PHYSICAL REVIEW B **77**, 115324 (2008)

Chemisorption of acetic acid on Si(100)-2×1 at room temperature

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(Received 28 October 2007; published 14 March 2008)

We have investigated adsorption of acetic acid on Si(100)-2×1 at room temperature using high-resolution photoemission spectroscopy and near edge x-ray adsorption fine structure (NEXAFS) measurements in the partial electron yield mode. At room temperature, an acetic-acid molecule is found to chemisorb on Si(100)-2×1 surface through the formation of the O—H dissociation structure. NEXAFS was conducted to characterize the adsorption geometry of acetic acid on Si(100). The π^* orbital of the C═O bond shows a good angle dependence in carbon *K*-edge NEXAFS spectra, and we estimate the adsorption angle between chemisorbed acetic acid of C═O bond and the Si(100) surface normal as ~41° ± 2° using an analytical solution of NEXAFS intensity.

DOI: 10.1103/PhysRevB.77.115324 PACS number(s): 68.43.−h

Adsorption of organic molecules on group semiconductor surfaces have attracted growing interest because of their scientific and technological importance.[1–5] Their potential applications are microelectronics, sensor design, and electrochemistry. The interaction of small organic molecules with silicon surfaces has been employed for understanding reaction mechanisms in organic functionalization of semiconductors. Especially, the Si(100) surface is a particularly important semiconductor because of its potential future device applications in molecular devices.[6] Recently, there have been a number of theoretical[7,8] and experimental[9–13] studies on the adsorption of a carboxyl (—COOH) group molecules on Si(100) using x-ray photoelectron spectroscopy, low-energy electron diffraction (LEED), near edge x-ray adsorption spectroscopy (NEXAFS), and high-resolution electron energy loss spectroscopy. Kim and Cho performed a theoretical study[7] for the adsorption of acetic-acid molecule, one of the simplest organic molecules containing a carboxyl group, on Si(100)-2×1 surface using first principles density-functional calculations within the generalized gradient approximation. They show that there are two different reaction pathways forming the O—H dissociative and di-σ configurations. The attraction of the lone pair of the hydroxyl O to the down Si atom proceeds to the dissociation of the O—H bond, resulting in the formation of the dissociative configuration. The di-σ configuration is formed via a precursor, where the carbonyl O is attracted to the down Si atom. Although the former configuration is energetically favored over the latter one, its calculated energy profiles along the two reaction pathways reveal that formation of the two chemisorption configurations are almost equally feasible via their precursor states because of their shallow energy barriers. However, at room temperature, CH_3COOH desorption from the di-σ configuration can be easily activated, while that from the O—H dissociative configuration cannot. Thus, they expect that at room temperature, adsorbed CH_3COOH molecules on Si(100) mostly occupy the dissociative configuration, similar to other carboxylic acids on Si(100). In this paper, we focus on identifying chemisorption geometry and bonding reaction of adsorbed acetic-acid molecules on Si(100) surfaces by photoemission spectroscopy (PES) and NEXAFS using synchrotron radiation at room temperature. PES provides information on the chemical shift of the Si 2*p*, C 1*s*, and O 1*s* core levels. NEXAFS was used to characterize the unoccupied molecular orbital states and the adsorption geometry of acetic acid on Si(100). Our experimental results show that the adsorbed acetic-acid molecules on Si(100) surfaces have the O—H dissociation structure and the average tilting angle between the double bond and the Si(100)-2×1 surface normal of ~41° ± 2°. This study provides a good example for the reaction between the Si substrate and the simplest carboxyl containing molecules with two identical functional groups.

