

Bonding and Structure of 1,4-Cyclohexadiene Chemisorbed on Si(100)(2×1)[†]

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The adsorption state of 1,4-cyclohexadiene on a Si(100)(2×1) surface is studied with synchrotron radiation photoelectron spectroscopy (PES), high-resolution electron energy loss spectroscopy (HREELS), and scanning tunneling microscopy (STM). The existence of one π bond in the chemisorbed 1,4-cyclohexadiene is confirmed by valence band PES and HREELS measurements. The bonds between the 1,4-cyclohexadiene molecule and Si surface are characterized by the observation of a Si–C stretching mode in HREEL spectra and the interface component due to the Si–C bond in high-resolution Si 2p spectra. The remaining outermost π states in the adsorbed molecule are observed directly in the STM images. From HREELS and PES results, it is also clarified that the chemisorption state is basically invariable at any coverage.

I. Introduction

In recent years, a large number of studies have been reported on organic molecules adsorbed on semiconductor surfaces. They are attracting much attention not only for their fundamental scientific interest but also for their possibilities of applications in functional devices such as chemical and biological sensors, molecular electronics, and so on. Especially, the surfaces of Si are very important with respect to their large potential for application in various devices. The bulk truncated (100) surface of Si^{1,2} reconstructs, and the surface atoms bond to the neighbor atoms, forming surface dimers. These dimers compose dimer rows showing a (2×1) structure.

On this surface, cycloaddition reactions with unsaturated hydrocarbons have been reported. For instance, ethylene (C₂H₄) reacts one to one with a silicon dimer on the Si(100)(2×1) surface with the interaction between the C=C bond and the dangling bonds of the silicon dimer, forming di- σ Si–C bonds.^{3–6} Since Si is a very important material for electronic devices as well as scientific studies, many unsaturated hydrocarbons have been investigated in their adsorbed states upon Si(100)(2×1) surfaces other than ethylene, such as acetylene,^{7–10} 1,3-butadiene,^{11,12} benzene,^{13–18} cyclopentene,^{19–21} 1,5-cyclooctadiene,^{20,22} and 1,3-cyclohexadiene.^{20,23}

In this study, we have chosen 1,4-cyclohexadiene (C₆H₈) as an adsorbate molecule on the Si(100)(2×1) surface. In the previous studies^{24,25} by low-energy electron diffraction (LEED) and synchrotron radiation photoelectron spectroscopy (PES)

measurements, we have concluded that 1,4-cyclohexadiene chemisorbs on Si(100)(2×1) one to one with one of the two π bonds reacting with the Si dangling bond. The molecules are anisotropically aligned on the surface, and the molecular plane is inclined from the surface normal, where the remaining π bond is located at the vacuum side. The proposed adsorption model is depicted in Figure 1. This 1,4-cyclohexadiene–Si(100)(2×1) system involves various potentials. The subsequent chemical reactions with these remaining π bonds may provide us the possibilities of fabrications of functionalized organic films on the atomic scale²⁶ and also of elucidations of the novel properties, which originate from the strong anisotropy reflecting the (2×1) structure. In this study, we performed detailed studies on the interface bonding and structure of chemisorbed 1,4-cyclohexadiene on Si(100)(2×1) surfaces and the coverage dependence by means of PES and high-resolution electron energy loss spectroscopy (HREELS). In addition, the real space observation of chemisorbed 1,4-cyclohexadiene was performed by scanning tunneling microscopy (STM).

II. Experimental Section

All experiments were performed in an ultrahigh vacuum (UHV) chamber achieving a base pressure of $<1 \times 10^{-10}$ Torr.

Two kinds of boron-doped p-type Si(100) wafers (10 Ω cm) were used in the present experiments. One was a double-domain flat wafer, and the other was a vicinal wafer with an off-angle of 5° toward the [011] direction. By being outgassed at ~400 °C, flashed up to 1250 °C several times, and cooled slowly from ~900 °C to room temperature, a double-domain Si(100)(2×1) flat surface and a single-domain Si(100)(2×1) vicinal surface were prepared. In the latter case, the terrace contains eight silicon dimers in a dimer row and is separated by double-layer

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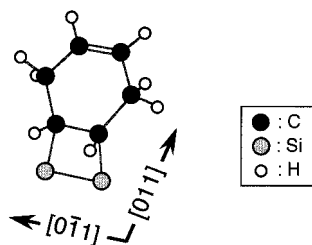


Figure 1. Adsorption model of 1,4-cyclohexadiene on Si(100)(2×1), where the 1,4-cyclohexadiene forms the di- σ bonding to the silicon dimer. The filled circle, gray circle, and small open circle show C, Si, and H atoms, respectively.

steps.^{27–29} After this treatment, no contaminations, such as carbon, oxygen, etc., were detected by Auger electron spectroscopy, and the LEED patterns showed sharp double-domain and single-domain (2×1) patterns.

