Article

Ene-like Reaction of Cyclopentene on Si(001)-2 × 1: An XPS and NEXAFS Study

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Ⓢ *Supporting Information*

ABSTRACT: The control and the understanding of single-molecule covalent coatings on silicon surfaces is increasingly important in designing nanoscale electrical elements, such as organic/inorganic semiconductor hybrid structures. In this respect, ordered arrays of cyclopentene deposited on Si(001)-2 × 1 appear as promising buffer layers for further molecular crystal growth on the substrate. In this work, we examine the adsorption of cyclopentene on Si(001)-2 × 1 at 130 and 280 °C by means of C 1s XPS and NEXAFS. Until now cryogenic and room-temperature adsorption studies tended to prove that cyclopentene adsorption results from a formal cycloaddition ([2 + 2]-like) reaction of the C=C double bond with a silicon dimer. Our XPS/NEXAFS study reveals that an ene-like reaction competes with the [2 + 2]-like reaction channel, leading to the formation of products bearing a C=C bond, already at deposition temperature as low as ∼130 °C. This work helps to determine the optimum conditions leading to optimal chemical order in view of applications of cyclopentene as a buffer layer.
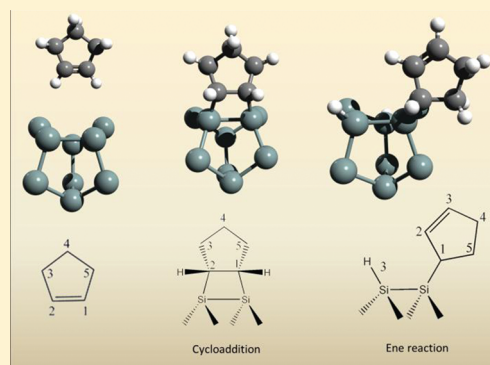
■ INTRODUCTION

The study of reactivity of organic molecules on the Si(001)-2 × 1 surface is strongly motivated by potential applications in the field of nanotechnologies and fabrication of functionalized materials. A wide variety of organic molecules can be the potential test subjects and have attracted lots of researchers across the globe to study these at times complex interfaces.[1] The Si(001) surface reactivity is largely determined by its peculiar surface reconstruction, characterized by the formation of silicon dimers.[2] The presence of formal Si=Si double bonds on the surface has inspired many research directions aiming at exploring possible analogies with the reactivity of alkenes despite the fact that the Si_2 π bond is weak and that dimer tilting (buckling) is associated with charge transfer between the down atom (electron-deficient) and the up atom (electron-rich). In fact, rather than concerted, stepwise reactions are envisaged for the Si_2 dimers, with the formation of low-symmetry radical-like intermediates.[3,4]

The prototypical molecule ethylene adopts a di-σ bonded geometry on top of the silicon dimer after a [2 + 2]-like reaction.[4,5] Only recently was evidence gathered for another reaction channel leading to the end-bridge configuration between two dimers in the same row.[6] However, the end-bridge is a minority species (14%). The chemistry of nonconjugated alkenes was assumed to follow the main characteristics of ethylene adsorption; that is, the molecular

anchoring occurs also via a formal [2 + 2] cycloaddition of the C=C bond on top of silicon dimers.[7−11]

Among this class of molecules, cyclopentene, a cyclic alkene (Figure 1a), has aroused great interest, largely motivated by its use to produce well-ordered buffer layers facilitating the further growth of molecular crystals on Si(001).[12,13] Indeed, scanning tunneling microscopy (STM) images of cyclopentene dosed Si(001)-2 × 1 present particularly well ordered molecular arrays on the surface.[8,9] The molecular imprint suggests that the molecule is adsorbed on the dimer top, in agreement with a formal di-σ cycloaddition, as shown in Figure 1b. High-resolution electron energy loss spectroscopy (HREELS) study of the surface exposed to cyclopentene at 90 K points to the formation of di-σ adducts without dissociation (absence of Si—H stretching mode).[14] Infrared spectroscopy performed after an exposure at 300 K is in line with the HREELS study, however, a weak Si—H stretching peak is observed, leading to the following comment by the authors "[this] suggests there is some dissociation on the surface.[15] It is not yet clear whether the dissociation arises from impurities in the cyclopentene or if it is intrinsic to the preparation procedure". C 1s core-level X-ray photoelectron spectroscopy (XPS) exhibits three distinct structures at ∼284, ∼284.8, and at ∼295.4 eV.[14,16,17] There is
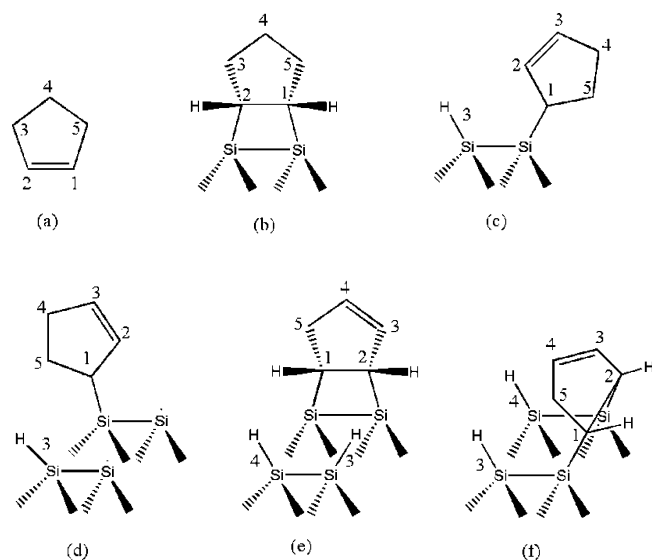
Figure 1. Schemes of the reaction products: (a) the free cyclopentene molecule, (b) the cycloaddition ([2 + 2]-like) product, (c) the ene-like reaction product (on-dimer), (d) the ene-like reaction product (interdimer), and (e,f) result of two successive ene-like reactions.