B-doped Si(100) wafer with a resistivity of 9–12 Ω cm and the dimension of $14\times4\times0.5\ \mathrm{mm}^3$ was used. The sample was degassed at 900 K for 12 h using direct resistive heating, and it was cleaned by the iteration of flashing for 2–3 s at 1500 K. During the cleaning process, the base pressure of the experimental chamber was kept below $\sim5\times10^{-10}$ Torr. The surface cleanness and crystallographic ordering of Si(100)-2×1 were verified by photoemission spectra and LEED. Acetic acid (99.8%, Aldrich) was purified by freeze-pump-thaw cycles prior to use. Dosing was accomplished by backfilling through a variable leak valve without ion gauge sensitivity calibration. The saturated acetic-acid surface was obtained by dosing at 2 L ($1\ \mathrm{L}=1\times10^{-6}$ s Torr). The photon was incident on the surface at 20° with respect to the surface normal. The experiments have been performed at the 2B1 beamline[14] of the Pohang Light Source (PLS).[15] The Si 2*p* core level spectra have been taken with photon energy of 130 eV with a total resolution of 200 meV. The C 1*s* and O 1*s* spectra have been obtained with photon energies of 330 and 650 eV with spectral resolutions of 350 and 500 meV, respectively. The binding energy and the spectral resolution have been determined by measuring the Au $4f_{7/2}$ core level and the Fermi level of sputtered Au film. The NEXAFS spectra have been measured in the partial electron yield detection mode by recording

1098-0121/2008/77(11)/115324(4)

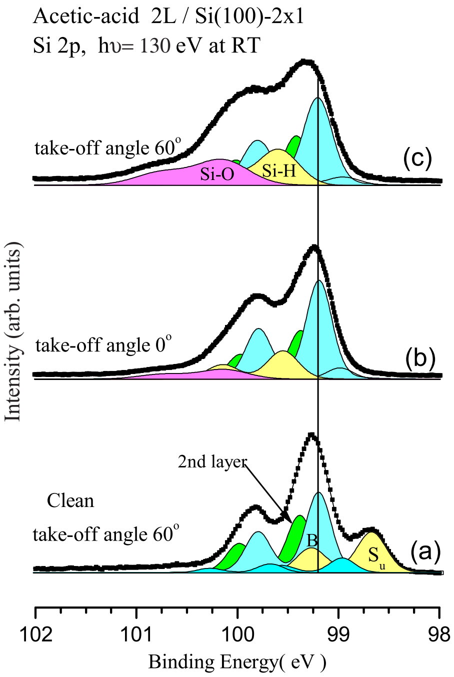

FIG. 1. (Color online) Si 2*p* spectra of 2 L acetic acid on Si(100)-2×1. (a) Clean Si at 60° take-off angle, (b) acetic acid on Si at 0° take-off angle, and (c) acetic acid on Si at 60° take-off angle. The prominent surface components for the up-dimer atoms (yellow) and for the second Si layer (green) in (a) are found to shift in opposite directions with adsorption of acetic acid in (b) and (c). The surface Si atoms bonded with H atoms (yellow), and O atoms (pink) grow as the take-off angle increases in (b) and (c). These spectra have been measured at the photon energy of 130 eV.

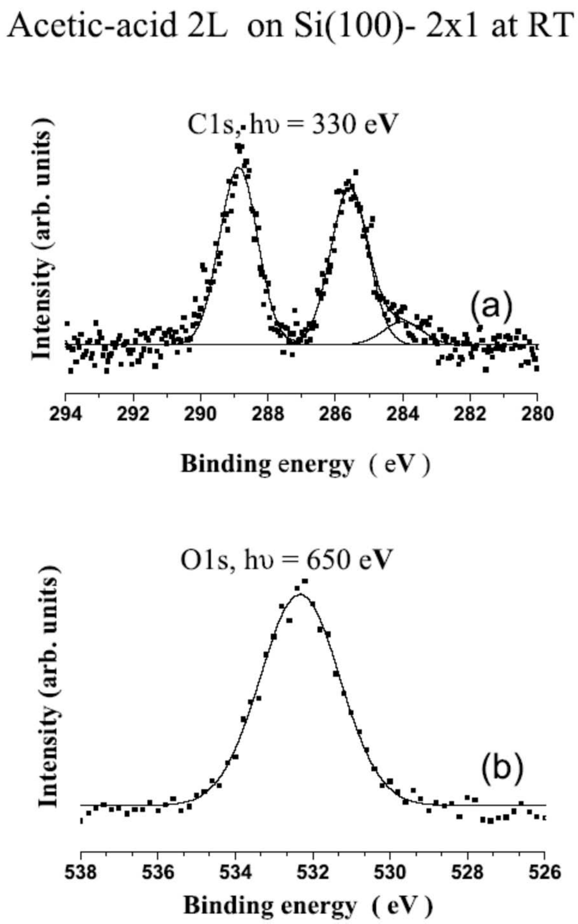

FIG. 2. (a) C 1*s* and (b) O 1*s* spectra obtained from the acetic acid chemisorbed on Si(100). These spectra were measured at the photon energies of 330 and 520 eV.

