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Adsorption of C_2H_2 and C_2H_4 on Si(001): Core-level photoemission

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The debating issue of Si 2*p* surface-core-level shifts and C 1*s* line shape for the Si(001) surface with unsaturated hydrocarbon molecules (C_2H_2 and C_2H_4) adsorbed is reexamined carefully with high-resolution photoemission. The present data unambiguously show the Si 2*p* components due to the Si-molecule bonding on the surface with binding-energy shifts from the bulk Si 2*p* of 0.24 ± 0.02 and 0.18 ± 0.01 eV for the C_2H_2 and C_2H_4 adsorbates, respectively. This result is consistent with the simple picture of the charge transfer from Si to the adsorbed hydrocarbon molecules, but is in contrast to some of the recent experimental reports and a recent theoretical expectation of almost no surface-core-level shifts for both adsorbate systems. The C 1*s* core levels are found to consist of two components for both C_2H_2 and C_2H_4 adsorbates with binding-energy shifts of 0.37 ± 0.02 and 0.43 ± 0.02 eV, respectively. The binding-energy shifts and the relative intensities of these components are invariant over the whole coverage range up to saturation. This supports the interpretation of the higher-binding-energy and smaller-intensity components as the C-H vibrational satellite.

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I. INTRODUCTION

Adsorption and self-organization of unsaturated hydrocarbon molecules on Si surfaces attract much recent attention partly due to its relevance to the Si-based molecular electronics and due to its importance in the heteroepitaxial growth of SiC or diamond and carbonization of Si layers. Among various molecular adsorption systems, C_2H_2/Si(001) and C_2H_4/Si(001) have played the role of model systems in studying the interaction and reaction of hydrocarbon molecules with the Si(001) surface atoms.[1–5] However, irrespective of the great amount of recent effort on these two adsorption systems, some of the fundamental physical and chemical nature of the adsorption of C_2H_2 and C_2H_4 molecules on Si(001) is not clear yet. Among the present issues under debate are (i) the determination of the stable local adsorption structure of the molecules, especially for C_2H_2,[6–10] and (ii) the detailed nature of the chemical bonding between the molecules and the Si surface dimers.[3,11–13] The structure of a molecular adsorbate bonded on top of each Si surface dimer through a di-σ bonding has been the most popular structure model up to recently for both C_2H_2 and C_2H_4.[3–5] However, the recent photoelectron holography[6] and scanning tunneling microscope (STM) (Ref. 10) studies introduced, for the C_2H_2 adsorption, a *tetra-σ-bonded structure* with molecules located between two adjacent Si dimers, and the so-called *end-bridge structure* with molecules bridging the adjacent ends of neighboring Si dimers, respectively. The recent *ab initio* calculations showed that the model with a tetra-σ bonding has relatively higher energy than the di-σ bonding, but that the end-bridge structure is energetically favorable.[7–10] Such new structure models indicate that the adsorption structure of C_2H_2 and C_2H_4 could be qualitatively different.

The adsorption configuration of the molecules is rather straightforwardly represented by the C 1*s* core-level photoemission spectra as the number of core-level components and their binding energies. As for the C_2H_2 and C_2H_4 adsorption on Si(001), the previous photoemission studies reported a single asymmetric C 1*s* component[13–15] or two symmetric components,[16] for which the origin of the high-binding-energy structures was not clear at all. This has made the interpretation of the C 1*s* line shapes in terms of the adsorption configuration difficult.

A closely related issue is the surface-core-level shift (SCLS) of Si 2*p*—the binding-energy shift of the Si 2*p* core level for the surface Si dimers bonded with C_2H_2 or C_2H_4 adsorbates from that of the bulk Si atoms.[11–15] Basically, the SCLS reflects the charge transfer between the hydrocarbon molecular adsorbates and the Si surface atoms, which is affected by the local adsorption structure and the nature of the Si-molecule bonding. While an earlier Si 2*p* study reported no discernible SCLS for C_2H_4/Si(001),[11] Xu *et al.* assigned a Si 2*p* surface component with a SCLS of −0.245 eV as due to the Si-C_2H_2 bonding.[12] A subsequent *ab initio* calculation of the SCLS's based on the di-σ bonding model indicated only marginal SCLS's for both C_2H_2 and C_2H_4 adsorbates.[14] This discrepancy may be interpreted as due to the possible difference of the local bonding structure of the two adsorbate systems mentioned above, that is, the deviation from the di-σ bonding model for C_2H_2/Si(001). However, in further contrast to these studies, a very recent high-resolution Si 2*p* study[15] for C_2H_4/Si(001) suggested a positive SCLS of +0.25 eV, but another one[13] suggested −0.227 eV and +0.169 eV for C_2H_2/Si(001) and C_2H_4/Si(001), respectively. Note that the negative binding-energy shifts reported is not compatible with the simple picture of charge transfer from the Si surface atoms to the adsorbed hydrocarbon molecules.