Commercial 1,4-cyclohexadiene (purity 97%) was purified by several freeze–pump–thaw cycles. After this treatment, gaseous molecules were introduced into the UHV chamber through a pulse gas doser (for HREELS and PES measurements) or a variable leak valve (for STM measurements). The coverage of the chemisorbed layer was controlled by changing the number of shots of the pulse gas dosing. The multilayer was formed by the adsorption of an excess amount onto the silicon substrate cooled to 90 or 140 K.

Valence band PES measurements were performed at BL 5A of UVSOR in the Institute for Molecular Science. The incident photon energy was 50 eV. The electric field vector (**E**) of the incident photon was set parallel to the silicon surface in the same plane as the detected plane, and the photoelectrons were detected at a takeoff angle of 50°. The remaining π bond of the chemisorbed 1,4-cyclohexadiene molecule can be observed only when **E** of the s-polarized incident photon is set parallel to the Si dimer row direction.^{24,25} Therefore, **E** was set parallel to the Si dimer row direction. Single-domain vicinal Si(100)(2×1) surfaces were used as the substrates, and the samples were cooled to 140 K. The overall resolution of the PES system was ~ 0.1 eV.

High-resolution Si 2p PES measurements were made at PF BL-16B with an undulator radiation source in KEK under PF-PAC approval (no. 99-G178). The incident photon energy was 129 eV, and the photoelectrons were detected at 0°, 15°, 30°, 45°, and 60° off normal. The angle between the incident photon and the electron analyzer was fixed at 45°. The substrate was a double-domain flat Si wafer, and the experiments were carried out at 140 K. The overall instrumental resolution of this PES system was ~ 80 meV.

HREELS measurements were carried out at RIKEN. Double-domain flat Si wafers were used as the substrates, and the samples were cooled to 90 K during the measurements. The primary energy was 5 eV, and the energy resolution was 9 meV (the full width at half-maximum, FWHM, of the elastic peak). The spectra were taken at both in- and off-specular conditions, where the incidence angle was 60° and the emission angle (θ_e) was 60° and 55° from the surface normal, respectively.

STM measurements were carried out at JEOL. Double-domain Si(100)(2×1) flat surfaces were used as the substrates, and the samples were kept at room temperature (RT) during the measurements. Since it has been confirmed by PES and HREELS measurements that the chemisorption state does not change up to RT, the results of these STM measurements can be comparable to those of PES and HREELS measurements.

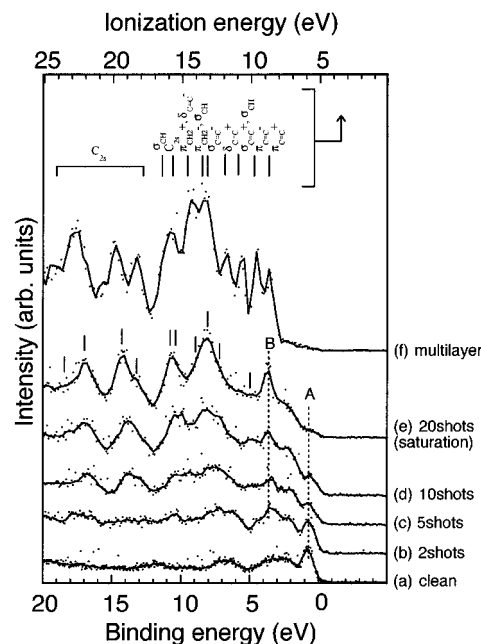


Figure 2. Synchrotron radiation valence PES spectra with a normal incident angle. The photon energy was 50 eV. The sample was kept at 140 K. (a) is the spectrum of the clean vicinal Si(100)(2×1) surface. (b)–(d) are the spectra of the chemisorbed layer of 1,4-cyclohexadiene on Si(100)(2×1) with exposures of 2, 5, 10, and 20 shots, respectively. (e) corresponds to the saturation coverage. The peak positions of adsorbate-derived states are indicated in Figure 2e. (f) is the spectrum of the multilayer of 1,4-cyclohexadiene. The peak assignments for the condensed molecules are based on the data from refs 30–32. The ionization energy for gaseous species is shown in the upper axis.