sample currents normalized to the signal acquired simultaneously with the gold mesh current in UHV. The carbon *K*-edge spectra have been measured in the photon energy region of 280–320 eV, with −210 V retarding voltage and 2.2 kV accelerating voltage. These conditions could provide the clear NEXAFS spectra that contain the structural information of the top few layers of the multilayer films by considering the probing depth less than 20 Å. The photon had a degree of polarization of about 85% and the incident photon energy resolution of 350 meV near the carbon *K*-edge region. All measurements were performed at room temperature. PES measurements have been employed to investigate the chemical states and the adsorption behavior of acetic acid on Si(100)-2×1.

Figure 1 shows surface sensitive Si 2*p* core level spectra of the clean and 2 L acetic acid dosed Si(100) surface at 300 K. At the 2 L exposure, the surface was saturated with the acetic-acid species. The photon energy was set at 130 eV. The spectral change of Si 2*p* can be seen more clearly through a proper curve-fitting procedure with spin-orbit split Voigt functions for quantitative analyses.[16] The clean surface spectrum [Fig 2(a)] has the characteristic shape associated with the Si 2*p* core level, which has been fitted with one bulk and four surface related components.[13,17] The major surface components for the up-dimer atoms (S_u) and for the second Si layer are observed with the core-level shifts of -0.57 ± 0.02 and 0.17 ± 0.02 eV from the bulk component B. The branching ratio and spin-orbital splitting are set to 0.5 and 0.6 eV, respectively. Using the Lorentzian width of 85 meV, the optimized Gaussian width value for the bulk (surface) component is 270 (240) meV. Following the dosing of acetic acid, the core level has been most consistently fitted by two chemically shifted components at binding energies of 0.37 and 0.96 eV with respect to the bulk peak, with the surface core-level shifted components completely attenuated. The core-level shift of the 0.37 and 0.96 eV components has been assigned to the surface Si atoms bonded with the H atoms and the O atoms of adsorbed acetic-acid molecules.[13,18–20] Figure 1(b) shows the Si 2*p* spectra at the take-off angle of 0° with a decreased surface sensitivity. Si—H and Si—O intensities decreased with the bulk peak. We suggest that acetic acid is chemisorbed on Si(100)-2×1 surface through the cleavage of O—H, forming a Si—O linkage between the substrate silicon dimer and oxygen atom of the acetic acid.

