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Adsorption state of 1,4-cyclohexadiene 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 using low-energy electron diffraction (LEED) and photoelectron spectroscopy (PES). LEED shows a sharp 2×1 pattern at saturation after the adsorption of 1,4-cyclohexadiene indicating that the Si dimer structure is maintained. Judging from the PES results, almost all the dangling bonds react on adsorption of 1,4-cyclohexadiene, and one of the two π bonds in 1,4-cyclohexadiene reacts with the Si dimer. Thus, the molecule adsorbs on a Si(100)(2×1) dimer one to one with di-σ bonding, and the ideal saturation coverage is expected to be 0.5 monolayer. It is concluded that the molecules are anisotropically aligned and the molecular plane is inclined from the surface normal, with the remaining π bond located at the vacuum side.

I. INTRODUCTION

In recent years, various organic thin films have attracted a great deal of attention, especially for applications to functional devices such as chemical and biological sensors, molecular electronics, and so on. In order to improve performance and allow further for innovation of atomically controlled structures, the initial bonding on the surface (that is, the interface bond formation) should be perfect and stable, and the adsorbed molecules should be well ordered at the atomic scale.

Our goal is to fabricate hybrid structures using organic molecules on a Si(100)(2×1) surface by several successive reactions. In order to establish relatively stable interface bonding and coherent adsorbed structures on the substrate, we have adopted an elementary reaction between the C═C double bond and the dangling bonds on the Si dimer as the first step. For instance, ethylene (C_2H_4) reacts one to one with a silicon dimer on a Si(100) surface with the interaction occurring between the C═C bond and the dangling bonds of the silicon dimer, forming di-σ Si—C bonds.[1] These Si—C bonds are stable up to 550–600 K.[1,2] As for the di-σ bond formation reaction of small alkene and alkine molecules on Si(100)(2×1), there has been some discussion whether or not the Si—Si σ bond at the dimer is broken.[1,3–7] The latest calculations[8–12] and experimental[13] results support the di-σ model maintaining the Si dimer bond.[1]

Cyclic hydrocarbons on Si(100)(2×1) have also been recently studied. Several studies have been reported on benzene,[14–18] cyclopentene,[19–21] and 1,5-cyclooctadiene.[20,22] According to recent theoretical and experimental studies by angle-resolved photoelectron spectroscopy, benzene adsorbs onto the Si(100)(2×1) surface with a form of butterflylike structure, maintaining two π bonds.[14] The cyclopentene molecule reacts with the silicon dimer one to one and makes an ordered structure.[19–21] Hovis and co-workers have reported that cyclooctadiene also reacts one to one with the silicon dimer by breaking only one of the two C═C bonds, making a four-membered ring with the Si surface.[20,22]

In this study, we have chosen 1,4-cyclohexadiene (C_6H_8) as the adsorbate molecule. Based on past studies of the adsorption structures of cyclohydrocarbons, two adsorption models can be anticipated for 1,4-cyclohexadiene, as depicted in Fig. 1. (1) If both of the two π bonds react with the two silicon dimers, a pedestal structure is expected [Fig. 1(a)]. (2) If only one of the two π bonds reacts with the silicon dimer, the molecule stands on the substrate [Fig. 1(b)]. In the present experiments, the adsorption state of 1,4-cyclohexadiene was investigated by means of photoelectron spectroscopy (PES) and low-energy electron diffraction (LEED).

II. EXPERIMENT

All experiments were performed in an ultrahigh vacuum (UHV) chamber achieving a base pressure of less than 1×10^{-10} Torr. The system was equipped with the apparatus