III. Results and Discussion

1. Valence Band PES. Figure 2 shows valence band PES spectra measured by the incident photon of 50 eV at a normal incident angle. Figure 2a is the spectrum of the clean vicinal Si(100)(2×1) surface. Parts b–e of Figure 2 are the spectra of the chemisorbed layers of 1,4-cyclohexadiene on Si(100)(2×1) with exposures of 2, 5, 10, and 20 shots. Twenty shots of exposure corresponds to the saturation coverage. Figure 2f is the spectrum of the multilayer of 1,4-cyclohexadiene.

Observed peaks for the multilayer can be assigned as compared with gaseous molecules. The peak positions and their assignments of gaseous species are indicated above Figure 2f.^{30–32} The peaks at binding energies (E_B) of 3.2 and 4.1 eV originate from two π states of 1,4-cyclohexadiene. These two peaks do not appear in the chemisorbed layer (Figure 2b–e). The distinct peak at 0.8 eV in Figure 2a, which is labeled as A, is attributed to the Si dangling bond state.^{33,34} The peak at 3.8 eV, which is labeled as B, is ascribed to the remaining π bond in chemisorbed 1,4-cyclohexadiene on Si(100)(2×1).^{24,25} In Figure 2b–e, corresponding to the chemisorption layer on Si(100)(2×1), the observed peaks between 5 and 10 eV are assigned to the C–C σ bonds and C–H bonds and there appear mainly C 2s derived peaks above $E_B = 10$ eV.²⁵

In Figure 2, peak A decreases and peak B increases in intensity with increasing coverage. This indicates that the dangling bonds of the Si surface and the π bonds of 1,4-cyclohexadiene molecules react, leaving one π bond unreacted. The intensity of peak A at saturation (Figure 2e) is $\sim 10\%$ of that on the clean surface (Figure 2a). This indicates that about 90% of the Si dangling bonds reacted with 1,4-cyclohexadiene molecules upon the saturated adsorption at 140 K. Comparing parts b–e with part f of Figure 2, some peaks of the multilayer

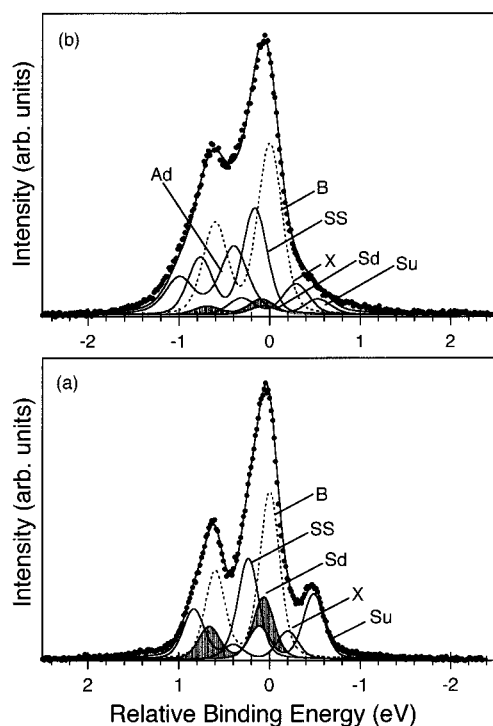


Figure 3. Si 2p spectra at a normal emission angle for (a) clean Si(100)c(4 \times 2) surface and (b) the same surface exposed to 1,4-cyclohexadiene at saturation at 140 K. Filled dots are experimental data, and the solid line between them is the fitted result. The assignment of each component is indicated in the figure (see the text). The relative binding energy is referred to the energy position of the B (bulk) component.

do not appear in the chemisorption layer. For example, the peaks at 4.5 and 5.5 eV which are related to C=C double bonds appear in Figure 2f but not in Figure 2b–e. Since chemisorbed 1,4-cyclohexadiene has only one π bond, some energy states do not split in the chemisorption layer.