Figure 2 shows the C 1*s* and O 1*s* spectra of 2 L dosing acetic acid on Si(100) at 300 K. We notice that the C 1*s* spectrum [Fig. 2(a)] has two peaks of similar intensity, and a weak, low-binding energy component (284.2 eV). When fitting this peak, we find that this procedure gives two peaks with a relative chemical shift of 3.4 eV and full width at half maximum (FWHM) ~1.14 eV, implying the existence of two kinds of chemically inequivalent carbons. We have employed the Voigt function and the least-squares approach to determine the quality of the fitting. This energy shift corresponds to carbon atoms in a different chemical environment:[13,21] the component at higher binding energy can be assigned to the carbonyl carbon atoms (—C═O— bond) in the acetic acid and the peak at lower binding energy is attributed to the methyl carbon atoms (CH_3— bond). The intensity of these two peaks is in a 1:1 ratio, as expected for a surface bound acetic acid. This assignment can be confirmed by a similar binding energy position of the C 1*s* core level for acetic acid adsorbed on the Ge(001)-2×1 surface.[21] The weak, low-binding energy component (284.2 eV) has been attributed to the Si—C species resulting from a photon irradiation effect. This component grows with time of beam irradiation, but considering the low intensity (~6%), it is negligible as a minority species on the surface, as observed for some compounds on the related Si(100)-2×1 surface.[22–24] Photoelectron diffraction effects have not been considered. The O 1*s* core-level spectrum, recorded at a photon energy of 650 eV, is shown in Fig. 2(b). It consists of a single component with a sharp peak at 532.2 eV and FWHM=2.1 eV, which can be assigned to the C═O, —C—O—Si bond. O 1*s* chemical shifts are usually not large and it is possible that two or more unresolved oxygen species are present within the peak at 532.2 eV.[21] These PES results show that acetic acid was nondissociatively adsorbed on the Si(100)-2×1 surface through the cleavage of O—H, forming a CH_3COO—Si linkage between the substrate silicon dimer and the oxygen atom of the acetic acid. Similarly, previous studies of carboxyl group molecules on Si(100) have reported that the adsorption of carboxylic acids such as formic acid (DCOOD),[9] vinylacetic acid (CH_2CHCH_2COOH),[12] 4-aminobenzoic acid ($H_2NC_6H_4COOH$),[13] and benzoic acid[11] (C_6H_5COOH) on Si(100) resulted in the cleavage of the O—H bond,[10] therefore forming the DCOO—Si, CH_2CHCH_2COO—Si, $H_2NC_6H_4COO$—Si, C_6H_5COO—Si, and H—Si species. On the adsorption of these carboxylic acids on Si(100), it is interesting to notice that only one adsorption configuration involving the O—H bond cleavage was observed at room temperature.

Figure 3 shows NEXAFS spectra of 2 L dosing acetic acid on the Si(100) at 300 K at different incidence angles, between the direction of propagation of incident synchrotron light and the surface plane. These features were assigned to transitions from the C 1*s* orbital to the π^* (C═O) orbital at 288.6 eV and to the σ^* orbital in the region of 292–303 eV, respectively.[9,25] The curve fits were accomplished by performing a nonlinear least-squares routine using Gaussian functions for π^* resonant features, the Gaussian-broadened step functions for the edge jumps, and the asymmetrically broadened Gaussian functions for σ^* resonant features.[26,27] In order to determine the average angle between the double bond and the Si(100)-2×1 surface normal, we assume that the Si(100)-2×1 surface has the properties of a fourfold symmetry.[28] For the case of a substrate of fourfold symmetry, it is easy to obtain an analytical solution of NEXAFS intensity problem. The expression can be written as $I_P \propto \frac{2P}{3}\{1-\frac{1}{4}(3\cos^2\theta-1)(3\cos^2\gamma-1)\}+\frac{(1-P)}{2}(1+\cos^2\gamma)$, where γ and θ denote the angle between the surface normal and the normal to the molecular plane, and the angle between the light polarization and the surface plane, respectively; while P denotes the degree of polarization, assuming a polarization factor of $P=0.85$.[29]