a general agreement to attribute the first two lines to C−Si bonds and CH$_2$ bonds, respectively. The third high BE structure is ascribed to physisorbed cyclopentene.[18] Alternately, only two asymmetric core level components can describe the spectrum taking into account the vibrational series,[17] which are indeed observed in the C 1s XPS spectrum of free cyclopentene.[19] Ultraviolet photoelectron spectroscopy (UPS) confirms the absence of C=C bonds surviving the adsorption at 140 K, in agreement with the cycloaddition view.[14,20] Further refinement of cyclopentene geometry was sought by using X-ray photoelectron diffraction (XPD).[17] The angular dependence of the C 1s peaks is accounted for by a cis-type molecule di-σ bonded to an on-dimer site.

A possible dissociation state of cyclopentene on Si(001)-2 × 1 has not yet been considered, except in the special case where dissociation is induced purposely under an STM tip by current injection.[21] In fact, within the scheme of an ene-like reaction,[22] cyclopentene could react with one Si$_2$ dimer to give a silicon monohydride and a π-bond bearing adsorbate on top of the silicon dimer (Figure 1c). The end-bridge site (consisting of two Si radicals) could equally be involved to give the same final product, but the detached H atom should stay on the neighboring dimer (Figure 1d) and two Si atoms remain uncapped. Two successive ene-like reactions (leading to the abstraction of two H) on two adjacent dimers could lead to the adsorbate geometries given in Figure 1e,f, with all Si dangling bonds saturated.

Although ene-like reactions are not documented on Si(001)-2 × 1, chloroacetonitrile reacts with an ad atom/rest atom pair on Si(111)-7 × 7 (deposited at cryogenic temperature followed by annealing to room temperature) via the scheme given in ref 23. (The chlorine is abstracted by a silicon dangling bond.) In a similar way, acetone adsorbs on Ge(001)-2 × 1 (a surface akin to Si(001)-2 × 1) via C−H bond cleavage.[24]

In the present Article, we raise the issue of a possible dissociative adsorption of cyclopentene via an ene-like reaction and look for signatures of π-bond bearing adducts in the C 1s XPS and near-edge X-ray absorption fine structure spectra.[25] We show that the [2 + 2]-like reaction and an ene-like reaction

compete on the surface, already at 130 °C, and that the proportion of π-bond bearing adducts increases with substrate temperature.

■ EXPERIMENTAL SECTION

The experiment was carried out at TEMPO beamline at the French synchrotron facility (SOLEIL) at Saint-Aubin, France. Highly doped (phosphorus) n^+-type Si(001) wafers (resistivity of 0.003 Ω × cm, N_D 2 × 10^{19} cm^{-3}) were cleaned from their native oxide by prolonged degassing (600 °C for ∼8 h) and flash annealing (Joule effect) at 1100 °C in ultrahigh vacuum (10^{-10} mbar base pressure).

The resulting clean Si(001)-2 × 1 surface was then exposed to 6.75 L (1 L = 10^{-6} Torr × s) of cyclopentene by dosing for 15 min under pressures in the range of 5 × 10^{-9} to 10^{-8} mbar. The cyclopentene dosage was carried at two different substrate temperatures of 130 °C and of 280 °C. These temperatures were estimated afterward using a C-type thermocouple attached to the backside of similar samples with UHV-compatible cement. Detailed experimental setup is described in ref 26. Cyclopentene molecule (C$_5$H$_8$), liquid at room temperature, was purchased from Aldrich (99.99%) and purified by several freeze−pump−thaw cycles before dosing.

