. J.; Huang, K.; Polanyi, J. C. Electron Attachment Leads to Unidirectional In-Plane Molecular Rotation of Para-Chlorostyrene on Si(100). J. Phys. Chem. C 2019, 123, 18425–18431.
17. Flammini, R.; Cecchetti, D.; Tagliatesta, P.; Carbone, M. Multiple options for phenol on Si(111)×7×7 revealed by high resolution photoemission. Surf. Sci. 2020, 692, 121510.
18. Hovis, J. S.; Hamers, R. J. Structure and Bonding of Ordered Organic Monolayers of 1,5-Cyclooctadiene on the Silicon(001) Surface. J. Phys. Chem. B 1997, 101, 9581–9585.
19. Ferraz, A. C.; Miott, R. A comparative study of the interaction of cyclopentene, cyclohexene, and 1,4-cyclohexadiene with the silicon (001) surface. Surf. Sci. 2004, 566–568, 713–718.
(20) Tao, F.; Wang, Z. H.; Qiao, M. H.; Liu, Q.; Sim, W. S.; Xu, G. Q. Covalent attachment of acetonitrile on Si(100) through Si–C and Si–N linkages. J. Chem. Phys. 2001, 115, 8563–8569.
(21) Bourrel, F.; Gallet, J.-J.; Kubsky, S.; Dufour, G.; Rochet, F.; Simeoni, M.; Stroff, F. Adsorption of acetonitrile and acrylonitrile on Si(001)-2×1 at room temperature studied by synchrotron radiation photoemission and NEXAFS spectroscopies. Surf. Sci. 2002, 513, 37–48.
(22) Mui, C.; Filler, M. A.; Bent, S. F.; Musgrave, C. B. Reactions of Nitriles at Semiconductor Surfaces. J. Chem. Phys. B 2003, 107, 12256–12267.
(23) Cho, J.-H.; Kleinman, L. Ab initio calculations of the adsorption and reaction of acetonitrile on Si(001). J. Chem. Phys. 2003, 119, 6744–6749.
(24) Miotto, R.; Oliveria, M. C.; Pinto, M. M.; de Leon-Perez, F.; Ferraz, A. C. Acetonitrile adsorption on Si(001). Phys. Rev. B: Condens. Matter Mater. Phys. 2004, 69, 235331.
(25) Waltenburg, H. N.; Yates, J. T. Surface Chemistry of Silicon. Chem. Rev. 1995, 95, 1589–1673.
(26) Takayanagi, K.; Tanishiro, Y.; Takahashi, M.; Takahashi, S. Structural analysis of Si(111)-7×7 by UHV-transmission electron diffraction and microscopy. J. Vac. Sci. Technol., A 1985, 3, 1502–1506.
(27) CRC Handbook of Chemistry and Physics, 68th ed; Chemical Rubber Company: Boca Raton, FL, 1987.
(28) Tao, F.; Chen, X. F.; Wang, Z. H.; Xu, G. Q. Binding and Structure of Acetonitrile on Si(111)-7×7. J. Phys. Chem. B 2002, 106, 3890–3895.
(29) Bourrel, F.; Carniato, S.; Dufour, D.; Gallet, J. J.; Ilakovac, V.; Rangen, S.; Rochet, F.; Stroff, F. Adsorption of acetonitrile (CH$_3$CN) on Si(111)-7×7 at room temperature studied by synchrotron radiation core-level spectroscopies and excited-state density functional theory calculations. Phys. Rev. B: Condens. Matter Mater. Phys. 2006, 73, 125345.
(30) Shirotta, N.; Yagi, S.; Taniguchi, M.; Hashimoto, E. Molecular adsorption of CH$_3$CN and C$_2$H$_5$N on Si(111)-7×7. J. Vac. Sci. Technol., A 2000, 18, 2578–2580.
(31) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169–11186.
(32) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15–50.
(33) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865–3868.
(34) Blöchl, P. E. Projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953–17979.
(35) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758–1775.
(36) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010, 132, 154104.
(37) Lu, X.; Wang, X.; Yuan, Q.; Zhang, Q. Diradical Mechanisms for the Cycloaddition Reactions of 1,3-Butadiene, Benzene, Thiophene, Ethylene, and Acetylene on a Si(111)-7×7 Surface. J. Am. Chem. Soc. 2003, 125, 7923–7929.
(38) Tersoff, J.; Hamann, D. R. Theory and Application for the Scanning Tunneling Microscope. Phys. Rev. Lett. 1983, 50, 1998–2001.
(39) Tersoff, J.; Hamann, D. R. Theory of the scanning tunneling microscope. Phys. Rev. B: Condens. Matter Mater. Phys. 1985, 31, 805–813.
(40) The VASP Visualization Tool, http://www.p4vasp.at.
(41) Lock, D.; Rusimova, K. R.; Pan, T. L.; Palmer, R. E.; Sloan, P. A. Atomically resolved real-space imaging of hot electron dynamics. Nat. Commun. 2015, 6, 8365.