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Adsorption and reaction of acetylene and ethylene on the Si(001)2×1 surface

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The electronic structures and the thermal reaction of chemisorbed C_2H_2 and C_2H_4 on the Si(001)2×1 surface have been investigated by carbon *K*-edge near-edge x-ray absorption fine structure (NEXAFS) and ultraviolet photoemission spectroscopy (UPS) using synchrotron radiation. The bonding and antibonding states due to the interaction of the molecules and the Si surface atoms are identified by detailed polarization-dependent UPS and NEXAFS measurements, respectively. These bonding and antibonding states are shown to originate from the hybridization between the occupied Si dangling bonds and the lowest unoccupied molecular orbitals ($\pi^*_{\text{C-C}}$) of C_2H_2 and C_2H_4 double-σ-bonded on the top of the Si dimer. The thermal evolution of mainly C_2H_2 is investigated in detail for a wide temperature range of $60-1500$ K from the condensation to the surface alloy formation. The coexistence of the *physisorbatelike* and the chemisorbed molecular species is observed at 70−90 K for C_2H_2 and C_2H_4, for the coverages greater than ~0.25 monolayer (ML). The $\pi^*_{\text{C-C}}$ resonance of those physisorbatelike C_2H_4 species in NEXAFS exhibits an unusual polarization dependence indicating adsorption with their molecular planes aligned perpendicular to the surface. The dissociation of C_2H_2 chemisorbates is shown to occur at 600−700 K as observed by UPS. After the dissociation of molecules, the atomic hydrogen adsorbates are identified by the monohydridelike surface resonance states in the UP spectra at 800−950 K. Most of the Si dangling bonds are passivated by, at least partly, the hydrogen adsorbates at this stage. At ~1000 K, the desorption of hydrogen occurs, which accompanies the appearance of a broad SiC-like feature in the UP spectra at ~3 eV below Fermi level.

I. INTRODUCTION

The adsorption and dissociation of hydrocarbon molecules on Si surfaces have drawn considerable interest in recent years.[1–4] Technologically such reactions are the crucial initial stages of the heteroepitaxy of SiC and diamond thin films on Si surfaces.[5–8] Also, the chemical modification of the surface by the adsorption of various hydrocarbon molecules can provide a noble way to the microscopic decoration of semiconductor surfaces.[9] The interaction between the Si(001) surface and the unsaturated hydrocarbon molecules of C_2H_2 and C_2H_4 has been the prototypical system in this line of research. However, in spite of the vigorous efforts, there are still many uncertain points especially when it comes to the atomic-scale details of the adsorption, dissociation, and reaction processes.

For example, the geometric structures of the C_2H_2 and C_2H_4 chemisorbates on the Si(001)2×1 surface have been under debate. Although these molecules are thought to chemisorb on the top of Si dimers, mainly two conflicting local configurations were proposed: one has the underlying Si dimers cleaved,[10,11] while the other has the Si dimers preserved.[12,13] Among the experimental investigations so far, no quantitative structural analysis is available. Although the various semiempirical calculations[14–20] have reached contradictory conclusions, the recent *ab initio* molecular dynamics calculations[21–23] supported the model with the Si dimers preserved. The recently obtained scanning tunneling microscopy (STM) images of C_2H_2 on Si(001)2×1 (Ref. 24) were consistently interpreted with the results of the *ab initio* calculations.[21] Our previous photoemission and C *K*-edge near-edge x-ray absorption fine-structure (NEXAFS) study, then, confirmed the retainment of the Si dimers for both C_2H_2 and C_2H_4 adsorption.[25]

In an electronic point of view, a C_2H_2 or C_2H_4 chemisorbate is known to form double σ bonds (called the di-σ bond) with a Si dimer.[12,13] This bonding involves the π molecular orbitals (MO's) and the Si dangling bond state.[25,26] However, the detailed nature of the di-σ chemical bonding is not established yet mostly due to lack of direct experimental information.[1–3,27–29]

Furthermore, very recently, Xu *et al.* have proposed a tetra-σ-bond model for the C_2H_2 adsorption based on the photoemission and the photoelectron diffraction studies.[30,31] In their model, C_2H_2 is rehybridized to sp^3 and is absorbed in between two neighboring Si dimers. Thus the information on the electronic structure is expected to give an essential criterion for determining the debating adsorption geometry of C_2H_2.

Another remaining issue concerns the saturation coverage and the adsorption kinetics. Several experimental studies suggested that C_2H_2 and C_2H_4 adsorb on the alternate Si dimers to result in a saturation coverage of about 0.25 monolayer (ML),[24,32,33] while others indicate the filling of all of the Si dimer sites (0.5 ML).[3] This is related to the issues of

(1) the direct or indirect adsorbate-adsorbate interaction, (2) the temperature and/or coverage dependence of the sticking probability of molecules, and (3) the existence of adsorption precursors.[17,34,35] Evidence of the direct adsorbate-adsorbate interaction by the MO overlapping of the neighboring adsorbates was found recently for the C_2H_4 adsorbate at low temperature[29] but no such information is available for C_2H_2. A more extensive experimental study for the low-temperature adsorption behavior could be helpful to resolve these issues.

At an elevated temperature, the thermal reaction process of C_2H_2 and C_2H_4 adsorbed on the Si(001) surface is important for the SiC formation. Indeed this topic has been extensively studied by means of thermal desorption spectroscopy (TDS),[11,34,35] high-resolution electron energy-loss spectroscopy (HREELS),[10,12,13] x-ray photoemission spectroscopy (XPS),[1,3,5,6,36] STM,[24] and reflection high-energy electron diffraction (RHEED).[1,37] A common scenario is as follows. The C_2H_2 and C_2H_4 chemisorbates at room temperature undergo dissociation at 550–750 K with partial desorption. The atomic hydrogen adsorbates and the carbon complexes exist on the surface above this dissociation temperature. Above 800–1000 K, the hydrogen adsorbates start to desorb and thin SiC-like films start to form. However, the detailed chemical and structural nature of the dissociation/reaction products is not clear before the formation of the stoichiometric SiC on the surface.