The beamline X-ray spot (normally focused in a spot 45 μm long in the horizontal direction by 10 μm wide in the vertical dimension) was defocused on purpose to a spot of dimensions 1 mm × 2 mm without losing photoelectron count rate while the sample was moved before and after each acquisition to limit beam damage. Photoelectrons were detected at 0° from the sample surface normal and at 46° from the polarization vector **E**. The C 1s XPS core-level spectra were recorded at $h\nu$ = 350 eV with an overall experimental resolution better than 100 meV. The zero BE (i.e., the Fermi level) was taken at the leading edge of a clean molybdenum foil in electrical contact with the silicon sample.

To quantify the amount of deposited carbon, we recorded the C 1s spectra at $h\nu$ = 390 eV (kinetic energy (KE) ≈ 105 eV) close to that of the Si LVV Auger peak (∼80−88 eV range). The C 1s photoemission peak integrals are normalized with respect to an equal Si LVV height.

C 1s NEXAFS spectra of the adsorbed layer were recorded in Auger yield mode using a KE window of 12 eV, centered at 263 eV. The measurement of the C 1s edge is made feasible thanks to a procedure allowing the cleaning of the mirrors (using mercury UV lamp in 400 mbars of ultrapure O$_2$ in the beamline) and leading to a minimization of the absorption dips in the photon flux at C 1s absorption edge about 285 eV and at photon energy above 800 eV due to antireflection coating effects.[27] Raw spectra divide the spectrum of the clean surface to correct modulations in the X-ray beam intensities. The Auger yield spectra are normalized to equal intensity jumps between 280 and 320 eV. NEXAFS measurements are done at different angles θ between the normal to the sample surface and the polarization vector **E**, in the range of 10 (grazing incidence) to 90° (normal incidence). The orientation of the molecular orbitals is derived using these angle-dependent normalized spectra.[25] The spectrum of a thick layer of solid cyclo-octatetraene (C$_8$H$_8$) condensed on a silicon substrate is measured in the total electron yield mode. (The raw spectrum is divided by that of the clean surface, also measured in total yield.) The spectrum of this 100% sp^2 molecule is used as a reference to evaluate the concentration of sp^2 carbons in the deposited cyclopentene layers.
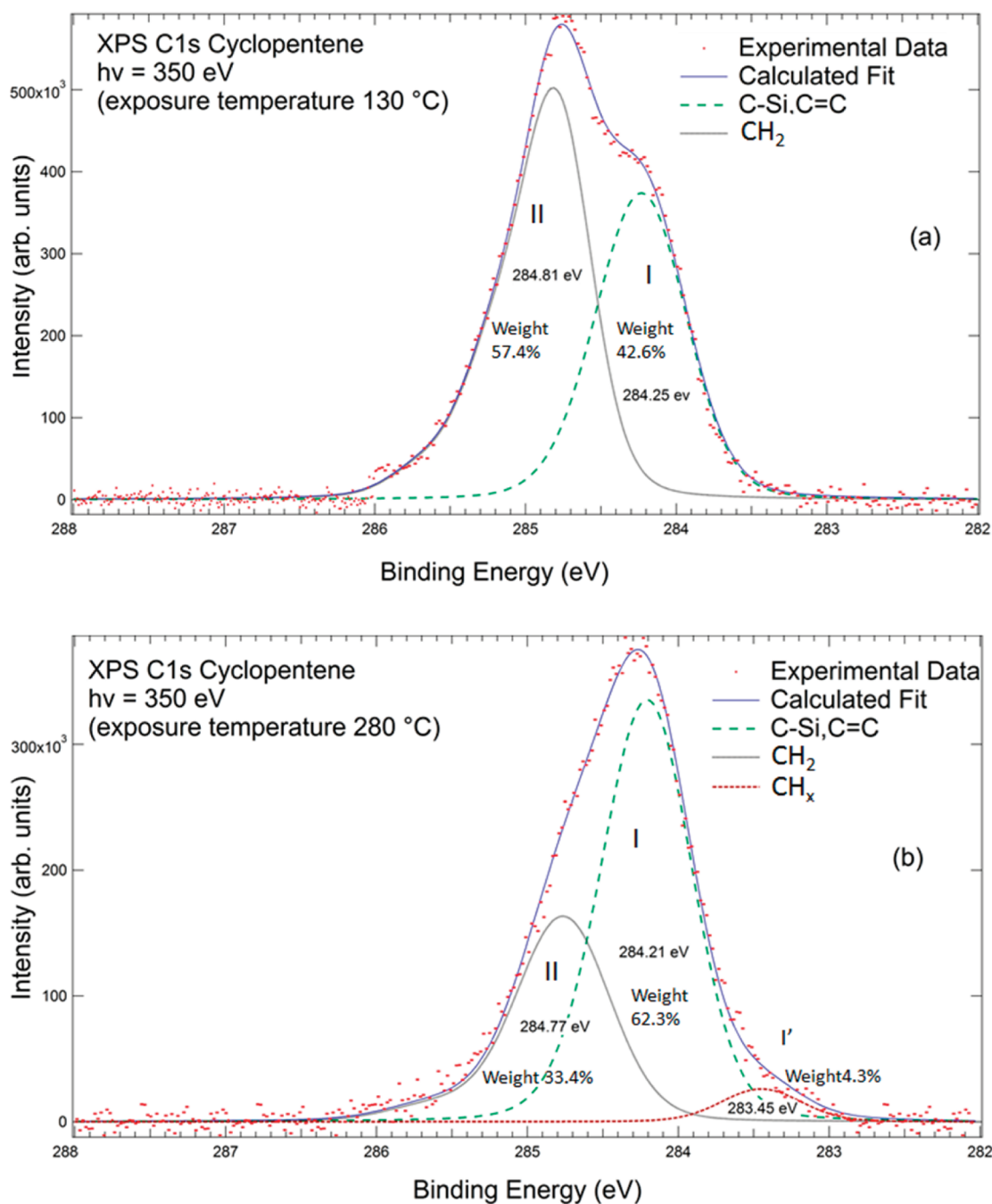
Figure 2. C 1s XPS photoemission spectra recorded at photon energy of 350 eV for (a) 130 and (b) 280 °C exposures. The Si(001)-2 × 1 surface was exposed to cyclopentene for 15 min under a pressure of 10^{-8} mbars.