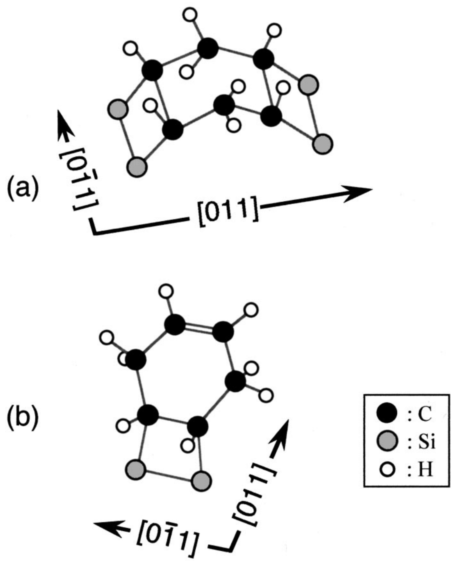

FIG. 1. The possible adsorption models for 1,4-cyclohexadiene on Si(100)(2×1). The filled circles, gray circles, and small open circles show C, Si, and H atoms, respectively. (a) The pedestal structure with the two π bonds reacting with two silicon dimers. (b) The upright structure where the 1,4-cyclohexadiene forms a di-σ bonding to the silicon dimer using one of its two π bonds.

for LEED, PES, Auger electron spectroscopy (AES), and pulse gas dosing.

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 outgassing at ~400 °C, flashing up to 1250 °C several times, and cooling slowly from ~900 °C down to room temperature, the double-domain Si(100)(2×1) flat surface and 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 the terraces are separated by double-layer steps.[23–25] After this treatment, no contaminants such as carbon, oxygen, etc., were detected by AES, and sharp double- and single-domain (2×1) LEED patterns were obtained.

Commercial 1,4-cyclohexadiene (purity 97%) and cyclohexene (purity 99%) were purified by several freeze-pump-thaw cycles. After this treatment, gaseous molecules were introduced into the UHV chamber through a pulse gas doser.

Synchrotron radiation ultraviolet photoelectron spectroscopy (UPS) measurements were performed at beam line 5A of UVSOR in the Institute for Molecular Science (Okazaki, Japan). The incident photon energy was 50 eV. The electric field vector (**E**) of the incident photon was in the same plane as the detected photoelectron, and the angle between the incident light and the electron analyzer (Omicron EA125) was fixed at 50°. The spectra were taken at two different incident angles of 0° and 50°. In one case, **E** was set parallel to the silicon surface, and the photoelectrons were detected at a take-off angle of 50°. In the other case, the incident angle was 50° and the photoelectrons were detected at a normal emission angle. In order to determine the adsorbate structure on the vicinal Si(100) surface, the spectra were obtained using two different directions of the *s* component of **E** ($\mathbf{E}_s$), i.e., $\mathbf{E}_s$ was set parallel or perpendicular to the silicon dimer rows on the Si(100)(2×1) surface. Photoelectron spectra were measured for a clean Si(100)(2×1) surface, a chemisorbed layer and a multilayer of 1,4-cyclohexadiene, and a multilayer of cyclohexene. The chemisorbed layer was prepared by adsorbing a saturation amount of 1,4-cyclohexadiene onto the silicon substrate at 300 K, and the multilayer was formed by the adsorption of an excess amount onto the silicon substrate at 90 K. The overall resolution of the PES system (ΔE) was ~0.1 eV.

UPS measurements using an unpolarized He I discharge lamp were performed for the valence-band region at the Institute for Solid State Physics, University of Tokyo, where the photoelectrons were detected at a normal emission angle ($\Delta E = 60$ meV).

III. RESULTS

A. LEED

The bulk-truncated Si(100) surface consists of silicon atoms having two dangling bonds, and reconstructs by a pairing mechanism, forming surface dimer rows.[26,27] Figure 2(a) is a LEED pattern of the clean double-domain Si(100)(2×1) surface. It displays a sharp (2×1) structure, reflecting the ordered structure of the silicon dimer rows on the surface. After adsorption of the saturation amount of 1,4-cyclohexadiene at room temperature, a clear (2×1) LEED pattern still remains [Fig. 2(b)]. This indicates that the (2×1) dimer structure is conserved upon adsorption. In addition, it argues against the pedestal adsorption model [Fig. 1(a)], because the formation of a local (2×2) structure would be expected in this model.