The combined use of NEXAFS and UPS is a direct and powerful method in extracting the information on the electronic structures of the adsorbates and the Si surface atoms for the states above and below the Fermi level, respectively. In the present study, we apply these methods to characterize the interaction between the Si(001) surface and the C_2H_2 and C_2H_4 molecules. The evolution of adsorbates from the condensation stage to finally the surface reaction to form SiC is systematically studied, emphasizing the characterization of the chemical and electronic nature of the adsorbates and the reaction products. Through the NEXAFS and UPS study, the detailed mechanism of the chemical bond formation at the chemisorption stage is made clear. At the low temperatures of 70–90 K, we found the extra *physisorbatelike* C_2H_2 and C_2H_4 molecules in addition to the chemisorbed molecular adsorbates of about 0.25 ML, which provides an important insight into the adsorption kinetics. At elevated temperatures, the hydrogen atoms originating from the dissociated C_2H_2 are characterized as forming the monohydride species. The desorption of atomic hydrogens is well correlated to the onset of the formation of the SiC-like surface layers/clusters.

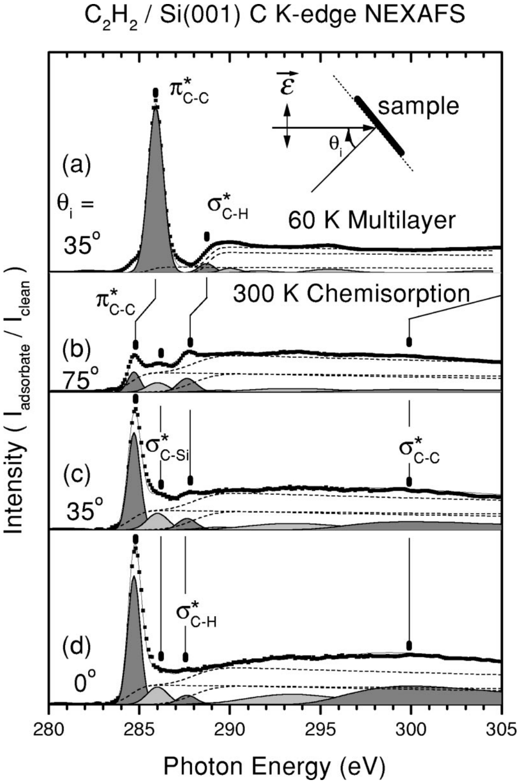

FIG. 1. C-*K* NEXAFS spectra of C_2H_2 adsorbed on the Si(001)2×1 surface. (a) The spectrum of the C_2H_2 multilayer at 60 K with incidence photon angle of 35° from the surface normal. (b)–(d) The NEXAFS spectra of chemisorbed C_2H_2 at 300 K taken with different θ_i. The setup for the measurements is shown in the inset. The results of curve fitting analyses are given together with the raw spectra (dots). See the text for the details of the curve fitting and peak assignments.

II. EXPERIMENTAL DETAILS

The NEXAFS and XPS experiments were carried out at the soft-x-ray beam line BL-7A (Ref. 38) and the UPS measurements at the vacuum ultraviolet beam line BL-7B (Ref. 39) of the Photon Factory, KEK, Japan. The ultrahigh vacuum chamber at BL-7A is equipped with a microchannel plate (MCP) detector for NEXAFS, a double-pass cylindrical-mirror analyzer for XPS, a LEED optics, and a sample manipulator with a cryostat. The sample can be resistively heated up to 1500 K and cooled down to 50 K by the liquid-helium flow. An angle-resolved photoelectron spectrometer (ADES 400, Vacuum Generators, U.K.) was used at beam line BL-7B.[40] The details of the Si(001)2×1 surface preparation were described before.[25] The Si(001)2×1 surface was exposed to C_2H_2 and C_2H_4 at various temperatures of 60–300 K by back-filling the chamber with high-purity gas at a pressure of 1×10^{-6} to 1×10^{-5} Pa. The typical dosage was, then, 1–10 Langmuir (L, $1=10^{-6}$ Torr s). As reported previously, C_2H_2 and C_2H_4 adsorb preferentially on alternating dimer sites.[24,32,33] Further adsorption to saturate all of the dimer sites (0.5 ML) is accomplished only by a significantly large exposure due to the greatly reduced sticking coefficient at high coverages.[3] Most of the data reported here for the room-temperature adsorption are obtained after the completion of the ‘‘rapid adsorption’’ with a quasisaturation coverage of ~0.25 ML. A capillary gas doser was used for much higher doses in preparing the condensed multilayers of C_2H_2 and C_2H_4 at the low temperature. The sample temperature was monitored by a thermocouple (<900 K) or by an optical pyrometer (>850 K).

The polarization-dependent C *K*-edge NEXAFS spectra were obtained by the partial-electron-yield mode with a MCP detector using a retarding voltage of 100 V. The geometry of the incident x ray and the sample is shown in the inset of Fig. 1. The x-ray incidence angle (θ_i) was varied from 0° (the electric field vector $\vec{\epsilon}$ in the surface plane) to 85° ($\vec{\epsilon}$ close to the surface normal) to investigate the polar-

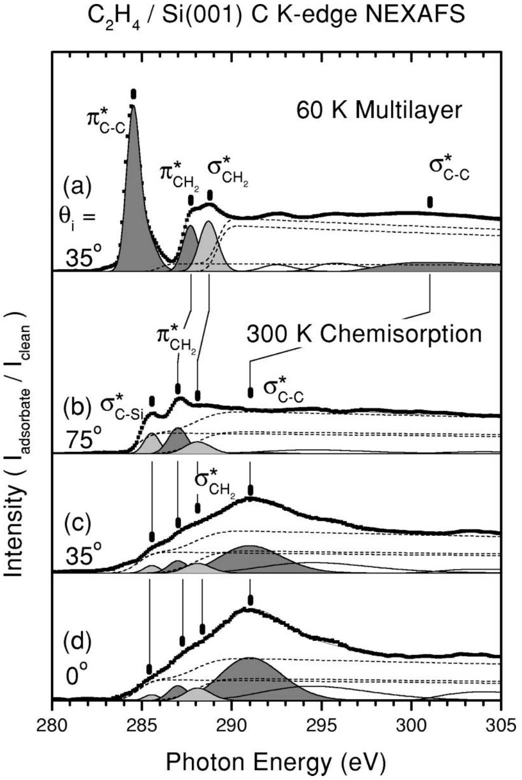

FIG. 2. Similar to Fig. 1 but for C_2H_4 on the Si(001)2×1 surface.