■ RESULTS AND DISCUSSION

XPS Core-Level Spectroscopy. The exposure to cyclopentene was done at two temperatures, 130 and 280 °C, under a pressure of 10^{-8} mbar for duration of 15 min for each case. The coverages are close to saturation as nearly all of the Si 2p surface states are quenched. (See the Supporting Information.)

C1s XPS spectra are reported in Figure 2a,b, corresponding to the substrate temperatures during cyclopentene exposure of 130 and 280 °C, respectively. The excitation energy was 350 eV, and the spectra were recorded at normal emission. A Shirley background was subtracted from all core-level spectra presented here. The spectrum corresponding to an exposure at 130 °C has been fitted using only two components, with an asymmetrical shape to account for vibrational progressions.[17] Asymmetric peaks have been created by broadening experimental gas phase data, as detailed in the Supporting Information.[19] The spectrum corresponding to an exposure at 280 °C needs the introduction of an extra small Gaussian component at low binding energy (BE). The fitting components, BE, and spectral weights (%) are also reported in Figure 1.

In the C1s spectrum of the 130 °C surface (Figure 2a), we find peak I at 284.25 eV (spectral weight = 42.6%) and peak II at 284.81 eV (spectral weight = 57.4%). The decomposition and the BE are similar to the one obtained by Weier at normal emission ((peak I/peak II) = (41%/59%)).[17] Following refs 15 and 17, we can attribute peak I to carbon atoms directly bonded
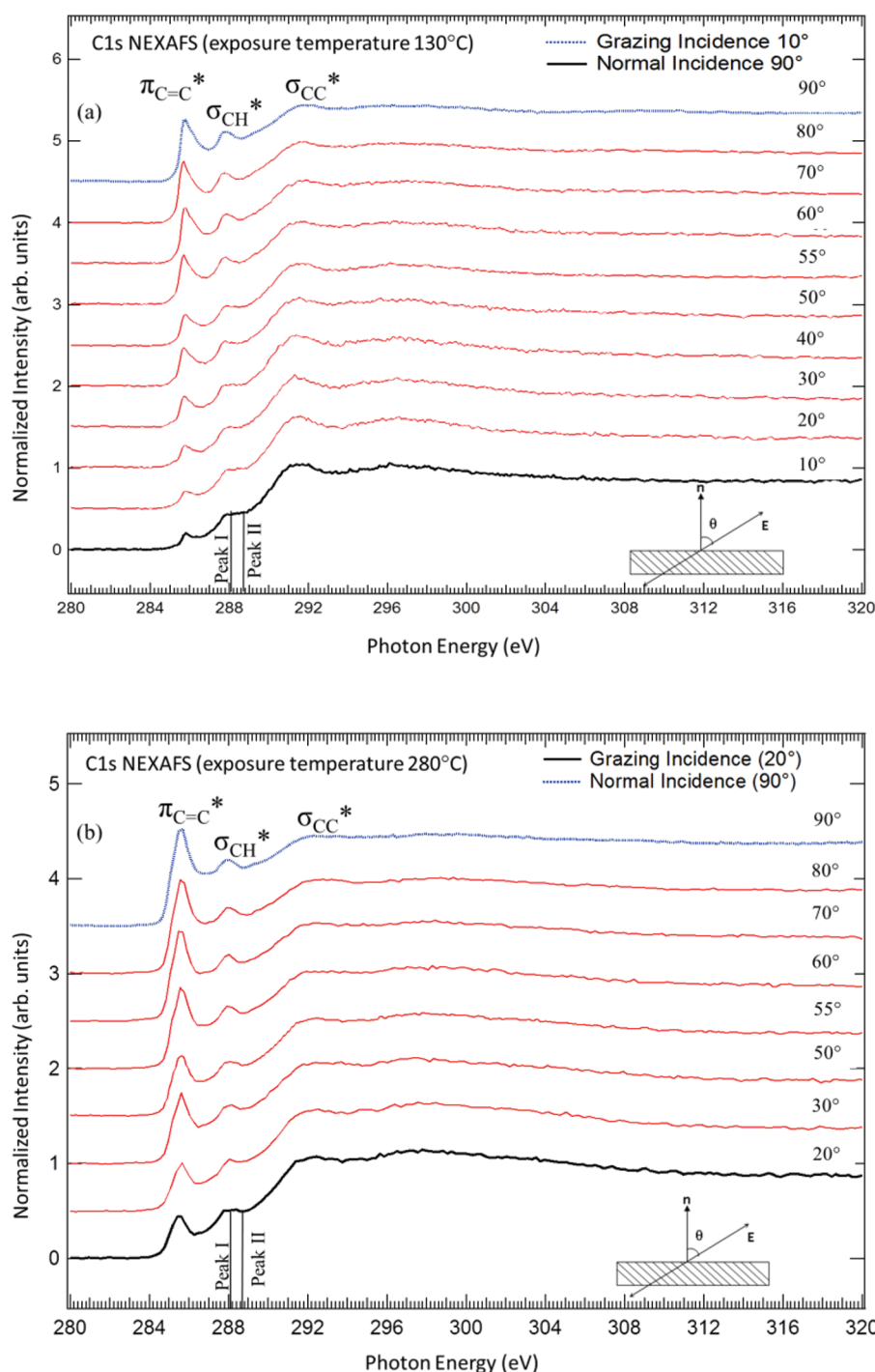
Figure 3. C 1s (Auger yield) NEXAFS spectra for (a) the 130 °C and (b) the 280 °C adsorption, for various values of θ, the angle between the radiation polarization and the normal to the surface. The ionization potentials IP (peak I) and IP (peak II) are indicated as vertical bars. The spectra are normalized to equal intensity jumps measured before the edge (at $h\nu = 280$ eV) and far after the edge (at $h\nu = 320$ eV).