Note that the relative intensities of adsorbate-derived peaks at 3.8, 5.0, 7.2, 8.1, 8.9, 10.4, 10.8, 13.2, 14.3, 17.0, and 18.4 eV in Figure 2b–e almost monotonically increase with increasing coverage. This indicates that the adsorbed state does not change at any coverage.

2. Si 2p PES. Parts a and b of Figure 3 show the Si 2p spectra recorded at a normal emission angle for the clean Si(100)(2 \times 1) surface and the same surface exposed to the saturation coverage of 1,4-cyclohexadiene at 140 K, respectively. The experimental data are plotted as filled circles, and the solid line between them represents the result of the fitting. The peak components in the line-shape analysis are shown as dotted lines, solid lines, and filled curves.

According to the previous studies^{35,36} and the present analysis, Si 2p PES spectra can be deconvoluted into five components (B, SS, S_u, S_d, and X). Here, we have used a Shirley background subtraction, and have imposed a spin–orbit split of 0.602 eV and a branching ratio from 0.49 to 0.53. The FWHM is 0.26 eV for the bulk component and slightly larger, 0.27 eV, for the surface components. In the previous study by Landmark et al.,³⁵ the assignments were made for these components as follows: component B originates from the bulk Si atoms; components S_u and S_d correspond to the up and down Si atoms of the asymmetric dimers, respectively; component SS is assigned to the Si atoms of the subsurface layer; component X is probably derived from the third-layer Si atoms or defects. In our results,³⁷ the core level shifts relative to the bulk component for the SS, S_u, S_d, and C components are 0.235, –0.485, 0.065, and –0.200

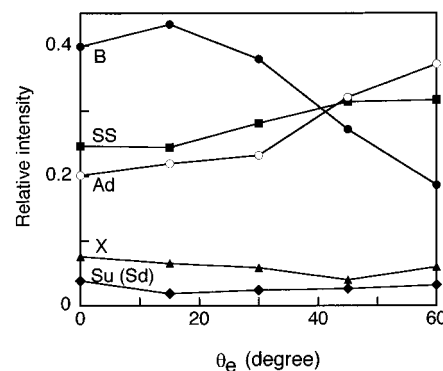


Figure 4. Fractional intensities of the B, SS, X, S_u (S_d), and A_d components as a function of the emission angles. The circle, square, triangle, diamond, and open circle represent the B, SS, X, S_u (S_d), and A_d components, respectively.

eV, respectively. These results are similar to those reported by Landmark et al. They concluded that the core level shifts were 0.230, –0.500, 0.062, and –0.225 eV, respectively.³⁵

At first glance, the relative intensities of S_u and S_d components are decreased after adsorption. This indicates that up and down dimer Si atoms react with 1,4-cyclohexadiene. Therefore, for the 1,4-cyclohexadiene chemisorbed Si surface, the Si 2p spectra were decomposed into six components; we have to introduce a new component (labeled A_d) as shown in Figure 3b. The peak deconvolution was performed for all the spectra taken at emission angles of 0°, 15°, 30°, 45°, and 60° off normal. The FWHM and peak position of each component were fixed in all the Si 2p spectra, and only the relative peak intensities were altered. To fit the convoluted results to all the measured spectra at different emission angles, the best set of values for the FWHM and peak positions were found. The relative peak positions to B of the SS, S_u, S_d, X, and A_d components are 0.165, –0.530, 0.090, –0.290, and 0.395 eV, respectively. Owing to the lifetime and/or inhomogeneous broadening by adsorption, the FWHM's become larger than those for the clean surface in Figure 3a. The FWHM's of B, SS, S_u, S_d, X, and A_d are 0.32, 0.32, 0.34, 0.34, 0.34, and 0.365 eV, respectively.

