



Supporting Information

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Kinetic and Thermodynamic Control via Chemical Bond Rearrangement on Si(001) Surface

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To help identify the surface species which are produced upon adsorption of acetone on the Si(001) surface, we performed spectroscopic studies using FT-IR spectroscopy and X-ray photoelectron spectroscopy (XPS). Those results have demonstrated that the four-member ring and the dissociation species are produced upon adsorption. We describe experimental procedures, results, and discussion as to how we have identified the adsorbates.

1. Experiments

FT-IR and XPS studies were carried out in ultrahigh vacuum (UHV) systems with base pressures of $<1 \times 10^{-10}$ Torr. Highly doped (<0.004 ohm \cdot cm resistivity, As-doped) samples were used for the XPS experiments. Lightly doped (15 ohm \cdot cm resistivity, B-doped) samples were used for the FT-IR experiments in order to reduce free-carrier adsorption in the bulk. The Si(001) samples at ~ 340 K were exposed to acetone, and the XPS and FT-IR measurements were performed for the samples at room temperature. In the XPS experiments, the sample was oriented so that the detection angle for the photoelectrons was 65° with respect to the surface normal, in order to enhance surface sensitivity and minimize emission from the bulk silicon. Monochromatic Al- K_α ray (1486.6 eV) was used. Spectra in the C(1s) and O(1s) regions were obtained using a pass energy of 5.85 eV. The spectra have been corrected to yield a constant 99.4 eV binding energy for the bulk Si(2p_{3/2}) peak, ensuring that peak shifts in binding energies are solely due to changes in the local chemical environment. Curve fittings for the XPS spectra using Voigt line shapes were evaluated based on a reduced chi-square. When a reduced chi-square is less than or equal to 1.0,

the fit is statistically a good representation of the data [1]. FT-IR spectra were obtained using multiple internal-reflection geometry [2] with a Mattson RS-1 FT-IR spectrometer coupled to a UHV system through BaF₂ windows. InSb and HgCdTe detectors were used for the spectral region above 2000 cm⁻¹ and for the region below 2000 cm⁻¹, respectively.

2. Results

Figure 1 shows XPS spectra taken after a Si(001) sample at ~340 K was exposed to 20 Langmuir (5×10^{-8} Torr for 400 sec) of acetone. The spectrum of the O(1s) core level in Figure 1a is distinctly asymmetrical, showing two peaks at binding energies of 532.5 eV and 531.8 eV with an intensity ratio of 60:40. The fit results in a full-width at half-maximum (FWHM) of 0.96 eV for each peak and a reduced chi-square of 0.96. Because the FWHM is only slightly broader than the instrumental line width and because the reduced chi-square is less than 1.0, it is concluded that there are two types of chemically inequivalent oxygen atoms. Previous work has shown that an intact carbonyl oxygen has an O(1s) binding energy of 532.7 eV when acetone forms a multilayer on the Si(001) surface [3]. The O(1s) binding energies we obtained are shifted down by 0.2 eV and 0.9 eV in comparison with that observed for the physisorbed molecule.

The C(1s) spectrum in Figure 1b apparently consists of three peaks with binding energies of 286.7, 285.8, and 284.8 eV, with an intensity ratio of 14:18:69. Fitting to three Voigt line profiles yields a reduced chi-square of 0.98 and FWHM of 0.81, 0.85, and 1.2 eV for the peaks at 286.7, 285.8, and 284.8 eV, respectively. Although the reduced chi-square is less than 1.0 and the FWHM of the 286.7 and 285.8 eV peaks are almost the same as the instrumental resolution, the peak at 284.8 eV has the larger FWHM than the instrumental line width. This suggests that several chemically different carbons are not distinguishable and included in the peak at 248.8 eV, because their binding energies are within the instrumental line width.

Prior studies have shown that an intact carbonyl carbon in an acetone multilayer has a C(1s) binding energy of 287.6 eV [3], which is much higher than those observed in the C(1s) spectrum in Figure 1b. Changes in the C(1s) spectra compared to acetone multilayers suggest that the carbonyl bond is perturbed upon chemisorption. In recent studies, we found that adsorption of methyl iodide on the Si(001) surface creates a methyl group bound directly to the Si surface atom with the methyl carbon showing a C(1s) binding energy of 284.1 eV [4]. Acetone

on the Si(001) surface shows higher C(1s) binding energies than that for the CH₃-Si group, indicating that a similar species is not produced upon acetone adsorption.