In the present paper, we report on the reexamination of the C 1*s* and Si 2*p* spectra for both C_2H_2 and C_2H_4 adsorbates on the Si(001) surface. The high-resolution measurements performed here unambiguously identify the positive Si 2*p* SCLS's of an order of 0.2 eV for both adsorbate systems supporting the idea of electron transfer from the Si surface dimers to the adsorbed molecules. The analyses of the C 1*s* spectra indicate the existence of the two symmetric components for both C_2H_2 and C_2H_4 adsorbates in the whole coverage range. These components are interpreted as due not to the different adsorption configurations but to an intrinsic property of the C 1*s* photoemission of the molecules, i.e., the C-H vibrational satellites.

II. EXPERIMENTAL ASPECTS

The measurements were performed on a newly built soft x-ray beam line (BL-8*A*1) connected to an undulator at Pohang Accelerator Laboratory in Korea.[17] The endstation is equipped with a high-performance electron-energy analyzer (SCIENTA-200, Gamma Data).[18] Before C_2H_2 or C_2H_4 doses, well-ordered Si(001)2×1 surfaces were obtained by flash heating up to 1200 °C and annealing at 1000 °C.[4,5] The C_2H_2 or C_2H_4 exposure to Si(001)2×1 was carried out by back filling the chamber at room temperature (RT).[4,5] The source gases were carefully purified by cycles of freezing and pumping. The spectra were obtained at normal emission to the surface if not specified. The overall instrumental resolution was better than 60 (250) meV for Si 2*p* (C 1*s*) at a photon energy $h\nu$ of 134 (330) eV.[19] For higher-resolution measurements, the sample was quickly cooled down to 90 K after gas doses at RT in order to reduce the thermal broadening. The core-level photoemission spectra were then carefully analyzed by a standard nonlinear least-squares fitting procedure using Voigt functions or asymmetric Doniach-Sunjik functions. In case of Si 2*p*, spin-orbit doublets are used with a spin-orbit splitting of 0.605 eV and a $2p_{1/2}/2p_{3/2}$ branching ratio of 0.5 and Lorentzian width of 0.085 eV.[20,21]

III. RESULTS AND DISCUSSION

Figure 1 shows the evolution of the C 1*s* spectra taken at a photon energy of 330 eV upon increasing the C_2H_2 dose from 0.2 to 20 L. The molecular uptake almost saturates at 5–8 L as measured from the variation of the C 1*s* intensity. The quasisaturation at 5–8 L is thought to be 0.8–1.0 ML, roughly one molecule per 2×1 unit cell.[3,5,13] The spectra are aligned in binding energy by the maximum peak positions in order to compare the line shape in detail. This compensates the apparent energy shifts caused mainly by the adsorption-induced band bending. The band-bending shift (of an order of 0.2 eV) is discussed later for the Si 2*p* spectra. For the low coverage of 0.2 L (0.02–0.03 ML) the band-bending shift is marginal and the C 1*s* binding energy is measured to be 238.70 eV (the main peak, see below). This binding energy is consistent to the previous reports.[13,16]

As also reported, the asymmetry of the raw spectra themselves is apparent. More details of the line shape can be elucidated by careful curve-fitting analyses. Examples of the optimized curve-fitting results are also shown in Fig. 1 for 0.2 and 5 L—the dots connected by the solid lines are the raw data and the gray lines are the results of fits. All spectra are fitted excellently and consistently by two symmetric Voight functions with an energy shift of 0.37 ± 0.02 eV. This is in contrast to the result of Fink *et al.*,[13] which claimed that the spectra cannot properly be fitted by two symmetric components. Another previous result by Lui and Hamers is similar to the present one but the energy shift between the two components reported is twice larger than the present one (0.8 eV). The energy shift and the intensity ratio [80/20% (±4%)] of the two components is invariant over the whole coverage range making the line shape unchanged upon increase of the coverage. This fact is important in considering the origin of these two components, which will be discussed further below.