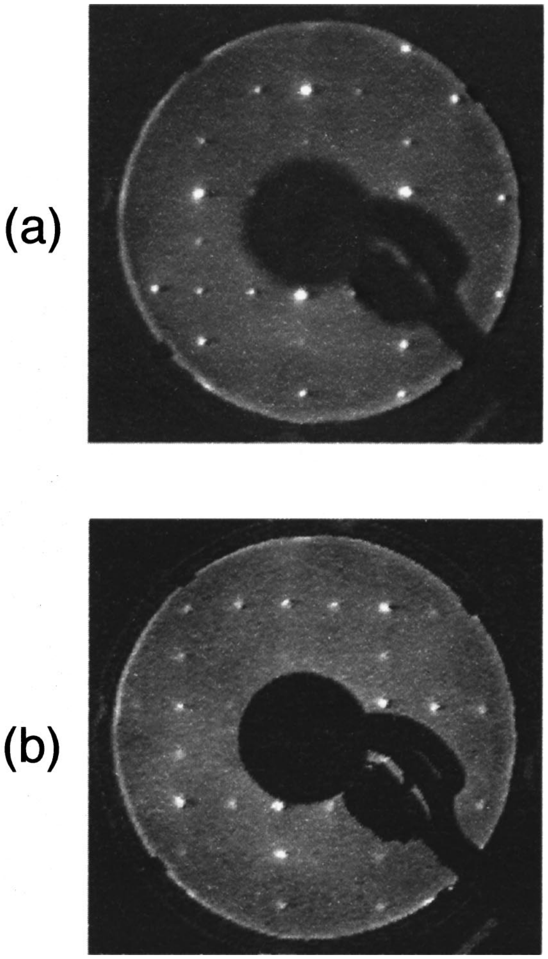

FIG. 2. The LEED patterns of (a) clean Si(100)(2×1), and (b) chemisorbed 1,4-cyclohexadiene on Si(100)(2×1) at saturation. The primary energy was 121 eV.

B. He I UPS

Figure 3 shows the valence-band UPS spectra measured with unpolarized He I light. The spectra (a) and (b) correspond to the clean Si(100) surface and chemisorbed 1,4-cyclohexadiene at saturation (θ_{sat}), respectively. A distinct peak at the binding energy (E_B) of 0.8 eV in Fig. 3(a), which is attributed to the silicon dangling-bond states,[28,29] disappears almost completely upon adsorption [Fig. 3(b)]. Thus, after the adsorption of 1,4-cyclohexadiene up to saturation, all the dangling bonds on Si(100)(2×1) have reacted. Together with the LEED observation, these results indicate that one 1,4-cyclohexadiene molecule bonds to one silicon dimer and the θ_{sat} of 1,4-cyclohexadiene is estimated to be 0.5 monolayer (ML) (defined as molecules per surface Si atom).

This adsorption model is similar to those for acetylene[3,9,10,13] and ethylene[1,8,11] on Si(100)(2×1), where a *di-σ* Si—C bond is formed between the molecule and the (2×1) dimer. Matsui *et al.*[13] have observed that the silicon

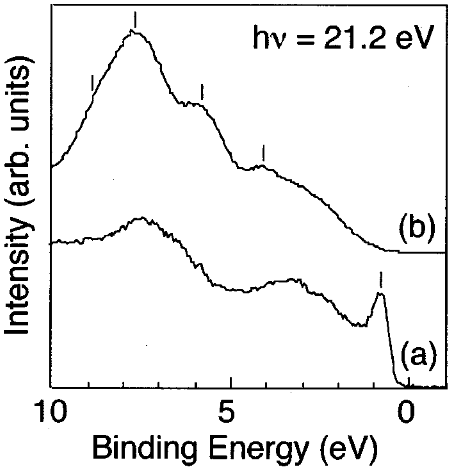

FIG. 3. He I ($h\nu = 21.2$ eV) UPS spectra at normal emission for (a) the clean Si(100)(2×1) surface, and (b) adsorbed 1,4-cyclohexadiene at saturation.

dangling-bond state also disappears completely after the saturated adsorption of acetylene and concluded that $\theta_{\mathrm{sat}} = 0.5$ ML. In contrast, in the case of benzene on Si(100)(2×1), it has been reported by Gokhale *et al.* that one-half of the silicon dangling bonds still remain even after saturation because of the butterflylike structure,[14] and thus θ_{sat} is estimated to be 0.25 ML.[14,15,17]

In Fig. 3(b) adsorbate-derived peaks are observed at 3.9, 5.5, 7.3, and 8.5 eV. These peaks are observed more clearly with synchrotron radiation UPS and will be discussed in the next section.