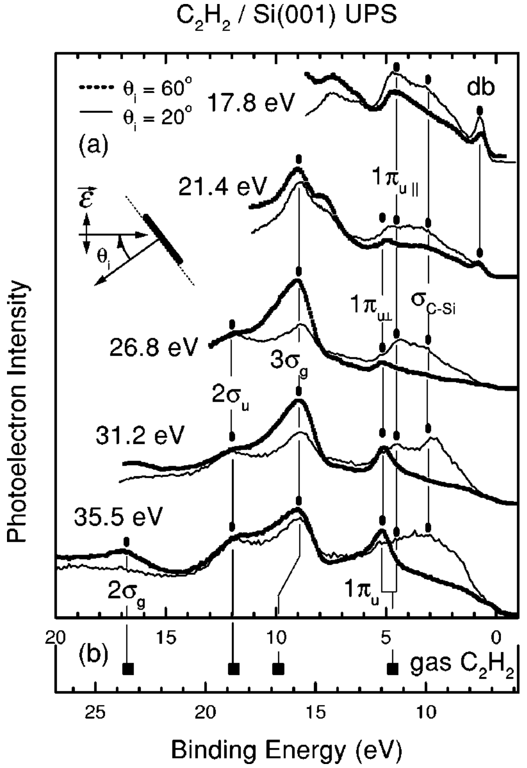

FIG. 3. (a) The polarization dependence of photoemission spectra of C_2H_2 chemisorbed on the Si(001)2×1 surface at 300 K with various incident photon energies of 17.8–35.5 eV. The solid lines and dots represent spectra taken with normal ($\theta_i = 60°$) and grazing ($\theta_i = 20°$) incidence photons. The setup for the measurements is shown in the inset. (b) The molecular orbitals of the gas-phase C_2H_2 used for reference purpose (Refs. 48 and 49).

ization dependence. The NEXAFS spectra were normalized by the absorption-edge jump after being divided by the clean Si(001) surface spectrum taken at the same measurement conditions.[41]

The geometry for the UPS measurements is shown in the inset of Fig. 3. The photon incidence angle, θ_i, was set to 20°, 45°, or 60°. The analyzer was fixed along the surface normal. The incident photon energy used was between 17.8 eV and 39.8 eV.

III. RESULTS AND DISCUSSION

A. NEXAFS study of the room-temperature chemisorption: The unoccupied MO's and the adsorption geometry

NEXAFS is a powerful experimental probe, especially for the unoccupied MO's of a *molecular* adsorbate. The details of the interaction between the molecules and the substrate can be investigated by comparing the NEXAFS spectra of the adsorption phase and those of the condensed phase.[42] Figures 1(a) and 2(a) show the C *K*-edge NEXAFS spectra of the C_2H_2 and C_2H_4 multilayers condensed on the Si(001)2×1 surface at 60 K, respectively. These are to be compared with the spectra of the chemisorption phases at room temperature, shown in Figs. 1(b)–1(d) and 2(b)–2(d). For quantitative comparison, the spectra taken at the magic angle geometry ($\theta_i = 35°$) are used to cancel out the apparent polarization dependence of the well-oriented chemisorbates.

For the fully quantitative discussion of the chemisorption-induced changes on MO's, the careful curve fittings were performed for the NEXAFS spectra. The optimized parameters are listed in Table I. The NEXAFS resonance peaks below the ionization threshold (located at ~289 eV) were fitted with the symmetric Gaussian curves, and the remaining peaks were fitted with the asymmetric Gaussian curves.[41] The $\pi^*_{C\text{-}C}$ resonance peak of the C_2H_4 multilayer is shown to be asymmetric due to vibrational excitations: mainly C-C and CH_2 stretching modes.[43] It was fitted with two symmet-

TABLE I. The summary of curve fitting for the C *K*-edge NEXAFS spectra of C_2H_2 and C_2H_4 adsorbates on Si(001)2×1. Multilayers are condensed at 60 K. Chemisorbed surfaces are prepared by dosing gas at 300 K.

	C_2H_2		C_2H_4	
	multilayer (eV)	chemisorbate (eV)	multilayer (eV)	chemisorbate (eV)
Fermi level	286.1	284.5	286.0	284.8
Vacuum level	289.3	288.0	289.2	288.0
$\pi^*_{C\text{-}C}$	286.4	284.7	284.5	
$\sigma^*_{C\text{-}Si}$		286.0		285.6
$\sigma^*_{C\text{-}H}$	289.2	287.6		
$\pi^*_{CH_2}$			287.7	287.0
$\sigma^*_{CH_2}$			288.7	288.1
Shake up	290.5	289.4	292.5	294.5
	292.1	293.4	296	304
	296		300	
	305			
$\sigma^*_{C\text{-}C}$	310	300	301	291.0

ric Gaussians. In contrast, the $\pi^*_{\text{C-C}}$ resonance of C_2H_2 appears symmetric because of the coupling of the C-C and C-H stretching modes as also observed in the spectra shown in Fig. 1.[43] In addition to the resonance peaks, the *continuum steps* were fitted with the error functions, whose centers correspond to the ionization thresholds located at the vacuum level. However, there are some remaining intensities below the vacuum level in every spectrum in addition to the resonance peaks. Those additional structureless features can be attributed to the excitations to the adsorption-induced states between the Fermi level ($\sim$284.5 eV) and the vacuum level.[42,44] These background features were also fitted with the error functions.