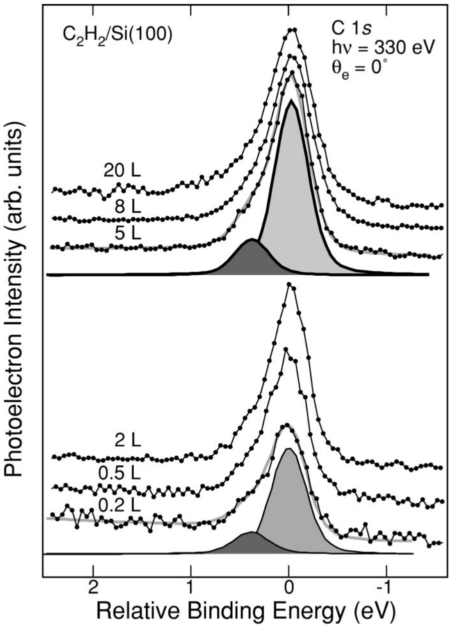

FIG. 1. C 1*s* spectra (dots and solid lines) for the Si(001) surface dosed with C_2H_2 of 0.2–20 L at RT. All spectra are taken along the surface normal (emission angle θ_e of 0°) with a photon energy $h\nu$ of 330 eV. The spectra are aligned in energy to compare the line shapes in detail by compensating the band-bending shift, where the main peak position for the 0.2-L spectrum corresponds to 283.70 eV. Decompositions of the spectra using Voight functions are shown for 0.2 and 5 L where the gray lines overlaid are the results of the fits. The Lorentzian and Gaussian widths used were 0.12 and 0.31–0.38 eV, respectively. The energy shift between the components is 0.37 ± 0.02 eV.

Similar results for the C_2H_4 adsorption are shown in Fig. 2. In contrast to C_2H_2, the sticking rate of molecules is much lower and the saturation is obtained only at above 500 L. The binding energy of the C 1*s* level is 238.95 eV for the main peak and the band-bending shift is only 0.05 eV at maximum. Similar to C_2H_2 the line shape of C 1*s* is independent of the adsorbate coverage with two symmetric components—the energy shift is 0.43 ± 0.02 eV and the intensity ratio is 75/25% (±3%). This result is consistent to the previous report although the previous study could not resolve the high-binding-energy component clearly.[14]

As the origin of the high-binding-energy components of the C_2H_2 and C_2H_4 adsorbates, one can at first think of the possibility of different adsorbate configurations. However, it has been established well that, at least for the C_2H_4 adsorption, the molecules have a unique adsorption site of on-top di-σ structure.[3–5,7] Furthermore, the similarity of the line shapes for the C_2H_2 and C_2H_4 adsorbates and their coverage-

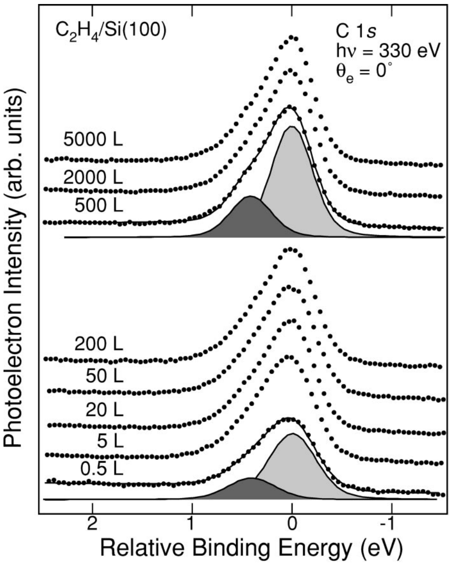

FIG. 2. C 1*s* spectra (only dots) similar to Fig. 1 but for the C_2H_4 doses of 0.5–5000 L at RT. The spectra are aligned in energy to compare the line shapes in detail by compensating the band-bending shift, where the main peak position for the 0.5-L spectrum corresponds to 283.95 eV. Decompositions of the spectra are shown for 0.5 and 500 L, where the solid lines overlaid are the results of the fits. The Lorentzian and Gaussian widths used were 0.12 and 0.46–0.50 eV, respectively. The energy shift between the components is 0.43 ± 0.02 eV.