Figure 4 shows the fractional area intensities of the six components as a function of θ_e . The area intensity of the B component decreases with higher θ_e , while SS and A_d components have larger intensities at higher θ_e . This indicates that the B component originates from the bulk, and that SS comes from the subsurface Si atoms. Thus, the A_d component can be assigned to the top-layer Si atoms, that is, the interface Si atoms newly bonded to C atoms of 1,4-cyclohexadiene. The core level shift of 0.395 eV is mainly due to the different electronegativities of the Si atom (1.90) and C atom (2.55).^{37,38}

Next we will estimate the amount of reacted surface Si atoms at the saturation adsorption of 1,4-cyclohexadiene. Visual inspection of Figure 3b shows that some of the up and down Si dimer atoms remain unreacted. At all θ_e values, the relative intensity of the remaining S_u (S_d) to that of the B component is 0.10 ± 0.05 of that in the clean surface. This indicates that ~90% of the Si dimer atoms react with 1,4-cyclohexadiene at saturation. This is consistent with the valence band PES result as shown in Figure 2. The incomplete consumption of the Si dimers may be due to the steric hindrance between 1,4-cyclohexadiene molecules at adjacent adsorption sites.

3. HREELS. In Figure 5a–d, we show the HREEL spectra of the clean Si(100)c(4 \times 2) surface and the same surface exposed to 1,4-cyclohexadiene at 90 K as a function of exposure. The exposure of Figure 5b–d is 2, 4, and 5 shots, respectively. The

TABLE 1: Assignments of Observed HREELS Peaks of Chemisorbed 1,4-Cyclohexadiene and a Multilayer of 1,4-Cyclohexadiene, Together with the Infrared and Raman Spectra of Liquid Cyclohexene⁴⁰ and 1,4-Cyclohexadiene⁴²

mode	chemisorbed 1,4-cyclohexadiene on Si(100)	cyclohexene (liquid) ⁴⁰	1,4-cyclohexadiene multilayer	1,4-cyclohexadiene (liquid) ⁴²	organic molecules on Si(100)
=CH stretch	3008	3022, 2993	3032	3032, 3019	
—CH ₂ stretch		2960, 2940, 2929			
—CH ₂ stretch	2879	2898, 2882, 2860, 2840	2871	2877, 2875, 2825, 2822	
C=C stretch	1613	1653	1661	1680, 1639	
—CH ₂ scissors	1395	1456, 1447, 1438	1411	1430, 1426	
—CH ₂ wag	1169	1392, 1321, 1138, 917, 878	1307	1358	
—CH ₂ twist		1264		1100	
=CH in plane bend			1194, 1040	1197, 1193, 1159, 1035	
=CH out of plane bend	669	720	645	1000, 985, 706, 622	
—CH ₂ rock	944	1038	968	956	
C—C (ring) stretching				1405, 1377, 956	
Ring motions ^b	839, 524, 371	670, 640, 452	847, 524, 411	887, 854, 574, 530, 403, 250, 210	
hindered mode	202				690, 820 (acetylene) ⁷ 670 (ethylene) ³ 615 (benzene) ¹⁷ 467, 523 (benzene) ¹⁸ 775 (cyclopentene) ⁴¹
Si—C stretch	669				

^a The Si—C peak positions of acetylene,⁷ ethylene,³ benzene,^{17,18} and cyclopentene⁴¹ adsorbed on Si(100)(2×1) are also presented in the last column. The bracket means that the peak is derived from the mixture of the two modes to the left side of the bracket. ^b Ring motions include ring bending, puckering, deformation, and breathing modes.

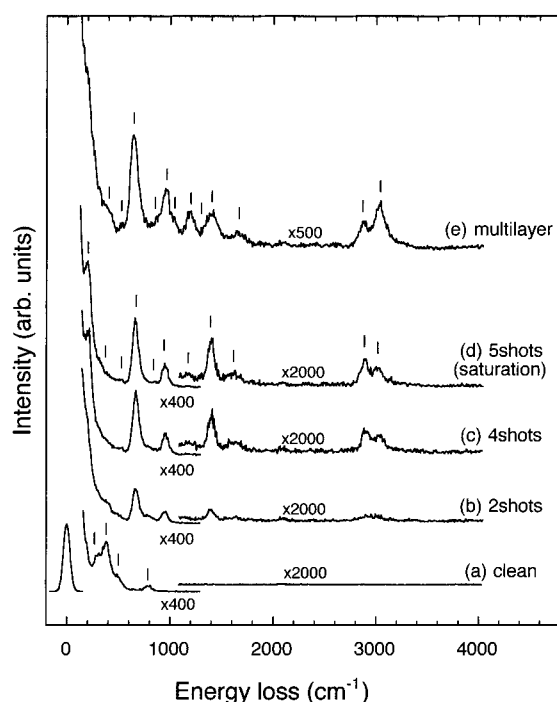


Figure 5. HREEL spectra measured at 90 K in the specular mode of (a) the clean Si(100)c(4×2) surface, (b)–(d) the surface exposed to 1,4-cyclohexadiene with increasing coverage, and (e) the multilayer of 1,4-cyclohexadiene. The primary electron energy, E_p , is 4 eV, and the intensity is normalized by the elastic peak intensity.

exposure of 5 shots corresponds to the saturation coverage in this case. The intensity is normalized by the elastic peak intensity.