The assignment of the spectral features of the multilayer NEXAFS spectra are straightforward from the *K*-shell absorption spectra of the gas-phase molecules[45,46] and of the multilayers condensed on metal surfaces.[43] The sharp peaks at 285.9 eV in the spectrum for the C_2H_2 multilayer and at 284.5 eV for the C_2H_4 multilayer are due to the transitions from C 1*s* into the aforementioned $\pi^*_{\text{C-C}}$ antibonding orbitals. The transition to $\sigma^*_{\text{C-C}}$ (called the shape resonance) appears at 310 eV (not shown here[25]) and 301 eV for the multilayer C_2H_2 and C_2H_4, respectively. Peaks at 288.7 eV for C_2H_2 and 287.7 and 288.7 eV for C_2H_4 are identified as the transitions into $\sigma^*_{\text{C-H}}$, $\pi^*_{\text{CH}_2}$, and $\sigma^*_{\text{CH}_2}$, respectively.[43]

For the C_2H_2 chemisorption phase at the saturation of the rapid adsorption (Fig. 1), the $\pi^*_{\text{C-C}}$ peak is observed at 284.7 eV shifted by -1.2 eV compared to the multilayer spectrum. This shift is associated with the C 1*s* chemical shift by the formation of the molecule-Si bonds. This indicates a charge transfer from the Si dimer atoms into the carbon atoms of C_2H_2 adsorbates. Indeed a consistent chemical shift was observed in the C 1*s* photoemission spectra for the condensed and chemisorbed adsorbates (data not shown). The peak at 287.6 eV for the C_2H_2 chemisorbates is assigned as due to the $\sigma^*_{\text{C-H}}$ resonance showing the same amount of the chemical shift as the $\pi^*_{\text{C-C}}$ peak. However, the peak at 286.0 eV, halfway between the $\pi^*_{\text{C-C}}$ and $\sigma^*_{\text{C-H}}$ peaks, cannot be explained from the multilayer spectrum. No such feature was observed for C_2H_2 chemisorbed on metal surfaces.[47,48] We thus assign this feature to *the transition into a state newly formed by the chemical bonding with Si dimers*, that is, the antibonding $\sigma^*_{\text{C-Si}}$ state.[25] In Fig. 2 and Table I, the similar assignments for the C_2H_4 chemisorbates are given. In this case, the $\pi^*_{\text{C-C}}$ peak is not observed but the $\sigma^*_{\text{C-Si}}$, $\pi^*_{\text{CH}_2}$, and $\sigma^*_{\text{CH}_2}$ resonances appear at 285.6, 287.0, and 288.1 eV, respectively. The $\pi^*_{\text{CH}_2}$ and $\sigma^*_{\text{CH}_2}$ states show a chemical shift of 0.7 eV, which is much smaller than that of C_2H_2. This is because each carbon atom in C_2H_4 is already bonded to two hydrogen atoms, which gives rise to less charge transfer from the Si dimer atoms. The line shape of the C_2H_2 and C_2H_4 chemisorption phase showed no essential change for the coverage up to $\sim$0.5 ML at room temperature.

As is obvious in Figs. 1 and 2, a conspicuous decrease of the $\pi^*_{\text{C-C}}$ resonance peak intensity is observed for the chemisorption-phase spectra. The intensity ratios of the $\pi^*_{\text{C-C}}$ resonance peaks to the edge jump (in the magic angle spectra) are 6.5 (C_2H_2) and 3.2 (C_2H_4) for the multilayer and 3.0 (C_2H_2) and 0.0 (C_2H_4) for the chemisorption phases. This clearly indicates the consumption of one $\pi^*_{\text{C-C}}$ state in forming the chemisorption and the rehybridization of MO's into sp^2 (C_2H_2) and sp^3 (C_2H_4) hybrids. Note that the $\pi^*_{\text{C-C}}$ state of C_2H_2 consists of two degenerate orbitals, which should be perpendicular ($\pi^*_{\text{C-C}_\perp}$) and parallel ($\pi^*_{\text{C-C}_\parallel}$) to the surface, respectively, for the adsorbed molecules lying parallel to the surface. The remaining $\pi^*_{\text{C-C}}$ resonance peak of the chemisorbed C_2H_2 chemisorbates has a larger intensity in the normal incidence spectra, indicating that the $\pi^*_{\text{C-C}_\perp}$ state of C_2H_2 is vanished while the $\pi^*_{\text{C-C}_\parallel}$ state is intact. Appearances of the $\sigma^*_{\text{C-Si}}$ resonance features in the chemisorbed phase imply the bond formation between the $\pi^*_{\text{C-C}_\perp}$ states and the Si dangling bond states.

Very recently, Xu *et al.* have proposed the tetra-σ-bond model of C_2H_2 adsorbed between the Si dimer with the sp^3 rehybridization based on their photoelectron holography study.[30,31] Since, the above NEXAFS data for C_2H_2 chemisorbed on Si(001) clearly show the remaining $\pi^*_{\text{C-C}_\parallel}$ states and at the same time the formation of C_2H_2-Si bonds through the interaction of $\pi^*_{\text{C-C}_\perp}$ and the dangling bond states, the di-σ-bond model with C_2H_2 adsorbed on the top of the dimer is strongly favored over the tetra-σ-bond model. At this moment, we can only comment that their tetra-σ-bond model is irreconcilable with the present electronic information and also with the recent STM studies.[24] The adsorption geometry of C_2H_2 has to be reconfirmed by an alternative structural probe.

As discussed in our previous paper,[25] the $\sigma^*_{\text{C-C}}$ shape resonances of both C_2H_2 and C_2H_4 chemisorbates shift to significantly lower energies: from 310 to 300 eV and from 301 to 291 eV, respectively. This has been interpreted as due to the well-known sensitivity of the $\sigma^*_{\text{C-C}}$ shape resonances to the change of the C-C bond length, which has been also reported for the adsorption on the transition metal surfaces.[42,49,50] Furthermore, quantitatively, using the well-established empirical relationship between the $\sigma^*_{\text{C-C}}$ shape resonances and the bond length, we previously estimated the C-C bond of C_2H_2 as 1.36 Å and C_2H_4 as 1.52 Å. This indicates the significant expansion of the C-C bonds and the rehybridization of the C_2H_2 (C_2H_4) molecular orbitals to the sp^2 (sp^3) hybrid. The clear polarization dependence of the $\sigma^*_{\text{C-C}}$ peaks, as shown in Figs. 1 and 2, indicates that the C-C bond are lying parallel to the surface. However, one can doubt the qualitative accuracy of the C-C bond length estimation by the $\sigma^*_{\text{C-C}}$ resonances, since the mechanism of the shape resonance and its relation to the bond length are still under discussion.[51,52] In any case, within the present work, the shifts of $\sigma^*_{\text{C-C}}$ to lower energies are in consistent with the decrease of $\pi^*_{\text{C-C}}$ and the UPS study discussed in the following section.