to Si(001) and peak II to CH_2 units. Assuming a [2 + 2]-like cycloadded product, 2 C atoms in 5 are bonded to Si, thus corresponding to a weight of 40%. The peak I/peak II intensity ratio apparently fits with this adsorption model. We shall see next that the situation is in fact more complex.

The C 1s XPS spectrum of the 280 °C sample presented in Figure 2b is markedly different from that of the 130 °C sample. A low BE peak (Peak I′) appears at 283.45 eV (spectral weight = 4.3%) and is attributed to carbonaceous species (CH_x) resulting from the decomposition of the molecule on the

surface.[28] Peaks I and II appear at practically the same BE as the spectrum for 130 °C surface, but their relative weights have changed much. Peak I weight is ∼62% of the spectral weight instead of 42.6% for the 130 °C sample. This means that peak I does not only contain the C−Si moiety contribution. Because of the strength of the C−H bond, its cleavage in an ene-like reaction is thermally activated.[29] Therefore, an increase in temperature can favor the production of adducts bearing a C=C bond. C=C and C−Si moieties are indistinguishable in the high-resolution XPS spectra of 1,3-butadiene [4 + 2]-cyclo-

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added to the silicon dimer forming a Si−CH₂−CH=CH−CH₂−Si unit.[30] Therefore, we can hypothesize that peak I is related both to C−Si and C=C moieties. With the process of dehydrogenation (see Figure 1) the proportion of CH_2 carbons decreases: 3/5 for a [2 + 2]-like cycloaddition, 2/5 for an ene-like reaction (one H abstracted), and 1/5 for two consecutive ene-like reactions (two H abstracted). This assumption explains qualitatively the temperature trend observed in Figure 2a,b.

We note also that the saturation coverage at 280 °C is less than that at 130 °C. The normalized XPS C 1s intensities (using Si LVV Auger line as explained above) I_{C1s}^{XPS} ratio, $(I_{C1s}^{XPS}(280\ °C))/(I_{C1S}^{XPS}(130\ °C))$, is ∼0.65. Considering that a [2 + 2]-like cycloadded product is dominant at low temperatures, this ratio suggests that the dissociated product occupies more than one silicon dimer. This may be indicative of the presence of two-H abstracted geometries.