Figure 2a shows an FT-IR spectrum taken after the Si(001) surface was exposed to 1.0 Langmuir (1×10^{-8} Torr for 100 sec) of acetone at ~ 340 K. After taking this spectrum, the sample surface was exposed to another 1.0 Langmuir dose of acetone and a second spectrum was obtained. The additional exposure did not increase the intensity of any adsorption peaks. Therefore, it is concluded that the spectrum in Figure 2a represents a surface saturated with acetone molecules. A weak peak is observed at 3114 cm^{-1} , which is within the region where C-H stretching modes of alkenes (C=C-H) are typically observed. The $2800\text{--}3000\text{ cm}^{-1}$ region shows several peaks; this spectral region corresponds to C-H stretching modes of saturated hydrocarbons. There is a sharp peak at 2080 cm^{-1} overlapped partially with a small peak at 2107 cm^{-1} , where Si-H vibrations are typically observed. The observation of the Si-H stretching suggests that some acetone adsorption involves C-H bond cleavage. A strong absorbance is also observed at 1624 cm^{-1} , where C=C stretching modes are typically observed. Figure 2b shows an FT-IR spectrum of acetone in the liquid phase, in which C=O stretching is observed at 1717 cm^{-1} . It has been reported that acetone in the gas phase has C=O vibration at 1731 cm^{-1} [5]. However, no absorption peak has been observed in the C=O stretching region for the spectrum in Figure 2a. Additionally, a peak at 3416 cm^{-1} in the liquid spectrum in Figure 2b, which is assigned to the overtone of the C=O stretching [5], has not been observed for the spectrum in Figure 2a. The absence of the C=O vibration indicates that the carbonyl bond is cleaved upon adsorption.

In prior studies, using samples of identical size in the same apparatus, it was found that the Si(001)-(2 \times 1)H monohydride surface, which has one H atom per surface Si atom, produced an integrated absorbance of 0.11 cm^{-1} . Integrating the area of the Si-H peak in the spectrum in Figure 3a yields a value of 0.024 cm^{-1} . This corresponds to hydrogen coverage of 0.22 monolayer for a surface saturated with acetone.

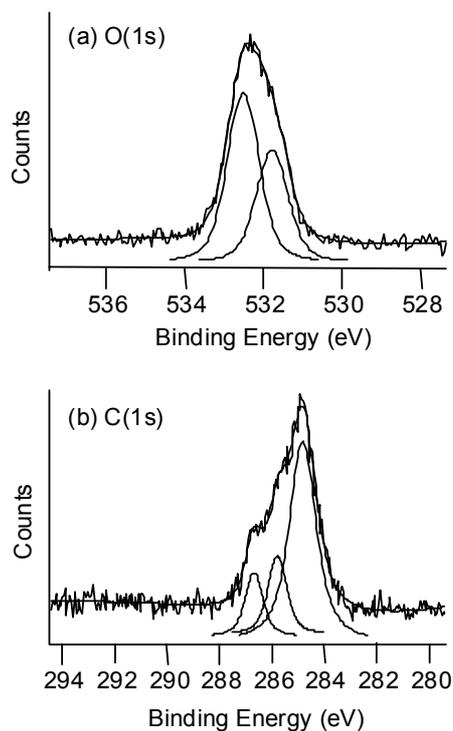


Figure 1. XPS spectra of Si(001) surface exposed to 20 Langmuir acetone at a temperature of 340 K: (a) O(1s) region; (b) C(1s) region.