B. UPS study of room-temperature chemisorption: The occupied MO's

To obtain a more comprehensive understanding of the mechanism of the C_2H_2- (C_2H_4-) Si bond formation, it is essential to investigate the occupied electronic states. The polarization-dependent valence-band photoemission spectra

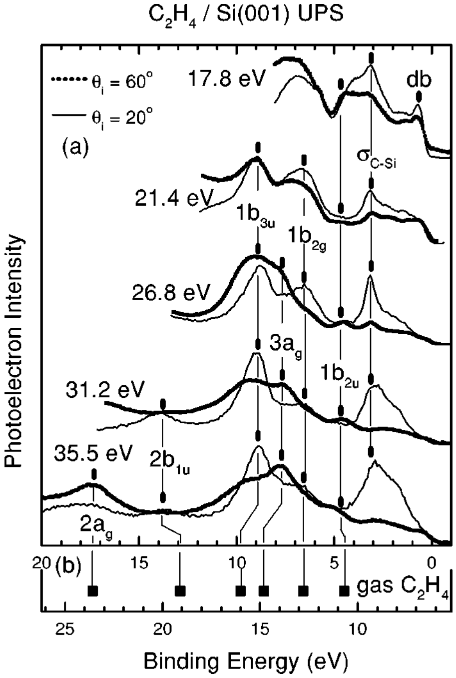

FIG. 4. Similar to Fig. 3 but for C_2H_4 on the Si(001)2×1 surface.

of C_2H_2 and C_2H_4 adsorbed on the Si(001)2×1 surface at 300 K are shown in Figs. 3(a) and 4(a), respectively, taken at the photon energies of 17.8–35.5 eV. Since the Si surface states and the adsorbate MO's are localized at the surface, their binding energies should exhibit no photon energy dependence. Such surface features can be picked out easily from the extensive series of the energy-dependent spectra shown partly in Figs. 3(a) and 4(a). At first, in comparison to the clean Si(001)2×1 surface spectra, the highest occupied states (lowest binding energies) just below the Fermi level is identified as the well-known dangling bond state of the bare Si dimers. The Si dangling-bond state (denoted as dB) is observed more clearly at a lower photon energy. As discussed previously,[25] the dB peak intensity is greatly reduced by the chemisorption of C_2H_2 and C_2H_4 molecules. Such peak-intensity reduction indicates the consumption of dangling bonds by the chemical bonding with the adsorbates. This observation of the depleted dangling bonds directly shows that the Si dimers beneath the adsorbates are preserved after chemisorption because, otherwise, the dimer-bond cleaving would create new dangling bonds.[25]

In addition to dB's, six (seven) nondispersing features are observed at the binding energies of 3.1, 4.6, 5.3, 9.0, 11.9, and 16.8 eV (3.1, 4.7, 6.6, 7.8, 8.9, 13.9, and 17.4 eV) for the surface with the C_2H_2 (C_2H_4) adsorbates. These states are confirmed not to be related to any bulk or surface features of the Si(001) substrate and thus are thought to come from the adsorbate MO's or the adsorbate-Si hybridization states. To assign the origin of these states, especially for the MO's, we compare the spectra with the standard UPS spectra obtained for the gas-phase molecules.[53,54] For a detailed assignment of the MO's, the symmetry selection rule is a very useful guide.[55] That is, as illustrated in the inset of Fig. 3(a), the incident light, its electric field vector, and the detector are all in the same plane and thus the transitions from an odd-symmetry initial state (with respect to the surface normal) are allowed at a normal incidence (s polarization), while those from an even-symmetry initial state are allowed at a grazing incidence (p polarization). The symmetry consideration of the adsorbate MO's is generally not trivial due to the symmetry reduction in the adsorption geometry. However, in the present case, we have already shown that the C-C bonds of C_2H_2 and C_2H_4 are parallel to the Si dimers through the NEXAFS measurements. Thus, the $D_{\infty h}$ and D_{2h} group symmetries of the free C_2H_2 and C_2H_4 molecules, respectively, is reduced to C_{2v} with the symmetry axis normal to the surface. Therefore, the MO's belonging to the A_1 representation,[56] which have an even symmetry (i.e., $2\sigma_g$, $3\sigma_g$, and $1\pi_{u\perp}$ of C_2H_2 and $2a_g$, $3a_g$, and $1b_{2u}$ of C_2H_4), should appear more strongly in the spectra at the grazing incidence, while others with an odd symmetry are probed with enhanced intensities in the spectra at the normal incidence.

From the above symmetry consideration and the comparison to the gas-phase standards [given at the bottom of Figs. 3(b) and 4(b)],[53,54] the peaks at the binding energies of 4.6, 5.3, 9.0, 11.9, and 16.8 eV in the chemisorbed C_2H_2 spectra are assigned to the $1\pi_{u\parallel}$, $1\pi_{u\perp}$, $3\sigma_g$, $2\sigma_u$, and $2\sigma_g$ MO's, respectively. Similarly, the peaks observed at 4.7, 6.6, 7.8, 8.9, 13.9, and 17.4 eV in the chemisorbed C_2H_4 spectra are assigned to $1b_{2u}$, $1b_{2g}$, $3a_g$, $1b_{3u}$, $2b_{1u}$, and $2a_g$, respectively. All these assignments fit well with the symmetry selection rules given above: the even-symmetry states, $2\sigma_g$, $3\sigma_g$, and $1\pi_{u\perp}$ of C_2H_2 and $2a_g$, $3a_g$ and $1b_{2u}$ of C_2H_4, are enhanced at the near-normal-emission geometry ($\theta_i = 20°$).

The peaks assigned to $3\sigma_g$ and $1\pi_{u\parallel}$ of the C_2H_2 chemisorbates and $1b_{3u}$ and $3a_g$ of the C_2H_4 chemisorbates shift to smaller binding energies compared to the gas-phase standard when we align the deepest MO's.[27] These MO's commonly have the C-C bonding character. On the other hand, the $2b_{1u}$ peak of the C_2H_4 chemisorbates, which has a C-C antibonding character, shifts to a larger binding energy. All these shifts are thought to reflect the distortion of the molecules and the expansion (weakening) of the C-C bond due to chemisorption. This is consistent with the NEXAFS results on the $\sigma^*_{\text{C-C}}$ shape resonances discussed above.