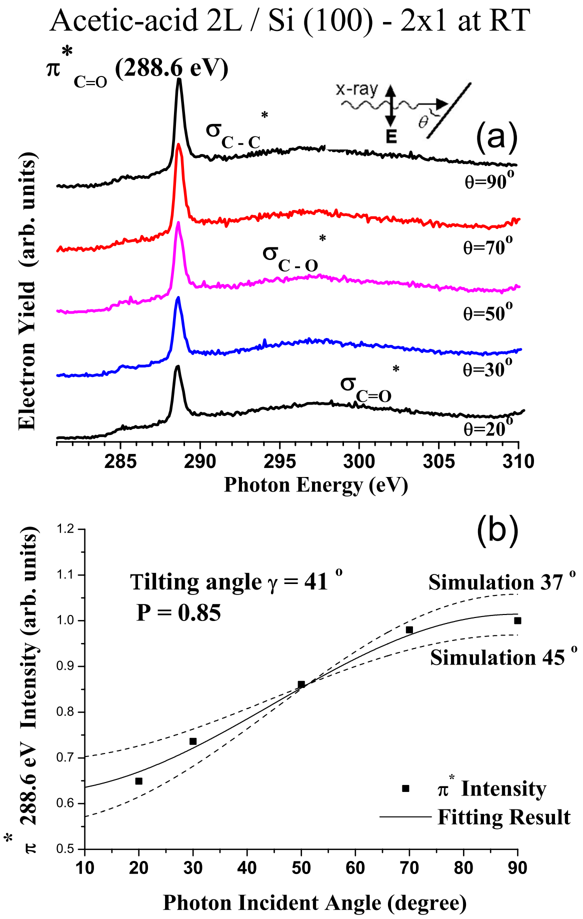

FIG. 3. (Color online) NEXAFS spectra measured from the 2 L acetic acid on Si(100)-2×1 at the different angles of incidence. (a) 288.6 eV resonance intensities as a function of the angle between the light polarization and the surface plane. (b) Results of fitting for the tilt angle: the experimental data (black square), the optimized curve fit (solid line), and the simulation results (dotted line).

The transition intensities depend on the orientation of the electric field vector components $E_\parallel$ and $E_\perp$ relative to the orientation of the molecule for the chemisorbed molecules. The π^* resonance intensity is strong when the incident photon angle is normal incident ($\theta=90°$), while it is weak when the incident photon angle is glancing incident ($\theta=20°$). Figure 3(b) shows the experimentally derived relative intensity for the 288.6 eV π^* (C═O) resonance as a function of the polarization vector angle. These values were obtained by measuring the height of the π^* (C═O) resonance intensity and the simulation, and the result of the curve fit, which was achieved by performing a nonlinear least-squares routine. As a result of quantitative analysis, the average angle γ obtained

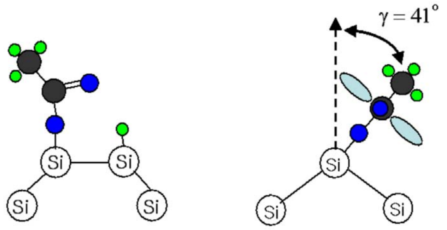

FIG. 4. (Color online) Geometrical representation of acetic acid chemisorbed on Si(100)-2 × 1. The O—H dissociation structure as shown on the left. The plane of the molecule is inclined at an angle of 41° with respect to the surface normal. This is indicated by the view down the plane of the molecule shown on the right. Black, blue, and green spheres represent C, O, and H atoms, respectively.

from these results is 41 ° ± 2° with respect to the surface normal, which is expected for a symmetric dimer with sp^3-like dangling bonds; the predicted geometry is schematically shown in Fig. 4. These angles are in good agreement with the O—H dissociation structure. This result is consistent with the room-temperature experimental observations and theoretical calculations that most of the carboxylic acids show the O—H dissociative adsorption on Si(100).[7–13] All these NEXAFS features (Fig. 3) are consistent with our PES results, suggesting the formation of a CH_3COO—Si and the cleavage of O—H, with the dangling bonds of silicon surface.

In the present work, we have investigated the Si 2*p*, C 1*s*, and O 1*s* core levels and NEXAFS for acetic acid on Si(100)-2 × 1 single-domain surface. The results indicate that acetic acid is nondissociatively chemisorbed on the Si(100)-2 × 1 surface at 300 K. The Si 2*p* core level results illustrate that the bonding interaction suggests the formation of Si—H and CH_3COO—Si bonds between the acetic acid and the silicon surface. The C 1*s* and O 1*s* core level results are consistent with the formation of the O—H dissociation structure. On the basis of the incident angle dependence of NEXAFS peak intensity of the transitions from the C 1*s* orbital to the π^* (C═O) orbital, we estimate the average angle between the double bond and the Si(100)-2 × 1 surface normal as ∼41 ° ± 2°. The selective chemisorption of acetic acid on the silicon surface may possibly serve as a functionality for further surface modification of Si(100)-2 × 1.

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2006-311-C00307). Experiments at PLS were supported in part by MOST and POSTECH. Useful discussion of the study by Hyung-Jin Kim, Department of Physics, Hanyang University, Korea is also gratefully acknowledged.