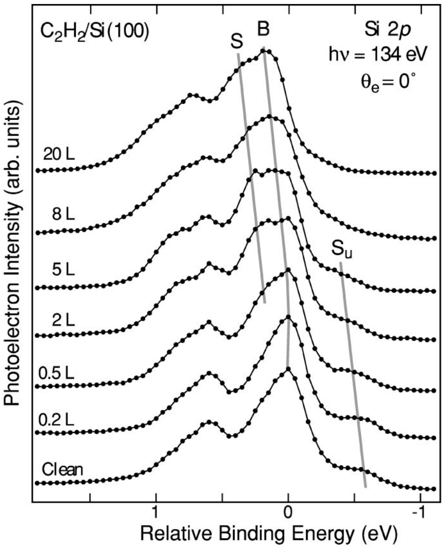

FIG. 3. Si 2*p* spectra (dots and lines) for the Si(001) surface dosed with C_2H_2 of 0.2–20 L at RT. All spectra are taken along the surface normal (emission angle θ_e of 0°) with a photon energy $h\nu$ of 134 eV. The gray lines indicate the positions of apparent spectral features.

independence strongly suggests that the two components are an intrinsic property of the molecules. This possibility has already been introduced,[13,14] since the C 1*s* spectra of C_2H_2 and C_2H_4 in gas phase were shown to have vibrational loss structures in the high-binding-energy side.[22] The most prominent and well-resolved vibrational satellite is due to the C-H stretching mode, which is shifted by about 410 meV.[22] This energy shift and moreover the fractional intensity of this loss feature is in good agreement with those of the high-binding-energy components observed presently for the adsorbates. The differences in the vibrational loss energy for the adsorbates from that of the gas molecules are in the order of 20–40 meV, which may reflect the distortion of the molecules in forming the local bonding with the Si surface atoms. Indeed, the electron-energy-loss spectroscopy observed the vibrational energy of the C-H stretching reduced to about 370 meV for the C_2H_2 adsorbates on Si(001), which is in good agreement with the present result.[23] In case of the C_2H_2 adsorption, a recent STM study have shown the coexistence of different adsorption structures for the very initial adsorption. This study further commented that the end-bridge structure becomes more and more popular as the coverage increases. However, as shown in Fig. 1, we do not observe no sign of such multiple adsorption sites.[10] This discrepancy may suggest that the coexistence of the different adsorption configurations happens only for the very initial adsorption,[10] or that the C 1*s* binding-energy differences between different adsorption configurations is too small to be resolved. If a systematic theoretical calculation is available for the C 1*s* binding energies and the C-H vibrational energies for different adsorption structures under debates, the present result may be used to determine the correct structure models.

Figure 3 shows the evolution of the Si 2*p* raw spectra taken at a photon energy of 134 eV upon increasing the C_2H_2 dose. In the figure, the overall shift of the spectra towards higher binding energy ($\sim$0.2 eV at saturation) is observed, which is thought to be due to the band bending induced by the adsorption as mentioned above. Together with the overall shift, the gradual decrease of the lowest-binding-energy peak of the clean surface contribution is noticeable. This component, denoted as S_u, represents the up-dimer atoms of buckled Si dimers on the clean Si(001) surface.[20] Thus the decrease of S_u straightforwardly indicates the expense of the Si dimer sites in bonding with the adsorbate molecules. Another distinct change of the Si 2*p* line shape upon C_2H_2 adsorption is the emerging shoulder at about 0.2 eV higher binding energy than the main bulk component *B*. This spectral feature is denoted as *S* and becomes almost a separate peak near the saturation coverage of 2–8 L.

The C_2H_2-induced feature *S* is resolved with better clarity in the spectra taken at 90 K due to the reduced thermal broadening. A few of such spectra are displayed in Fig. 4 for the 5-L dose with corresponding decompositions by curve-fitting analysis. At the more bulk-sensitive condition of $h\nu = 114$ eV (a lower kinetic energy and a larger mean free path of photoelectrons (Refs. 20, 21), the *S* component is an obvious shoulder and becomes a separate peak at 134 eV with almost the same intensity as *B* and even a dominant peak at 145 eV. This behavior clearly indicates that the higher binding-energy feature *S* is a surface-related component. The detailed decompositions of the spectra suggest additional but minor peaks such as S_u, *C*, and *D* around the two major components of *B* and *S*, as indicated in Fig. 4. While the S_u component is apparent as mentioned above, which is due to the unoccupied Si dimers remaining on the surface, the presence of other two components *C* and *D* are not evident from