One can also notice that the $1\pi_u$ states of C_2H_2 formerly degenerated split into two states by chemisorption, that is, into the surface parallel and perpendicular components. The perpendicular component ($1\pi_{u\perp}$) has a C-C bonding character, but shifts to a larger binding energy (5.2 eV) in contrast to the other MO's with a C-C bonding character. Similarly the $1b_{2u}$ state of C_2H_4, with a C-C bonding character, also shifts to a larger binding energy. This opposite trend in peak shifts for the highest occupied molecular orbitals (HOMO's) of chemisorbates thus cannot simply be explained by the aforementioned molecular distortion. We suggest that these shifts and the splitting for the HOMO's can come from the hybridization with the unoccupied Si dangling bond states.

In addition to the MO's assigned unambiguously from the gas-phase analogy, we observe a new feature at the binding energy of 3.1 eV for both C_2H_2 and C_2H_4 chemisorbates. These states are naturally related to the interaction between the Si surface dimers and the adsorbates and they are the most important feature of the molecule-Si bond formation.

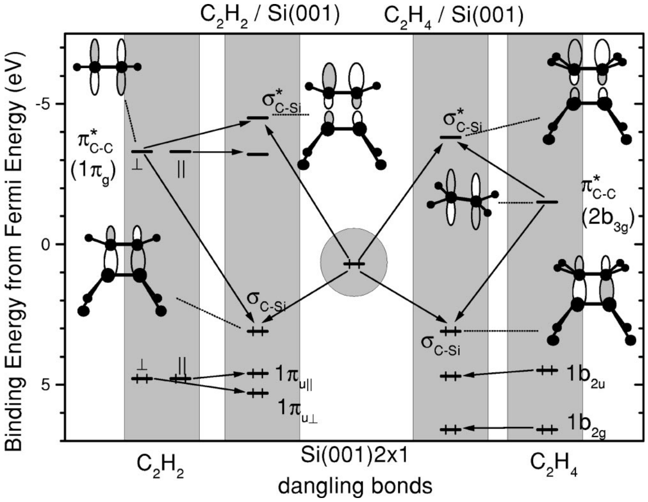

FIG. 5. A schematic electronic structure diagram of the C_2H_2 and C_2H_4 chemisorption on the Si(001)2×1 surface. The molecular orbitals of free C_2H_2 and C_2H_4 molecules are plotted at outside columns. The Si dangling-bond state is plotted in the center. In between the outside columns and the Si dangling-bond state, the molecular orbitals of chemisorbed C_2H_2 and C_2H_4 are shown as extracted from the present UPS and NEXAFS measurements.

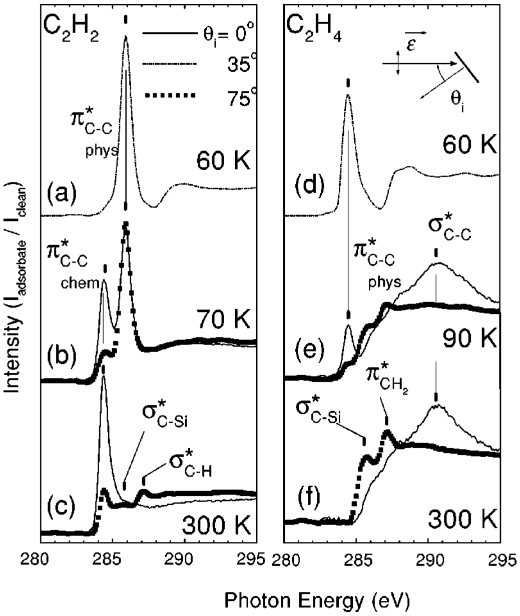

FIG. 6. The polarization and temperature dependence of the C-*K* edge NEXAFS of C_2H_2 and C_2H_4 adsorbates on the Si(001)2×1 surface. The spectra of multilayer C_2H_2 and C_2H_4 are shown in (a) and (d), respectively. The spectra in (b) [(e)] indicate the coexistence of physisorbatelike C_2H_2 [C_2H_4] with chemisorbates at 70 K [90 K]. The spectra in (c) and (f) show C_2H_2 and C_2H_4 chemisorbed at 300 K, respectively.

Since the disappearance of the Si db states and the $\pi^*_{\text{C-C}_\perp}$ states is observed clearly, the 3.1 eV states are understood as the $\sigma_{\text{C-Si}}$ states formed by the hybridization of the db state and the lowest unoccupied MO's (LUMO's) ($\pi^*_{\text{C-C}}$ or $1\pi_g$ of C_2H_2 and $1b_{3g}$ of C_2H_4 in gas-phase notation). Although there are no available calculations and experimental considerations for the electronic states of C_2H_2/Si(001), our assignments for C_2H_4/Si(001) are in good agreement with the recent report by Widdra *et al.*[29] The five (six) electronic states assigned above for C_2H_2 (C_2H_4) adsorbates are indeed a complete set for the whole number of surface electrons: ten (twelve) valence electrons of C_2H_2 (C_2H_4) and the two dangling-bond electrons of a Si dimer.

A schematic diagram of the electronic structures on the chemical bond formations by the molecule-Si interactions is shown in Fig. 5 as deduced from the above NEXAFS and UPS results. In the outside columns, the NEXAFS data of the condensed multilayers and the UPS data of the corresponding gas phases are plotted. In aligning the energy scale of the NEXAFS and UPS data, the core-hole relaxation effect of the $\pi^*_{\text{C-C}}$ resonance[42] in NEXAFS is assumed to be 3 eV.[57] The gas-phase UPS data of C_2H_2 (C_2H_4) are shifted by 6.7 eV (6.2 eV) to a lower binding energy so that the deepest MO peaks are aligned with those of the chemisorbed molecules as mentioned above. The occupied Si db state of the Si(001)2×1 surface is plotted in the center column of Fig. 5. The $\sigma^*_{\text{C-Si}}$ and $\sigma_{\text{C-Si}}$ states are observed, while the $\pi^*_{\text{C-C}_\perp}$ and the db states decrease in the NEXAFS and UPS of the chemisorbates on Si(001)2×1. The appearance of these new features can be explained by the hybridization of the LUMO's and the db states as indicated by the arrows in Fig. 5.