C 1s NEXAFS Spectroscopy. C 1s NEXAFS spectroscopy can provide a clear-cut confirmation of the presence of C=C bonds. It is known that the $\pi_{C=C}^*$ bound states appear at excitation energies of 285−286 eV, well-separated from the σ_{C-C}^* transitions at 291 to eV with a strong oscillator strength.[31]

In Figure 3a, we present the normalized angle-resolved NEXAFS spectra of cyclopentene adsorbed on Si(001)-2 × 1 surface at 130 °C, corresponding to the C 1s XPS spectrum given in Figure 2a for angle θ (the angle between the surface normal and the polarization vector **E**) specified on the graph. The measured ionization potentials (IPs) (referenced to the vacuum level) ∼288.1 eV (peak I) and ∼288.7 eV (peak II) are also indicated.

Three NEXAFS resonances are observed at ∼285.7, 287.8, and 291.7 eV. The shape and energy of the first one is clearly associated with a transition involving a $\pi_{C=C}^*$ (bound state). The intensity of this peak changes drastically with varying θ. Next to it is another bound state peak at 287.8 eV, which is attributed to antibonding C−H levels and labeled as σ_{C-H}^*. At excitation energies higher than the IP, there is a broad σ_{C-C}^* structure at 291.7 eV whose dichroic behavior is opposite to that of $\pi_{C=C}^*$. The presence of the double bonds cannot be explained if the molecule reacts through a [2 + 2]-like reaction. As a consequence, alongside cycloaddition, we believe that certain cyclopentene molecules attach to the surface via an ene-like reaction including a H abstraction already at 130 °C. The ene-like product shown in Figure 1c is one of those envisaged by Yoder et al. in their STM study of C−H breaking due to tip current injection.[21] The dichroic behavior of $\pi_{c=c}^*$ shows that the axis of the C 2p orbitals constituting the π system is rather aligned with the normal to the surface. (The absorption is maximum when the 2p orbital axis is parallel to **E**, and null when it is perpendicular to **E**.)[32] The angle α between the surface normal and the C 2p orbital axis of the $\pi_{c=c}$ system is calculated by the formula given in ref 33 valid for a substrate of three-fold or higher surface symmetry (the two-domain silicon surface reconstruction ensures a four-fold surface symmetry), which can be rewritten as

$$\frac{I_\theta}{I_{magic}} = 1 + \frac{1}{2}(3\cos^2\theta - 1)(3\cos^2\alpha - 1)$$

where I_θ is the θ-dependent absorption intensity of the $\pi_{C=C}^*$ transition and I_{magic} is the intensity at magic angle (55°).

By plotting $(I_\theta)/(I_{magic})$ against $(3\cos^2\theta - 1)$ (see Figure 4), we get the slope $(1/2)(3\cos^2\alpha - 1)$ from where we deduce

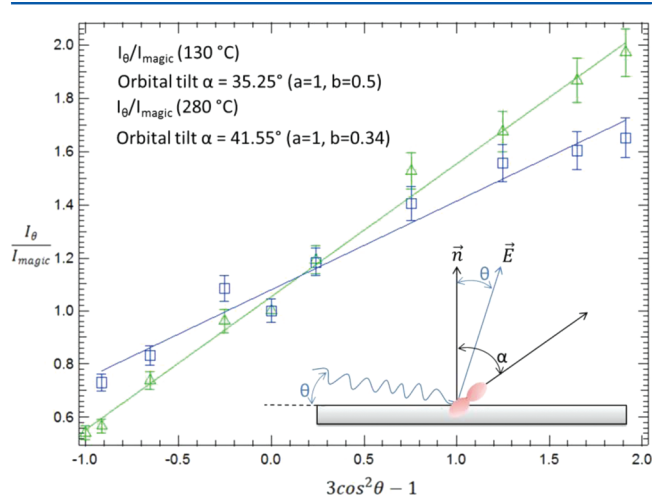the tilt angle α of the π bond C 2p orbital ∼35° by a linear fit (for the sample exposed to cyclopentene at 130 °C).

Figure 4. Plot of I_θ/I_{magic} against $(3\cos^2\theta - 1)$. The I_θ/I_{magic} curves are fitted by lines of intercept a and slope b. For the 130 °C adsorption $(a,b) = (1, 0.5)$ and for the 280 °C adsorption $(a,b) = (1,0.33)$. Slope b is equal to $1/2(3\cos^2\alpha - 1)$, where α is the tilt angle between the C 2p orbital axis (π bond) and the normal to the surface. Molecular tilt angles are indicated.