C. Synchrotron radiation UPS

Figure 4 shows the synchrotron radiation UPS spectra measured with incident photons of 50 eV at a normal incident angle. (a) is the spectrum of clean Si(100)(2×1) and (b) that of a multilayer of 1,4-cyclohexadiene. (c) and (d) are spectra of a saturated chemisorbed 1,4-cyclohexadiene layer on Si(100)(2×1) measured with **E** perpendicular and parallel to the silicon dimer rows, respectively. Figure 4(e) is the spectrum for a multilayer of cyclohexene on Si(100)(2×1). The cyclohexene molecular structure, with only one π bond, is shown in the inset in Fig. 4.

The observed peaks for condensed 1,4-cyclohexadiene [Fig. 4(b)] and cyclohexene [Fig. 4(e)] can be assigned by comparison with gaseous molecules; the peak positions and their assignments to gaseous species are indicated below each spectrum.[30–32] Note that the horizontal axes for gaseous species are somewhat shifted in order to adjust to the condensed species. The peaks in the inner valence region below ~12 eV mainly originate from the $C\,2s$ states.[33]

The distinct features in Fig. 4 are as follows. (i) The dangling-bond state at 0.8 eV in Fig. 4(a) disappears completely after saturation with chemisorbed 1,4-cyclohexadiene in Figs. 4(b) and 4(c) [see also Figs. 3(a) and 3(b)]. (ii) The peaks A at 3.2 eV and B at 4.1 eV in Fig. 4(b) originate from two π bonds in molecular 1,4-cyclohexadiene.[30–32] However, these peaks disappear after monolayer adsorption in Figs. 4(c) and 4(d). (iii) After saturation, a new peak C is observed at 3.8 eV in Fig. 4(d), but not in Fig. 4(c). It should be noted that the peak D (π bonding state) of condensed cyclohexene on Si(100)(2×1) in Fig. 4(e) is observed at 3.8 eV. (iv) The observed spectra between ~5 and 10 eV for chemisorbed 1,4-cyclohexadiene in Figs. 4(c) and 4(d) consist of several overlapping peaks, and the spectral shapes are somewhat different from those of condensed molecules [Figs. 4(b) and 4(e)].

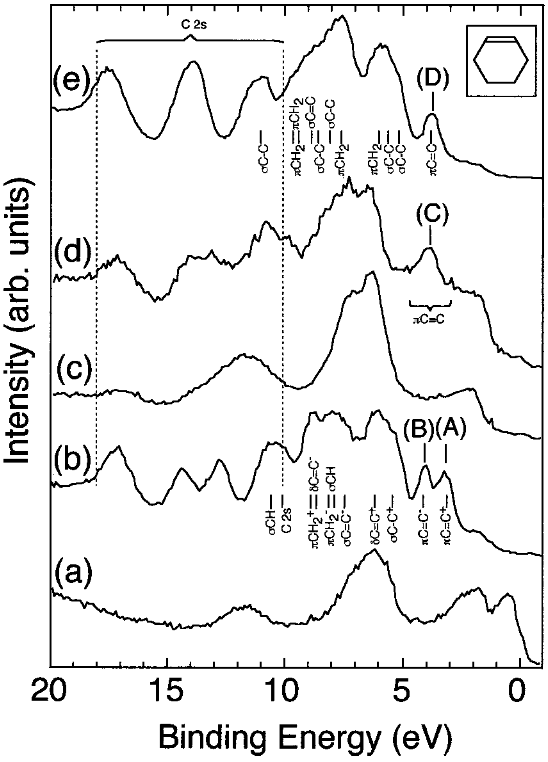

FIG. 4. Synchrotron radiation UPS spectra with a normal incident angle and an emission angle of 50° off normal (photon energy 50 eV). (a) The clean vicinal Si(100)(2×1) surface; (b) a multilayer of 1,4-cyclohexadiene; (c) and (d) a chemisorbed layer of 1,4-cyclohexadiene with **E** perpendicular and parallel to the silicon dimer rows, respectively; (e) a multilayer of cyclohexene. The inset above spectrum (e) is the molecular structure of cyclohexene. The peak assignments for condensed molecules are based on data from Ref. 32.