The present picture for the molecule-substrate bond formation is in contrast to the general trend of chemisorption on the transition metal surfaces where the electronic structure of *d* bands largely affect the adsorption of C_2H_2 and C_2H_4. On the transition metal surfaces, the hybridization of the HOMO and the *d* band generally yields an attractive interaction while the LUMO has only a minor overlap with the substrate orbitals.[58] Such hybridization of the HOMO and the *d* band is weak for the noble metals, [47,48,59] but significantly larger for the Ir(111) (Ref. 60) and Ru(0001) (Ref. 61) surfaces with the less-occupied and shallower *d* bands.[58] On the other hand, the adsorption behavior on the Si surface is governed by the well-localized db states, which produces the difference observed.

C. Adsorption kinetics of C_2H_2 and C_2H_4 at the low temperature: The NEXAFS study

After establishing the structural[25] and electronic details of the room-temperature chemisorption of C_2H_2 and C_2H_4 on Si(001)2×1, we discuss the adsorption and dissociation behaviors of the molecules at different temperatures. Figure 6 shows the C *K*-edge NEXAFS spectra of C_2H_2 (C_2H_4) on Si(001)2×1 dosed at 60, 70, and 300 K (60, 90, and 300 K). Since the exposures at 60 K were done using a capillary gas doser, the actual doses on the surface is an order of magnitude higher than the doses by back-filling the chamber at other temperatures. The spectra at 60 K and 300 K with the condensed multilayers and the room-temperature chemisorbates, respectively, are already discussed in the previous sections.

The spectra of 1 L C_2H_4 dosed at 90 K (not shown here) show no difference compared with the 300 K spectra. However a new peak appears at 284.4 eV with a further dosage of 10 L as shown in Fig. 6(e). This spectrum is easily understood by a mixture of the corresponding features of the multilayer and the chemisorbed species, indicating clearly the coexistence of the two different adsorption states: a physisorbatelike weakly adsorbed species and the chemisorbates. It should be noted that the $\pi^*_{\text{C-C}}$ peak intensity of the *physisorbatelike* C_2H_4 is larger in the normal incidence spectra, indicating a rather uniform adsorption configuration with each molecular plane aligned perpendicular to the surface, which is markedly different from the randomly oriented condensed phase. In contrast, the spectra of the surface dosed with 10 L C_2H_2 at 90 K (not shown here) exhibits no difference from the chemisorbed spectra of 300 K. However, the coexistence of the physisorbatelike C_2H_2 with the chemisorbates is observed at a slightly lower temperature of 70 K. Figure 6(b) shows the spectrum taken at 70 K with a dosage of 1 L C_2H_2. The near-edge structure is composed of two pronounced peaks. One appears stronger in the normal incidence spectrum at 284.7 eV, which is on the line of the $\pi^*_{\text{C-C}}$ peak of the C_2H_2 chemisorbate. The other peak at 285.9 eV coincides with that of the C_2H_2 multilayer. It shows no polarization dependence, eliminating the possibility of the coadsorbed C_2H_2 aligning. The physisorbatelike C_2H_2 coexisting at 70 K was also observed by a chemically shifted component in the C 1*s* core-level photoemission (data not shown). At this temperature of 70–90 K, no condensed multilayers were observed and the saturation coverages amount to ~0.5 ML with two different adsorption species together. It is interesting that the difference in the C-H bond structure leads to the unexpected alignment of the physisorbatelike C_2H_4.

The above findings give a hint to the issues of the adsorption kinetics and the saturation coverage. Before the saturation of the rapid adsorption, only the chemisorbates (di-σ-bonded to the Si dimers) exist at 70–300 K. According to the STM observations at room temperature, these molecules adsorb preferentially on the alternate dimer sites (~0.25 ML).[24,32,33] The C-H dipole repulsion between the chemisorbates was implied to explain this configuration.[24] Above 0.25 ML, the sticking coefficient of C_2H_2 and C_2H_4 on the Si(001)2×1 surface drops significantly at room temperature as observed in the present and previous experiments.[3,25] In contrast, physisorbatelike molecules were observed to adsorb on the surface covered with the chemisorbates of 0.25 ML at 70–90 K. Although the reason for this unique adsorption behavior at low temperature is not certain at this stage, the unexpected alignment of the molecular planes of the weakly adsorbed C_2H_4 species implies the existence of an adsorbate-adsorbate interaction above 0.25 ML, which depends strongly on the temperature.

Taylor and co-workers[34] have proposed the ''mobile precursor model'' for the C_2H_2 and C_2H_4 adsorption kinetics, where the adsorbate-adsorbate interaction was neglected up to the saturation coverage of 0.5 ML. However, as confirmed later by the STM and our present studies, the slow adsorption above 0.25 ML is significantly affected by the adsorbate-adsorbate interaction. They also claimed that below 140 K the mobile precursor populates on the surface. In contrast, we found no such precursor species at low temperature below 0.25 ML, casting doubts on the presence of the mobile precursor.

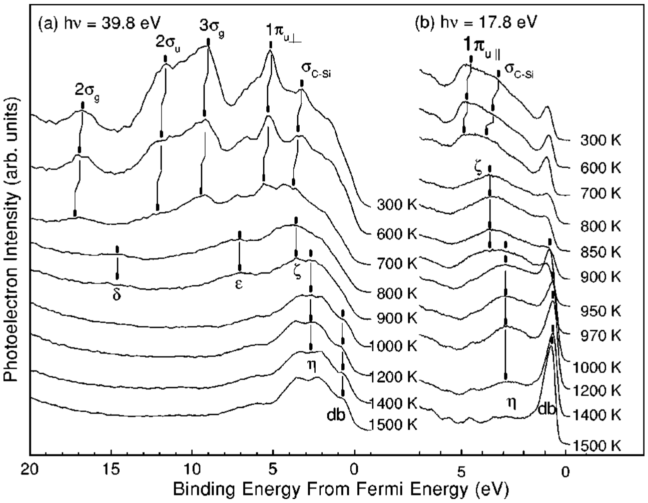

FIG. 7. The annealing temperature dependence of the valence-band photoemission spectra of C_2H_2 chemisorbed on the Si(001)2×1 surface. The incident photon energy is set to (a) 39.8 eV and (b) 17.8 eV. 10 L of C_2H_2 was dosed initially at 300 K.