For the clean surface, the loss peaks are observed at 272, 406, 500, and ~ 800 cm^{-1} . The peaks at 272, 406, and 500 cm^{-1} are related to the surface phonons; especially the 500 cm^{-1} loss peak is ascribed to the dimer stretching mode.³⁹ A small peak at ~ 800 cm^{-1} may be assigned to the Si—C stretching mode,³⁹ coming from C impurities. However, the amount of C impurities is quite small and is estimated to be $\ll 1 \times 10^{-3}$ monolayer from the normalized intensity of 3×10^{-5} .³⁹

For the 1,4-cyclohexadiene-exposed surfaces, no peaks appear at ~ 2020 cm^{-1} , where Si—H stretching modes should be observed if the molecule is dissociated. Thus, 1,4-cyclohexadiene adsorbs nondissociatively on Si(100)(2×1). In Figure 5b–d, loss peaks are observed at 202, 371, 524, 669, 839, 944, 1169, 1395, 1613, 2879, and 3008 cm^{-1} , which monotonically increase in intensity with increasing exposure. This indicates that the adsorption state does not change with the coverage. We can therefore conclude that 1,4-cyclohexadiene adsorbs nondissociatively on Si(100)(2×1) and the adsorption state is independent of the coverage.

Since the adsorption model shown in Figure 1 resembles the cyclohexene molecule in its structure where the six-membered C ring has one π bond, the vibrational modes of chemisorbed 1,4-cyclohexadiene can be assigned referring to the vibrational spectra of cyclohexene.⁴⁰ Comparing Figure 5b–e with the infrared and Raman spectra of cyclohexene⁴⁰ and EEL spectra measured for ethylene,³ acetylene,⁷ benzene,^{17,18} and cyclopentene⁴¹ chemisorbed on Si(100)(2×1) surfaces, the observed loss peaks can be assigned as shown in Table 1.

The Si—C-derived peak appears at 669 cm^{-1} , and C=C related peaks appear at 3008 and 1613 cm^{-1} . These peaks increase in intensity with increasing exposure. From these results, we can conclude that there exist Si—C σ bonds between the 1,4-cyclohexadiene molecule and Si(100)(2×1) surface and that the C=C double bond (π bond) remains in the chemisorbed 1,4-cyclohexadiene molecule. These are consistent with the previously reported PES results.^{24,25}

Figure 5e shows the HREEL spectra for a multilayer of 1,4-cyclohexadiene. The loss peaks are observed at 411, 524, 645, 847, 968, 1040, 1194, 1307, 1411, 1661, 2871, and 3032 cm^{-1} . The assignments can be made referring to the infrared and Raman spectra of 1,4-cyclohexadiene⁴² as shown in Table 1. The relative intensities of the peaks at 3032 and 2871 cm^{-1} in Figure 5e are the reverse of those in Figure 5b–d. The relative intensities of the peaks at 1194 and 1661 cm^{-1} are also larger than those in Figure 5b–d. This is because the condensed 1,4-cyclohexadiene molecule has two π bonds and two more =CH branches than the chemisorbed molecule.