In Figure 3b, we present the normalized NEXAFS spectra of cyclopentene adsorbed on Si(001)-2 × 1 surface at 280 °C, corresponding to the C 1s XPS spectrum given in Figure 2b. We observe the same transitions as in the NEXAFS spectrum of the 130 °C sample. However, qualitatively, it is clear that the intensity of the $\pi_{C=C}^*$ transition has strongly increased with respect to the 130 °C deposit. It suffices to compare (Figure 5) the 280 and 130 °C spectra measured at magic angle (θ = 55°), for which the $\pi_{C=C}^*$ intensity is independent of the π bond orientation in space.[33] As for the preceding case, we can determine the tilt angle α of the π bond C 2p orbital, which is now ∼42° (Figure 4).

To evaluate the distribution of sp³ and sp² carbons in the cyclopentene films, we can make use of the Thomas−Reiche−Kuhn sum rule stating that for a given electron in an atom the sum of the oscillator strengths of all transitions to all other states is unity.[34] For the K shell, the integration of the absorption spectrum (after subtraction of a background from lower energy shells) is approximately proportional to the number of electrons in the subshell. For an integration window between 280 and 320 eV, the sum rule works satisfactorily in the case of diamond (pure sp³) and graphite (pure sp², measured at magic angle).[35] Díaz et al.[35] determined the absolute sp² bonding concentration in carbon films, measuring the area of the π* band relative to the total area of the spectrum (in the 280−320 eV window), using a "100% sp²" reference (C₆₀).

We apply the same approach to evaluate the sp² carbon content in the deposited cyclopentene films. We measure the area of the $\pi_{C=C}^*$ transition A_π in the adsorbed cyclopentene spectra (measured at magic angle), which we divide by the integral INT_{abs} of the absorption curve, calculated in the 280−320 eV energy interval. (The ratio $(A_\pi)/(INT_{abs})$ is a number proportional to the number of sp² carbons.) In Figure 5, we compare the NEXAFS spectra of the deposited cyclopentene layer to that of solid cyclooctatetraene[36] (also measured at
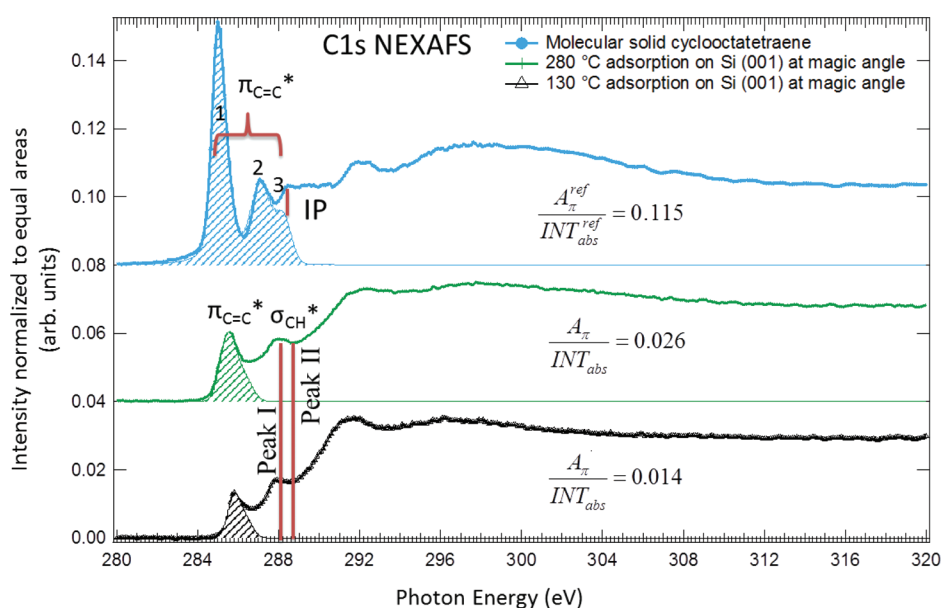
Figure 5. C 1s NEXAFS spectra measured at magic angle of solid cyclooctatetraene (top curve) and of cyclopentene adsorbed on Si(001)-2 × 1 at 280 °C (middle curve) and at 130 °C (bottom curve). All spectra are normalized to equal areas in the 280−320 eV energy window. The $\pi_{C=C}$* areas are hatched. The spectrum of the 100% sp² cyclooctatetraene molecule is used as a reference to estimate the ratio sp²/(sp² + sp³) in the deposited layers. (See the text.)

magic angle). Solid cyclooctatetraene fulfills the conditions for being a reference: (i) it is constituted of 100% sp² carbons, (ii) the molecule is nonconjugated and therefore the π* transitions (labeled 1 to 3) are well-identified,[37] and (iii) as it is a molecule, excitonic transitions affecting the intensity of the π* transition (as in sp² solids like graphite[35]) are not present. The spectra in Figure 5 are normalized to equal areas, integrated between 280 and 320 eV, and the $\pi_{C=C}$* areas are hatched.