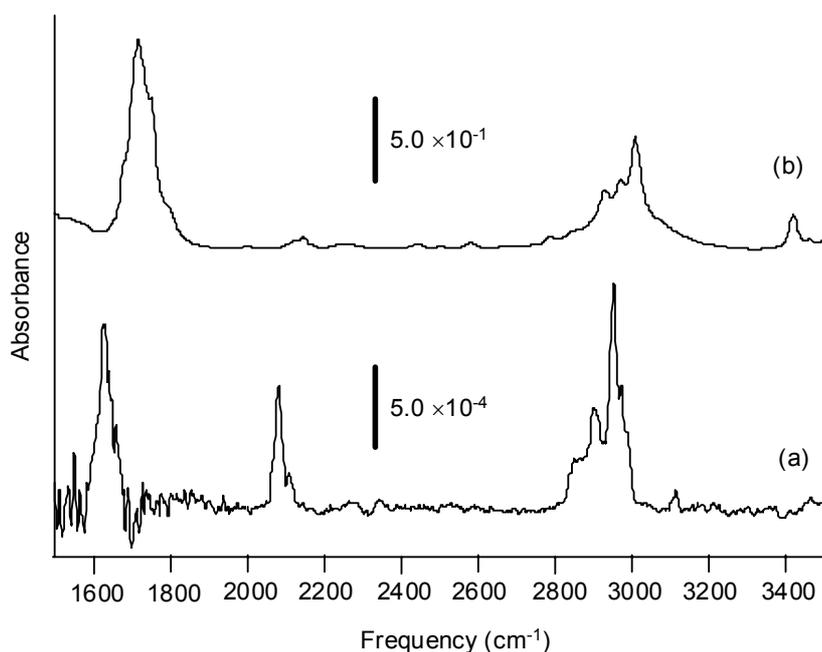


Figure 2. (a) FT-IR spectrum of Si(001) surface exposed to 1 Langmuir of acetone. (b) FT-IR spectrum of acetone in the liquid phase.

3. Identification of Bonding Configurations

Figure 3 schematically depicts five possible bonding configurations for acetone attached to the Si(001) surface. Because the XPS spectrum in the C(1s) region and the FT-IR spectrum clearly show that acetone adsorption perturbs the carbonyl bond and because the C(1s) XPS spectrum shows that no CH₃-Si group is present on the surface, the configurations shown in Figures 3c and 3d are ruled out as possible bonding configurations. The configuration in Figure 3e which is formed by the coordination through the non-bonding electrons on the carbonyl oxygen is also ruled out on the basis of the O(1s) spectrum in Figure 1a. Since the oxygen atom in Figure 3e is positively charged compared to the free molecule because of the donation of its non-bonding electrons to the surface silicon atom, it is expected that it has an O(1s) binding energy higher than that of the intact carbonyl oxygens. However, the O(1s) spectrum shows that

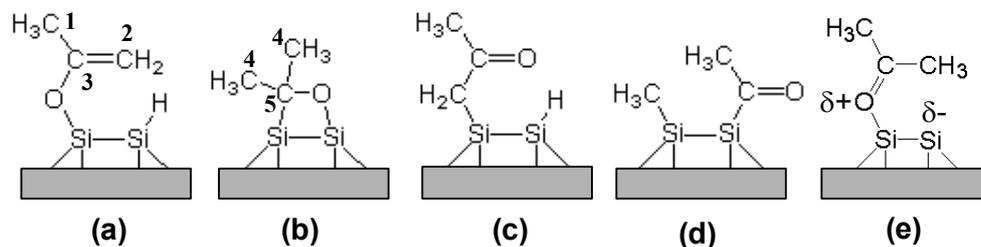


Figure 3. Five possible bonding configurations for acetone on Si(001) surface resulting from (a) dissociation reaction, (b) cycloaddition reaction, (c) C-H bond cleavage, (d) C-C bond cleavage, and (e) coordination via non-bonding electrons on a carbonyl oxygen.

the 1s core levels of oxygens exhibit lower binding energies than that of the acetone molecules in multilayers on the Si(001) surface, demonstrating that the configuration in Figure 3e is not present on the surface.

The presence of the dissociation species in Figure 3a is supported by the FT-IR spectrum in Figure 2a, in which the peaks at 1624 cm^{-1} and 3114 cm^{-1} are assigned to C=C stretching and alkene C-H stretching, respectively. The observation of Si-H stretching also provides evidence for the formation of the dissociation species. At the moment, it remains unclear why the Si-H absorbance is split into two peaks at 2080 and 2107 cm^{-1} , as shown in Figure 2a. It is known that a H-Si-Si-H species on the Si(001)-(2x1)H monohydride surface shows two IR adsorption peaks at 2087.5 cm^{-1} and 2098.8 cm^{-1} because of symmetric and asymmetric Si-H stretching modes [6]. The splitting of 27 cm^{-1} in the spectrum in Figure 2a, however, is not explained by the formation of the H-Si-Si-H species, because it is 2.4 times larger than a splitting of 11.3 cm^{-1} observed for the monohydride surface. Thus, we believe that the Si-H mode splitting occurs for other reasons.