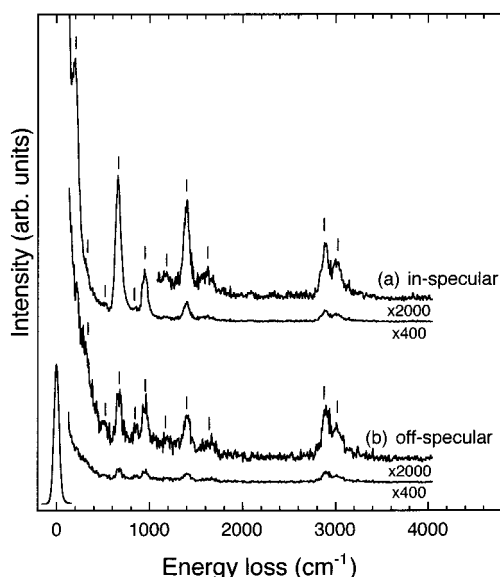


Figure 6. HREEL spectra of 1,4-cyclohexadiene chemisorbed on the Si(100)(2 \times 1) surface measured at 90 K with in-specular and off-specular modes. The coverage is saturation, and the intensity is normalized by the elastic peak intensity. (a) The incident and emitted angles of the electrons are both 60° off normal. (b) The incident and emitted angles of the electrons are 60° and 55° off normal, respectively.

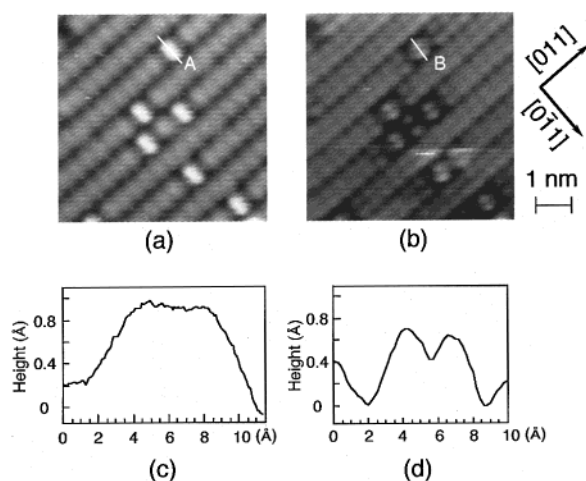


Figure 7. (a) and (b) are an occupied and an unoccupied state STM image of the 1,4-cyclohexadiene chemisorbed on the Si(100)(2 \times 1) surface, respectively. The scale is shown in the figure. (a) The sample bias is -1.5 V, and the tunnel current is 0.1 nA. (b) The sample bias is 1.3 V, and the tunnel current is 0.1 nA. The coverage is $\sim 3\%$ of the surface Si dimers. (c) and (d) are the cross sections across lines A and B, respectively.

Next we will discuss the adsorption structure more precisely, comparing the spectra measured at the in- and off-specular modes. In parts a and b of Figure 6, we show HREEL spectra measured at the in- and off-specular mode, respectively, for the chemisorbed 1,4-cyclohexadiene on Si(100)(2 \times 1). The most distinct feature in Figure 6 is that the loss peak at 669 cm^{-1} which comes from the Si–C stretching mode has larger intensity in the specular mode. Considering the dipole selection rules,⁴³ this Si–C stretching mode has a large dynamic dipole perpendicular to the Si surface.

4. STM. Figure 7a shows an occupied state STM image of 1,4-cyclohexadiene chemisorbed on the Si(100)(2 \times 1) surface. On the Si dimer rows, bright elliptic protrusions appear. Since the number of these protrusions increases as a function of the exposure and 1,4-cyclohexadiene is molecularly adsorbed on

Si(100)(2 \times 1), these bright elliptic protrusions can be assigned to the adsorbed 1,4-cyclohexadiene molecules. These adsorbate images are located at the center of the Si dimer row and almost symmetric to both the Si dimer and the dimer row direction.

In Figure 7b, we also show an unoccupied state image at the same area as in Figure 7a. The unoccupied state image of the Si(100)(2 \times 1) dimer splits into two protrusions. A little larger elliptic protrusions splitting into two, which lie on the Si dimer, are identified as an unoccupied state of adsorbed 1,4-cyclohexadiene.

Close inspection of Figure 7a,b shows that the occupied and unoccupied state images derived from the adsorbate also consist of two maxima. The cross section of the protrusion across line A in Figure 7a is trapezoidal as shown in Figure 7c. The protrusion may have two maxima, and the distance between them is $3.7 \pm 0.05\text{ Å}$. The cross section across line B of the unoccupied state image is shown in Figure 7d, where two peaks clearly exist, and the distance between them is $2.6 \pm 0.05\text{ Å}$.