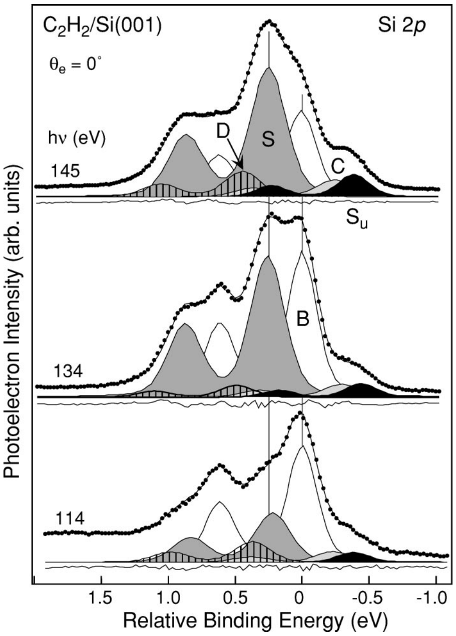

FIG. 4. Decompositions of the high-resolution Si 2p spectra for the Si(001) surface dosed with 5-L C_2H_2 at RT, which were taken with three different photon energies ($h\nu$'s) indicated along the surface normal (emission angle θ_e of 0°). The surface was cooled down to 90 K after the RT gas dose to reduce the thermal broadening. The solid lines overlapping the raw spectra given by the dots (the solid lines at the bottom of each spectrum) are the results (residues) of the fits. The bulk (B) and surface-related components (S, S_u, C, and D) are indicated with different hatchings.

only the raw spectra. A hint of D is provided from the very weak but extending high-binding-energy tails of the spectra. The binding-energy shifts (Gaussian width) of these components from B are 0.24 ± 0.02 (0.25 ± 0.01), 0.45 ± 0.05 (0.25 ± 0.01), -0.45 ± 0.05 (0.25 ± 0.01), and -0.25 ± 0.03 (0.25 ± 0.01) eV for S, D, S_u, and C, respectively. The Gausian width of bulk component optimized is 0.21 eV. These values are determined by a thorough and systematic curve fitting of five different spectra taken at different photon energies and emission angles.[21] An independent fitting of the lower-resolution RT spectra shown in Fig. 3 at 2–8 L gives a consistent result.

Figure 5 shows the Si 2p spectra similar to Fig. 3 but for C_2H_4 adsorption. As mentioned above, the band-bending shift is only marginal in contrast to C_2H_2/Si(001). In further contrast, no clear spectra feature induced by adsorption is noticed. One may suspect the appearance of a shoulder feature at a binding energy higher than B by ~0.2 eV as denoted by a dashed line in Fig. 5. The presence of this feature is, however, far from being conclusive. A consistent aspect with the C_2H_2 case is the gradual decrease of the up-dimer atom component S_u upon increasing the C_2H_4 coverage. However, the more extensive and higher-resolution measurements clearly elucidate the presence of an adsorption-induced Si 2p component.

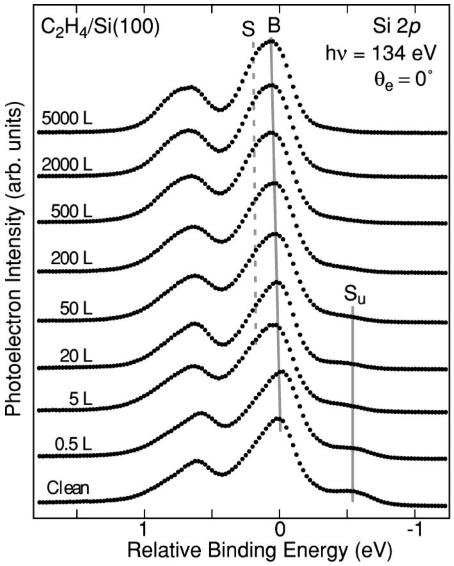

FIG. 5. Si 2p spectra similar to Fig. 3 but for the C_2H_4 doses of 0.5–5000 L at RT. The gray lines indicate the positions of apparent spectral features, and the gray dashed lines a weak spectral feature.