When covalent bonding between C atoms in the molecule and surface Si atoms occurs, the rehybridization of C atoms in the molecule takes place and thus significant changes of valence states are expected. Therefore, at the present stage, it may be difficult to assign every peak in the region between ~5 and 12 eV by a simple comparison with condensed molecules, as has sometimes been conducted for hydrocarbon molecules on transition metal surfaces. However, the detailed assignments will be made based on a first-principles calculation for this system.[34]

In the case of unsaturated hydrocarbon molecules chemisorbed on Si(100)(2×1), the observed peaks between 5 and 10 eV are assigned to C—C σ bonds and C—H bonds.[11–14] Above $E_B = 10$ eV, there appear mainly C $2s$–derived peaks.[12,14,33] On the other hand, π-bond peaks appear between E_F and 5 eV. For example, the π-bond peaks of benzene adsorbed on Si(100) appear at 2.3 and 4.0 eV,[14] and no other peaks such as C—C or C—H σ-bond peaks are observed in this region. In addition, no peaks have been ob-

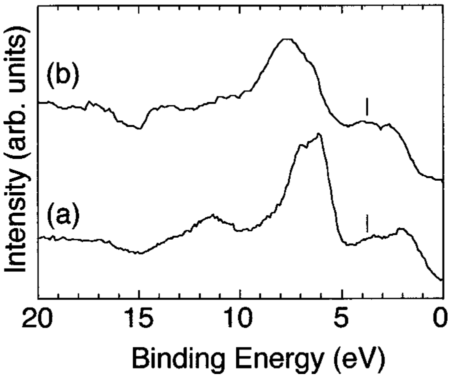

FIG. 5. Synchrotron radiation UPS spectra with an incident angle of 50° off normal and a normal emission angle (photon energy 50 eV). (a) and (b) are spectra of a chemisorbed layer of 1,4-cyclohexadiene with $\mathbf{E}_s$ perpendicular and parallel to the silicon dimer rows, respectively.

served between E_F and 5 eV in the case of cyclopentene or cyclohexene chemisorbed on Si(100)(2×1) where the π bond reacts to form di-σ bonds with the Si surface.[35] Therefore, the peak at 3.8 eV [Fig. 4(d)] is most probably assigned to a π-bond state of chemisorbed 1,4-cyclohexadiene on Si(100)(2×1), and we will discuss the adsorption models on the basis of this assignment.

Figure 5 shows the synchrotron radiation UPS spectra measured with incident photons of 50 eV with an incident angle of 50° and a normal emission angle. In this case, the incident photon has both s and p components of **E**: (a) and (b) are spectra of chemisorbed 1,4-cyclohexadiene on Si(100)(2×1) measured with $\mathbf{E}_s$ perpendicular and parallel to the silicon dimer rows, respectively. Some features of the silicon substrate are superposed on the spectra in Figs. 5(a) and 5(b).[29,36] Note that the peaks at 3.8 eV, which are assigned to the remaining π-bond state of adsorbed 1,4-cyclohexadiene on Si(100)(2×1), are observed in both geometries of $\mathbf{E}_s$, perpendicular and parallel to the silicon dimer rows [Figs. 5(a) and 5(b)].

IV. DISCUSSION

The disappearance of two peaks (A and B) in Fig. 4 and of the silicon dangling-bond state after saturated adsorption of 1,4-cyclohexadiene suggests a reaction between the π bonds of 1,4-cyclohexadiene and the silicon dangling bonds. The appearance of the peaks at 3.8 eV in Figs. 4(d), 5(a), and 5(b) indicates that one of the two π bonds of 1,4-cyclohexadiene still remains unreacted. Thus, the di-σ adsorption model [Fig. 1(b)] is supported rather than a pedestal model [Fig. 1(a)] judging from the present PES results as well as LEED observation.