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[1] J. Hamers, J. S. Hovis, S. Lee, H. Liu, and J. Shan, J. Phys. Chem. **101**, 1489 (1997); J. S. Hovis, H. Liu, and R. J. Hamers, Surf. Sci. **402**, 1 (1998).
[2] C. Joachim, J. K. Gimzewsky, and A. Aviram, Nature (London) **408**, 541 (2000).
[3] R. J. Hammers, Nature (London) **412**, 489 (2001).
[4] F.-J. Meyer Zu, H. Dorf, M. C. Reuter, and R. M. Tromp, Nature (London) **412**, 517 (2001).
[5] S. F. Bent, Surf. Sci. **500**, 879 (2002).
[6] M. A. Reed, Proc. IEEE **87**, 652 (1999).
[7] H.-J. Kim and J.-H. Cho, Phys. Rev. B **72**, 195305 (2005).
[8] X. Lu, Q. Zhang, and M. C. Lin, Phys. Chem. Chem. Phys. **3**, 2156 (2001).
[9] H. Ikeura-Sekiguchi and T. Sekiguchi, Surf. Sci. **549**, 433 (1999).
[10] T. Bitzer, T. Alkunshalie, and N. V. Richardson, Surf. Sci. **368**, 202 (1996).
[11] T. Bitzer and N. V. Richardson, Surf. Sci. **369**, 427 (1999).
[12] A. Lopez, T. Bitzer, T. Heller, and N. V. Richardson, Surf. Sci. **480**, 65 (2001).
[13] H.-N. Hwang, J.-Y. Baik, K.-S. An, S.-S. Lee, Y.-S. Kim, C.-C. Hwang, and B.-S. Kim, J. Phys. Chem. B **108**, 8379 (2004).
[14] K.-J. Kim, T.-H. Kang, and B. Kim, J. Korean Phys. Soc. **30**, 148 (1997); S. Rah, T. Kang, Y. Chung, B. Kim, and K. Lee, Rev. Sci. Instrum. **66**, 1751 (1995).
[15] I. S. Ko, J. Y. Huang, D. K. Seon, C. B. Kim, and T.-Y. Lee, J. Korean Phys. Soc. **35**, 411 (1999).
[16] H. J. Kim (private communication).
[17] K.-J. Kim, T.-H. Kang, K.-W. Kim, H.-J. Shin, and B. Kim, Appl. Surf. Sci. **161**, 268 (2000).
[18] M. P. Casaletto, M. Carbone, M. N. Piancastelli, K. Horn, K. Weiss, and R. Zanoni, Surf. Sci. **582**, 42 (2005).
[19] M. P. Casaletto, R. Zanoni, M. Carbone, M. N. Piancastelli, L. Aballe, K. Weiss, and K. Horn, Surf. Sci. **447**, 237 (2005).
[20] M. P. Casaletto, R. Zanoni, M. Carbone, M. N. Piancastelli, L. Aballe, K. Weiss, and K. Horn, Surf. Sci. **505**, 251 (2002).
[21] M. A. Filler, J. A. Van Deventer, A. J. Keung, and S. F. Bent, J. Am. Chem. Soc. **128**, 770 (2006).
[22] A. Fink, W. Widdra, W. Wurth, C. Keller, M. Stichler, A. Achleitner, G. Comelli, S. Lizzit, A. Baraldi, and D. Menzel, Phys. Rev. B **64**, 045308 (2001).
[23] H. Liu and R. Hamers, Surf. Sci. **416**, 354 (1998).
[24] J. W. Kim, M. Carbone, M. Tallarida, J. H. Dil, K. Horn, M. P. Casaletto, R. Flammini, and M. N. Piancastelli, Surf. Sci. **559**, 179 (2004).
[25] J. Stohr, *NEXAFS Spectroscopy* (Springer, New York, 1992).
[26] A. Fujimori, T. Araki, H. Nakahara, E. Ito, M. Hara, N. Matsuie, H. Ishii, Y. Ouchi, and K. Seki, Bull. Chem. Soc. Jpn. **76**, 663 (2003).
[27] D. A. Outka and J. Stöhr, J. Chem. Phys. **88**, 3539 (1988).
[28] A. V. Teplyakov, M. J. Kong, and S. F. Bent, J. Chem. Phys. **108**, 4599 (1998).
[29] S. Krinsky, M. L. Perlman, and R. E. Watson, in *Handbook on Synchrotron Radiation*, edited by E. E. Koch (North-Holland, Amsterdam, 1983).