As in Fig. 4, the Si 2p spectra of the Si(001) surface saturated with C_2H_4 (2000 L) were measured at 90 K at a couple of different photon energies and emission angles. Some of those spectra are shown in Fig. 6 with corresponding decompositions. At $h\nu=114$ eV, one can identify a clear shoulder feature at a higher binding energy than B, which becomes a dominating peak at the more surface-sensitive condition of $h\nu=145$ eV. At 134 eV, this surface-related peak and the bulk component B have comparable intensities making the apparent width of the Si 2p spectrum very broad. Qualitatively speaking, this behavior is completely consistent with the case of C_2H_2 as shown in Fig. 4. The surface com-

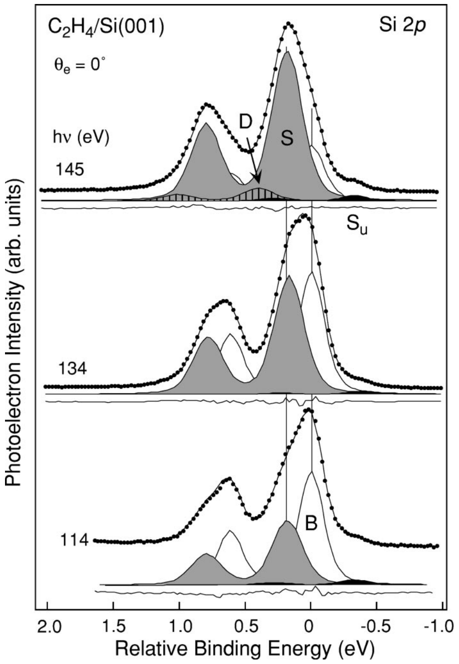

FIG. 6. Decompositions of the Si 2p spectra similar to Fig. 4 but for the 2000-L C_2H_4 dose at RT. The surface was cooled down to 90 K after the RT gas dose to reduce the thermal broadening. The bulk (B) and surface-related components (S, S_u, and D) are indicated with different hatchings.

ponent (denoted as *S* in analogy) is thus naturally assigned as due to the Si dimer atoms bonded with the molecular adsorbates. The SCLS of this component is accurately determined as 0.18 ± 0.01 eV. The Gaussian widths of *B* and *S* components are 0.18 ± 0.01 and 0.22 ± 0.01 eV, respectively.

As for the $C_2H_2/Si(001)$ system, Xu *et al.*[15] and Fink *et al.*[13] reported contradicting values of the Si 2*p* SCLS as -0.245 eV and $+0.227$ eV, respectively. Neither of those works, however, could resolve the surface component itself clearly. Comparing their spectra with the present ones, we can conclude that such discrepancy is mainly due to the insufficient spectral resolution of the previous studies, which leads to greater arbitrariness in the curve-fitting analyses. Although the Fink *et al.*'s report of $+0.227$ eV SCLS is qualitatively consistent to the present one of $+0.24$ eV, the decomposition therein is obviously unreasonable; the bulk component *B* used in the surface-sensitive spectrum of 70° emission is broader than the whole apparent width of the normal emission one.[13] In the case of $C_2H_4/Si(001)$, three different groups performed the Si 2*p* study: Rochet *et al.* claimed no SCLS,[14] Casaletto *et al.* claimed a SCLS of $+0.128$ eV (Ref. 12), and Fink *et al.* of -0.169 eV.[13] One can, however, notice that the reported Si 2*p* raw spectra themselves are all similar and thus the discrepancy here is also due to the insufficient resolution and a consequential arbitrariness of the curve fitting. In contrast, the present spectra were taken with a better resolution over a full range of different photon energies and emission angles. As shown in Figs. 4 and 6, the comparison of the spectral shapes at different measurement conditions clearly elucidates the presence of the surface-related features even before any curve-fitting analysis.

The present study indicates that the SCLS's of both C_2H_2 and C_2H_4 adsorbates are positive values and are of an order of 0.2 eV. Within the first approximation of the initial state picture, the electrons of the Si surface dimers are transferred to the adsorbate molecules when the dimers accommodate the adsorbates. This is fully natural if we consider the electronegativity difference of hydrogen, carbon, and silicon atoms. In contrast to the present determination, a recent *ab initio* calculation of the SCLS's based on a pseudopotential scheme suggested that both adsorbate systems have almost no SCLS's (less than 0.01 eV) in both the initial and the final states when the adsorbates adopt the di-σ boding on top of the Si dimers.[11] It is, however, not clear whether the discrepancy between that theory and the present experiment is due to the limitation/artifact of the calculation itself or to the deviation of the adsorbate structure from the di-σ bonding.