The two O(1s) peaks of the XPS data in Figure 1a suggest that the acetone adsorption gives rise to another surface species in addition to the dissociation product. Because the C=O bond is cleaved only in the bonding configurations in Figures 3a and 3b, we believe that a cycloaddition reaction occurs, resulting in a four-member ring as shown in Figure 3b. The several peaks in the $2800\text{-}3000\text{ cm}^{-1}$ region of the spectrum (a) in Figure 2 are, then, assigned to the C-H stretchings of the methyl groups of both of the four-member ring and the dissociation

species.

The ratio of the dissociation product (Figure 3a) to the four-member ring product (Figure 3b) can be determined from the XPS spectrum of the C(1s) core level. The carbon atoms are labeled from 1 to 5 in Figures 3a and 3b. The carbon atoms of C1-C5 in Figures 3a and 3b are separated into three groups based on chemical environment. Group 1 comprises the C1, C2, and C4 atoms, each of which are bonded to one carbon atom. It is expected that these carbon atoms are in a similar chemical environment, and that their binding energies would be similar. Groups 2 and 3 consist of C3 and C5, respectively. The neighboring atoms of C3 are carbon and oxygen, while the neighbors of C5 are carbon, oxygen, and silicon. Due to the difference in chemical environment, C3 and C5 are not expected to have similar binding energies. We attribute these three carbon groups to three peaks observed in the C(1s) spectrum in Figure 1b based on the electronegativity consideration. Pauling electronegativities of silicon, carbon, and oxygen are 1.90, 2.55, and 3.44, respectively [7]. Since oxygen is more electronegative than carbon, a carbon atom in a C-O bond donates its electron density to the oxygen atom, leading to a larger binding energy than a carbon atom in a C-C bond. Thus, one can expect that the group consisting of C1, C2, and C4 will have a smaller binding energy than the C3 atom. Because the total number of the C1, C2, and C4 atoms is greater than that of the C3 or C5 atoms, they also should show a peak with the largest area intensity. Therefore, the peak observed at 284.8 eV is assigned to the C1, C2, and C4 atoms. Because the FWHM of the 284.8 eV peak is relatively large compared to the instrumental line width, the binding energies of C1, C2, and C4 appear to be slightly different from each other. Since carbon is more electronegative than silicon, a carbon atom bonded directly to the silicon surface is expected to withdraw the electron density of the silicon atom and to have a smaller core-level binding energy. Hence, it is expected that C5 has a smaller binding energy than C3. Therefore the peaks at 286.7 and 285.8 eV are assigned to C3 and C5, respectively.

Since the peaks at 286.7 and 285.8 eV represent one carbon from each configuration, they can be used to estimate product ratio. The area ratio of the 286.7 and 285.8 eV peaks is 44:56, suggesting that the ratio of the dissociation product (Figure 3a) and the four-member ring product (Figure 3b) is approximately 40:60. This product ratio estimated from the C(1s) spectrum is consistent with the O(1s) spectrum in Figure 1a, in which two peaks observed at 531.8 and 532.5

eV show the intensity ratio of 40:60. The 531.8 and 532.5 eV peaks in the O(1s) region are then attributed to the dissociation species and the four-member ring product, respectively.

The area intensity of the Si-H stretching in Figure 2a shows that the H coverage is 0.22 monolayer at the saturation, indicating that 44 % of the Si dimers are occupied with the dissociation product. This suggests that the remaining 56 % Si dimers react with the acetone molecules to generate the four-member ring product at the saturation. This is again consistent with the XPS data, and indicates that acetone molecules react with each surface dimer.

4. Summary

The adsorption of acetone on the Si(001) surface at ~340 K has been investigated using XPS and FT-IR spectroscopy. The FT-IR and XPS studies have shown that acetone is adsorbed on the Si(001) surface through two bonding configurations. 60% of the molecules is bound to the surface via a cycloaddition reaction involving the carbonyl group and the silicon dimer. The remaining 40% undergoes a hydrogen abstraction to form a Si-H bond and a C=C-O group.

5. References

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