Using the cyclooctatetraene reference, we can give an estimate of the percentage of sp² carbons sp²(%) in the deposited layer using the formula:

$$\text{sp}^2(\%) = 100 \times \frac{A_\pi}{A_\pi^{\text{ref}}} \times \frac{INT_{\text{abs}}^{\text{ref}}}{INT_{\text{abs}}}$$

where $A_\pi^{\text{ref}}(INT_{\text{abs}}^{\text{ref}})$ are the $\pi_{C=C}$* area (280−320 eV window integral) of the cyclooctatetraene reference spectrum.

For the 130 °C sample, we find sp²(%) equal to 12%. For the 280 °C sample, sp² (%) increases up to 22.6%. The concentration of ene-like products C_{ene}, equal to (5/2) × sp²(%), would be ∼30% for the 130 °C experiment and ∼56% for the 280 °C experiment.

We examine now the consistency of NEXAFS and XPS data analyses. The concentration of carbons in CH₂ moieties (CH₂(%)) can be calculated from the C_{ene} values given by NEXAFS (with assumptions on the degree of dehydrogenation) and compared with the weight of peak II in the XPS spectra. (See Figure 2.) For the 130 °C sample, CH₂(%) is 54% for one abstracted H (two CH₂ moiety per molecule) and 48% for two abstracted H (one CH₂ moiety per molecule), to be compared with a peak II/(peak I + peak II) ratio of 57.4%. For the 280 °C sample, CH₂(%) is 47% for one abstracted H, and 35% for two abstracted H, to be compared with a peak II/(peak I + peak II) ratio of 35%. The NEXAFS/XPS comparison suggests that the number of abstracted H per adduct increases with increasing temperature, in accord with a molecular coverage lower at 280 °C than at 130 °C.

The present work that demonstrates the presence of $\pi_{C=C}$ bond bearing adducts (implying C−H bond cleavage), when the surface is exposed to cyclopentene at 130 °C and above, does not contradict, but instead complements, previous experiments. Adsorption at cryogenic temperature (90 K) leads to molecular adsorption via a [2 + 2] cycloaddition-like mechanism due to the absence of Si−H stretching (2090 cm⁻¹), C=C (1617 cm⁻¹) stretching, and sp² C−H stretching (3066 cm⁻¹) modes in the HREELS spectra.[14] As already emphasized in the Introduction, Hamers and coworkers observed a weak but significant Si−H stretching mode near 2070 cm⁻¹ after adsorption at room temperature.[9] However, nothing is known on the C=C bond stretching mode of the ene-like product (Si−CH₂−CH=CH) as the infrared window in ref 9 ends before 3000 cm⁻¹. In any case, in alkyl-substituted RCH=CHR the C=C stretching mode is reported to be weak.[38]

■ CONCLUSIONS

The reaction products of cyclopentene formed on the Si(001)-2 × 1 surface at 130 and 280 °C were examined using C 1s XPS and NEXAFS in combination. XPS C 1s spectra are strongly affected by the deposition temperature. Two main peaks are observed at 284.25 (peak I) and 284.81 eV (peak II). We show that the weight of peak I strongly increases when the temperature is increased. We attribute peak II to carbon in CH₂ moieties and peak I to C−Si and tentatively to C=C bonds, resulting from an ene-like reaction (implying C−H bond cleavage) competing with [2 + 2]-like cycloaddition. The presence of C=C π bonds is confirmed by NEXAFS spectroscopy, as a strong bound state transition is observed at $h\nu$ = 285.6 eV. The π bond concentration increases with increasing substrate temperature. An evaluation of the sp² carbon concentration in the deposited films is given by comparison with a solid cyclooctatetraene reference. XPS also shows that the saturation molecular coverage is less at 280 °C than at 130 °C. In view of the application of cyclopentene films

as buffer layers on Si(001)-2 × 1 for the growth of molecular crystals, the occurrence of a dissociative reactions (ene-like and carbonaceous) competing with cycloaddition will affect molecular ordering and likely the protective efficiency, especially when H-decorated dimers are formed. As silicon surfaces are generally cleaned via Joule heating (at temperatures higher than 1000 °C), a controlled cooling of the surface is strongly recommended to create condition leading to the selective formation of [2 + 2]-like adducts with high surface density.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Si 2p spectra for clean and cyclopentene covered Si(001)-2 × 1 substrate with the fit parameters used and asymmetrical fits for C1s. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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