Considering the fact that the SCLS of the C_2H_2 adsorbates is obviously larger than C_2H_4 the tetra-σ bonding for C_2H_2 (Ref. 6) is unlikely since the higher Si coordination of C atoms would lead to smaller charge transfer from each Si atoms and thus smaller SCLS values. However, the newly proposed structure of the end bridge,[9,10] where the adsorbates bridging the adjacent ends of neighboring Si dimers, is chemically very similar to the on-top di-σ bonding. It leads to an expectation of a very similar SCLS for both structures making it difficult to distinguish them by SCLS. If we assume the same adsorption structure for C_2H_2 and C_2H_4, the larger SCLS by C_2H_2 adsorbates is understood easily from the more electron-deficient nature of the C_2H_2 molecules due to the fewer C-H bonds than C_2H_4. However, more detailed discussion of the charge transfer between the molecules and the Si surface atoms should wait for a conclusive determination of the adsorption structures, especially for C_2H_2.

Further quantitative difficulty in the SCLS measurement is the possibility of the overlap of the surface Si 2*p* component with other unresolved components lying closely. Especially there is a possibility that the *S* component is overlaped with the component due to the second Si layer beneath the Si dimers, which has a SCLS of 0.22 eV on the clean surface.[20,21] Such overlap is plausible since the *preserved* Si dimers after adsorption would not bring about a large change in the SCLS for the second layers Si atoms.[21] Taking this situation into account probably, Casaletto *et al.* put the second layer component into their curve fitting.[12] However, in that case the fitting cannot be done without an assumption of the peak positions since the surface (Si atoms bonded with molecules) and the second layer components are too close, much closer than the apparent half width at half maximum. In turn, this suggests that the *S* component given in our work should also be treated as the integrated contribution of the first and second Si layers. Even in this case the above qualitative discussion of the SCLS would not be affected.[24]

As mentioned above, the minor component S_u and *C* in the above curve fitting are thought to have the same origin as the similar components of the clean surface spectra;[20,21] S_u is due to the up-dimer atoms of the bare Si dimers but the origin of *C* observed on the clean surface is still uncertain. However, the higher-binding-energy component *D* (SCLS $=0.45-0.48$ eV) is not found on the clean surface. We suspect this as due to the contamination from the residual gas or the source gas, since a very similar feature is frequently observed for the clean Si(001) surface in a few hour under ultrahigh vacuum condition after a flash cleaning. The partial dissociation of the adsorbate molecules and the subsequent hydrogen adsorption may also explain this feature since the Si-H and H-Si-H bonds on the dimers are reported to have SCLS's of ~0.3 and ~0.5 eV, respectively.[25]

IV. SUMMARY

The C 1*s* and Si 2*p* core-level line shapes for the Si(001) surface with unsaturated hydrocarbon molecules (C_2H_2 and C_2H_4) adsorbed are reexamined carefully and systematically. The present high-resolution data unambiguously show the Si 2*p* components due to the Si-molecule bonding on the surface with binding-energy shifts from the bulk Si 2*p* of 0.24 ± 0.02 and 0.18 ± 0.01 eV for the C_2H_2 and C_2H_4 adsorbates, respectively. This result is consistent with the simple picture of the electron transfer from Si to the adsorbed hydrocarbon molecules. The comparison of the present Si 2*p* data and the previous lower-resolution studies suggest that significant ambiguity can arise in the curve-fitting analyses for the complex core-level spectral line shape especially when the raw spectrum has no apparent spectral features and is taken with insufficient resolution. On the other hand, the C 1*s* core levels for both C_2H_2 and C_2H_4 adsorbates are found to be very similar consisting of two components with binding-energy shifts of 0.37±0.02 and 0.43±0.02 eV, respectively. The binding-energy shifts and the relative intensities of these components are invariant for the whole coverage range up to saturation. This supports the interpretation of the higher binding energy and smaller intensity components as a satellite structure due to C-H vibrational mode of the molecules.

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[1] A. J. Mayne, A. R. Avery, J. Knall, T. S. Jones, G. A. D. Briggs, and W. H. Weinberg, Surf. Sci. **284**, 247 (1993).