A qualitative C 1*s* core-level photoemission measurement indicated that most of the physisorbatelike C_2H_2 convert to the chemisorbates on annealing to room temperature (data not shown). This suggests that the coexisting physisorbatelike species introduce a new chemisorption path above 0.25 ML.

D. Dissociation and reaction of C_2H_2: UPS study

The significant valence-band changes upon annealing contain rich information on the bonding and stoichiometry of the adsorbates in the dissociation/reaction processes. Figures 7(a) and 7(b) show the temperature-dependent valence-band photoemission spectra of C_2H_2 on the Si(001)2×1 surface. 10 L of C_2H_2 was dosed at 300 K and the coverage corresponds to ~0.25 ML, as discussed in the previous section. The angle of the incident photon was 45° and normally emitted photoelectrons were detected. The measurements were done at room temperature after the sequential annealings of 1 min for each. The photon energy in Fig. 7(a) was set at 39.9 eV to focus on the temperature dependence of the chemisorbed C_2H_2 MO's and at 17.8 eV on the behavior of the dangling bond states and the molecule-Si bonding states. Five different C_2H_2 MO's observed at 300 K become smaller and shift to higher binding energies as the temperature rises up to ~700 K. The intensity change corresponds to the partial desorption of adsorbates and the dissociation. Roughly 30% of the room-temperature adsorbates was desorbed as measured by the C 1*s* photoemission peak intensity. However, the binding energy shift of MO's cannot be explained by desorption and/or dissociation. Since the db state exhibits no shift, this shift cannot be due to the possible band bending either. This shift, thus, suggests a certain change (stabilization) of the adsorbed molecules by annealing, although the details of this change remain to be studied.

All the MO's in the valence-band spectra disappear completely at 800–850 K as shown in Fig. 7(a). It is noticeable that the intensity of the db peak in Fig. 7(b) remains almost the same up to this temperature irrespective of the desorption and dissociation. This indicates that even after the dissociation of all the C_2H_2 molecules most of the db sites remain occupied by the atomic hydrogen or the dissociated carbon species. At 800–900 K, new features denoted as δ, ϵ, and ζ are observed at the binding energies of 14.6, 7.1, and 3.7 eV, respectively. The binding energies of ϵ and ζ agree well with those of the Si-H monohydride species of the Si(001)2×1 surface.[62] The feature δ cannot be attributed to any known hydride species[62] and it may be due to the carbon-containing fragments or atomic carbon species on the surface. This results clearly indicate that most of the hydrogen atoms from C_2H_2 remain as monohydride after dissociation.

At 970 K, δ, ϵ, and ζ disappear and the intensity of the db peak increases noticeably. These changes indicate the hydrogen desorption as also observed by previous HREELS studies.[10,12] It can be deduced that the carbon-containing fragments represented by ζ also undergo further dissociation/reaction. It is interesting that the hydrogen desorption temperature from the monohydride state on the Si(001)2×1 surface is reported to be 750 K,[63] which is significantly lower than the present observation. This suggests that the coexisting carbon atoms (or more complex fragments) play a role of hindering the recombination of hydrogen atoms. A more detailed study for the characterization of the dissociated carbon species is needed.

Along with hydrogen desorption, another structure η emerges, which is clear at >950 K. This feature is assigned to the valence bands of SiC from the similarity of its binding energy to that of the major valence-band peak of the SiC(001) surfaces.[7,64] This result is consistent with the recent STM study reporting that the dissociated C_2H_2 fragments scattered at 775 K start to form SiC clusters at ~950 K.[24] When the temperature reaches to 1500 K, the structure η disappears and clean Si surface spectra are reproduced. Indeed the disappearance of the structure η was used to confirm the surface cleanliness.

IV. CONCLUSION

We utilized NEXAFS and UPS using linear-polarized synchrotron radiation to clarify the electronic structure, the adsorption kinetics, and the dissociation mechanism of the simple hydrocarbon molecules of C_2H_2 and C_2H_4 on the Si(001)2×1 surface at a temperature range of 60–1500 K. A careful curve-fitting analysis was successfully applied to the NEXAFS spectra, which determines accurately the relative intensities and energies of the various near-edge resonance states. For room-temperature chemisorption, the molecule-Si bonding ($\sigma_{\text{C-Si}}$) and antibonding ($\sigma^*_{\text{C-Si}}$) orbitals were observed for both C_2H_2 and C_2H_4 in the detailed UPS and NEXAFS analyses, respectively. These bonding ($\sigma_{\text{C-Si}}$) and antibonding ($\sigma^*_{\text{C-Si}}$) orbitals are shown to result from the hybridization between the Si dangling bonds and the LUMO's ($\pi^*_{\text{C-C}}$) of C_2H_2 and C_2H_4. Further, the binding energies of the occupied MO's are affected by the molecular distortion (the C-C bond stretching[25]) accompanied by the chemisorption; on chemisorption the MO's of C-C bonding character were found to shift to a smaller binding energy and those of C-C antibonding character to a higher binding energy. The exceptions in these shifts are found for $1\pi_{u\perp}$ of C_2H_2 chemisorbates and $1b_{2u}$ of the C_2H_4 chemisorbates, which may suggest an interaction of these HOMO states with unoccupied Si dangling-bond states.

NEXAFS measurements for the adsorption of C_2H_2 and C_2H_4 at low temperatures show the coexistence of the physisorbatelike species with the chemisorbates of ~0.25 ML. This is in contrast to the adsorption beyond 0.25 ML at 300 K, where chemisorbates adsorbs further but with very small sticking probability.[3] Those physisorbatelike C_2H_4 were found to be aligned with their π^* orbitals parallel to the surface, i.e., their molecular plane perpendicular to the flat-lying chemisorbed C_2H_4.

The dissociation of C_2H_2 chemisorbates at elevated temperature was investigated mainly by means of UPS. C_2H_2 dissociates at 600–700 K and the UPS spectra indicate that the dissociated hydrogen atoms are bonded to the substrate as monohydrides. A SiC-like electronic feature emerges in the UP spectra at ~1000 K, concomitant with the desorption of hydrogen adsorbates. The desorption temperature of hydrogen in this case is found to be significantly higher than on the clean Si(001)2×1 surface, implying that the coexisting carbon species hinder the desorption of hydrogen.

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