Next we will discuss what orbitals are visualized in STM images. The highest occupied molecular orbital (HOMO) of chemisorbed 1,4-cyclohexadiene is the π bond state at 3.8 eV below E_F in PES measurements.^{24,25} The lowest unoccupied molecular orbital (LUMO) is the π^* state which is located just above E_F , and is located far from the σ^* state by more than 5 eV .⁴⁴ Note that the HOMO of the π state does not have a node and the LUMO of the π^* state has a node across the C=C bond. On the other hand, the remaining π bond is outermost in chemisorbed 1,4-cyclohexadiene, and STM measurements probe the local density of state. Since the π bond state is spatially close to the STM tip and is energetically located near E_F , the remaining π bond can be predominantly observed by STM. Therefore, adsorbate-derived images are attributed to the remaining π bond state of the chemisorbed 1,4-cyclohexadiene. The other states in chemisorbed 1,4-cyclohexadiene may not appear in this small sample bias condition, because they are σ and σ^* bond states which are located farther from E_F than π and π^* states.

In STM results of benzene and 1,3-cyclohexadiene adsorbed on Si(100)(2 \times 1) surfaces, the adsorbate images are also contributed mostly from π bond states.¹⁴ The present conclusion that the remaining π bond state appears in the STM images also confirms the existence of a π bond at the vacuum side in chemisorbed 1,4-cyclohexadiene.^{24,25}

The observation of these STM results also makes us aware of the fact that the adsorbate-derived images do not just lie upon the Si dimer but locate between the Si dimers. This is because the chemisorbed 1,4-cyclohexadiene molecule is tilted from the surface normal (Figure 1), and the π bond approximately locates above the middle of adjacent dimers.

Figure 8 shows an occupied state image of the 1,4-cyclohexadiene chemisorption layer of saturation coverage at 300 K. The sample bias is -2.30 V . The chemisorption layer conserves the row structure of the Si(100)(2 \times 1) substrate; the molecules are well arranged on Si(100)(2 \times 1). However, the estimated coverage is $\sim 60\%$ of the Si dimer sites, which is somewhat smaller than that at low temperature. This incomplete consumption of the Si dimers may be ascribed to the decrease of adsorption energy by the repulsive intermolecular interaction between neighboring molecules. Detailed analysis of STM images as a function of coverage will be discussed in a forthcoming paper.

IV. Summary

In this experiment, the interface bonding and the adsorbed state of 1,4-cyclohexadiene on Si(100)(2 \times 1) and its coverage

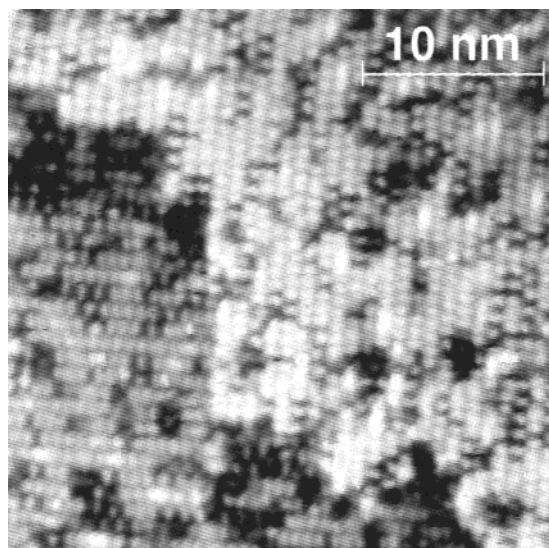


Figure 8. An occupied state STM image of 1,4-cyclohexadiene molecules chemisorbed on Si(100)(2×1) up to saturation at 300 K. The scale is shown in the figure. The sample bias is −2.3 V, and the tunnel current is 1.35 nA.

dependence were investigated in detail using valence band and Si 2p PES, HREELS, and STM measurements. It was clarified that 1,4-cyclohexadiene chemisorbs nondissociatively, and that the chemisorption state of 1,4-cyclohexadiene on the Si(100)-(2×1) surface is invariable at any coverage. We directly observed Si–C σ bonds between 1,4-cyclohexadiene molecules and Si dangling bonds by means of Si 2p PES and HREELS. The existence of the remaining π bond in the adsorbate molecule was evidenced by valence band PES, HREELS, and STM measurements. In particular, we observed the remaining π bond in STM images where the HOMO and LUMO of chemisorbed 1,4-cyclohexadiene may be predominantly visualized.

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