[2] L. Li, C. Tindall, O. Talaoka, Y. Hasegawa, and T. Sakurai, Phys. Rev. B **56**, 4648 (1997).

[3] W. Widdra, A. Fink, G. Gokhale, P. Trischberger, D. Menzel, U. Birkenheuer, U. Gutdeutsch, and N. Rösch, Phys. Rev. Lett. **80**, 4269 (1998).

[4] F. Matsui, H. W. Yeom, A. Imanishi, K. Isawa, and T. Ohta, Surf. Sci. Lett. **401**, L169 (1998).

[5] F. Matsui, H. W. Yeom, I. Matsuda, and T. Ohta, Phys. Rev. B **62**, 5036 (2000).

[6] S. H. Xu, M. Keeffe, Y. Yang, C. Chen, M. Yu, G. L. Lapeyre, E. Rotenberg, J. Denlinger, and J. T. Yates, Jr., Phys. Rev. Lett. **84**, 939 (2000).

[7] C.-H. Cho and L. Kleinman, Phys. Rev. B **63**, 193402 (2000).

[8] P. L. Silvestrelli, F. Togio, and F. Ancilotto, J. Chem. Phys. **114**, 8539 (2001).

[9] Y. Morikawa, Phys. Rev. B **63**, 033405 (2001).

[10] W. Kim, H. Kim, G. Lee, Y.-K. Hong, K. Lee, C. Hwang, D.-H. Kim, and J.-Y. Kim, Phys. Rev. B **64**, 193313 (2002).

[11] J.-H. Cho, L. Kleinman, C. T. Chan, and K. S. Kim, Phys. Rev. B **63**, 073306 (2001).

[12] M. P. Casaletto, R. Zanoni, M. Carbone, M. N. Piancastelli, L. Aballe, K. Weiss, and K. Horn, Phys. Rev. B **62**, 17128 (2000).

[13] A. Fink, W. Widdra, C. Keller, M. Stichler, A. Achleitner, G. Comelli, S. Lizzit, A. Baraldi, and D. Menzel, Phys. Rev. B **64**, 045308 (2001).

[14] F. Rochet, F. Jolly, F. Bournel, G. Dufour, F. Sirotti, and J.-L. Cantin, Phys. Rev. B **58**, 11 029 (1998).

[15] S. H. Xu, Y. Yng, M. Keeffe, G. J. Lapeyre, and E. Rotenberg, Phys. Rev. B **60**, 11 586 (1999).

[16] H. Lui and R. J. Hamers, Surf. Sci. **416**, 354 (1998).

[17] M.-K. Lee and H. J. Shin, Nucl. Instrum. Methods Phys. Res. A **467–468**, 508 (2001).

[18] Y. D. Chung, J. W. Kim, C. N. Whang, and H. W. Yeom, Phys. Rev. B **65**, 155310 (2002).

[19] H. Koh, J. W. Kim, and H. W. Yeom (unpublished).

[20] E. Landemark, C. J. Karlsson, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. Lett. **69**, 1588 (1992).

[21] H. W. Yeom, T. Abukawa, Y. Takakuwa, Y. Mori, T. Shimatani, A. Kakizaki, and S. Kono, Phys. Rev. B **54**, 4456 (1996); H. W. Yeom, Y.-C. Chao, S. Terada, S. Hara, S. Yoshida, and R. I. G. Uhrberg, *ibid.* **56**, R15525 (1997).

[22] B. Kempgens, H. Köppel, A. Kivimäki, M. Neeb, L. S. Cederbaum, and A. M. Bradshaw, Phys. Rev. Lett. **79**, 3617 (1997); S. L. Sorensen, M. Wiklund, S. Sundin, A. Ausmees, A. Kikas, and S. Svensson, Phys. Rev. A **58**, 1879 (1998).

[23] M. Nishjima, J. Yoshinobu, H. Tsuda, and M. Onchi, Surf. Sci. **192**, 383 (1987).

[24] Our own test fittings indicate that the two possible components (one for the Si dimers and the other for the second Si layer) should be closer than 0.1 eV in the energy separation. This is also corroborated by the fact that the width of the *S* component is not significantly broader than *B* in both adsorbate systems.

[25] E. Landemark, Ph.D. thesis, Linköping University, 1993.