Next, we will discuss the orientation of 1,4-cyclohexadiene adsorbed on Si(100)(2×1) at saturation. Since the photoelectrons were detected in the same plane as **E** in the present experimental geometry, the excitation of only even symmetric orbitals to the **E** plane is allowed.[37] In the synchrotron radiation UPS spectra measured at a normal incident angle in Fig. 4, only when **E** is set parallel to the silicon dimer rows is the π-bond state observed at 3.8 eV [Fig. 4(d)]. Thus, the C $2p$ orbitals that form the occupied π orbital by in-phase linear combination have an anisotropically aligned component parallel to the surface. This component parallel to the Si(100) surface has odd symmetry in the **E** plane perpendicular to the silicon dimer rows, and even symmetry in the **E** plane parallel to the rows. In this experiment, the π-orbital state was detected only when the **E** plane was parallel to the silicon dimer rows. Therefore, we can conclude that the adsorbed 1,4-cyclohexadiene molecules are almost perfectly aligned on the single-domain Si(100)(2×1) surface, where the unreacted C═C double bond is parallel to the Si dimer direction $[0\bar{1}\bar{1}]$.

We will next discuss the component perpendicular to the Si surface of C $2p$, i.e., C $2p_z$. The C $2p_z$ orbital has even symmetry in both **E** planes perpendicular and parallel to the silicon dimer rows. However, the interaction cross section between the C $2p_z$ orbital and $\mathbf{E}_s$ should be very small effectively. For this reason, the π state cannot be detected with **E** perpendicular to the silicon dimer rows, when **E** has only an s component. On the other hand, **E** has both s and p components when the incident angle is 50°. In this case, the C $2p_z$ can be detected with $\mathbf{E}_s$ both perpendicular and parallel to the dimer rows. In fact, the π-orbital state is observed at 3.8 eV in both geometries in Figs. 5(a) and 5(b).

Here we propose the adsorption model shown in Fig. 1(b). In this model, one of the two π bonds reacts with the Si dimer forming di-σ bond and the other remains unreacted. The remaining C═C bond is parallel to the Si dimer direction. The π orbital has two components parallel ([011] direction) and perpendicular (p_z) to the Si surface. These are consistent with the present experimental results (Figs. 4 and 5). Thus, the molecular plane is inclined from the surface normal. Further investigation is needed to determine whether the six-membered ring is flat or bent.

As shown in the proposed structural model [Fig. 1(b)], the unreacted π bonds of adsorbed 1,4-cyclohexadiene protrude over the uppermost molecular layer and they are ordered on Si(100)(2×1). Therefore, several interesting properties are expected. First of all, these unreacted π bonds can be used for fabricating further complex structures at the atomic scale, since the unreacted π orbitals can be involved in successive chemical reactions such as addition reactions.[38] Second, since the molecular layer on the single-domain Si(100)(2×1) surface has strong anisotropy reflecting the silicon dimer rows, it may show some features originating from one-dimensional electronic states; for instance, an anisotropic negative dispersion of the π state along [011] would be expected. In fact, in the case of ethylene on Si(100)(2×1), one-dimensional dispersion of electronic states was reported along the dimer row direction.[11] In addition, the anisotropic π-electron system on the surface may show nonlinear optical properties, including second-harmonic generation. Further experiments are needed to elucidate these properties. Therefore, this system will provide good opportunities not only for fundamental studies of surface chemistry and low-dimensional physics but also for the material science of functionalized surface devices and nonlinear optics.

V. SUMMARY

In this experiment, the adsorbed state of 1,4-cyclohexadiene on Si(100)(2×1) was investigated. One of the two π bonds of 1,4-cyclohexadiene reacts with one silicon dimer, forming di-σSi—C bonds. The molecules are ordered along the Si(100)(2×1) dimer rows. The molecular plane of adsorbed 1,4-cyclohexadiene is tilted from the surface normal, and the unreacted π bond sticks out into the vacuum side. Subsequent chemical reactions with this π bond may lead to the fabrication of functionalized organic films at the atomic scale; and unusual properties originating from the strong anisotropy of the (2×1) structure are expected.

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