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A Synchrotron Radiation X-ray Photoemission Spectroscopy Study of *n*-Propyltriethoxysilane Adsorption on Si(001)-2 × 1 at Room Temperature

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The reaction of *n*-propyltriethoxysilane (PTES) with clean Si(001)-2 × 1 at room temperature is studied by synchrotron radiation X-ray photoemission spectroscopy (XPS). It is shown that PTES dissociatively adsorbs on the surface via the scission of at least two Si−O bonds. Adsorbate geometries are proposed accounting for the XPS data, and possible reaction paths are discussed, considering the zwitterionic nature of the surface silicon dimers. The understanding of the reactivity of the triethoxysilane termination on clean silicon paves the way to its possible use as an anchoring unit enabling the grafting of complex multifunctional molecules.

Introduction

Because of potential applications in molecular electronics,[1] the reaction of organic compounds on clean silicon surfaces has been of considerable interest since the beginning of the silicon surface chemistry studies in the mid 1980s.[2] A number of review papers published on this subject during the past decade[3−7] testifies that this particular research field is flourishing. On the other hand, the reactivity of organometallics, or of organosilanes compounds (like alkoxysilanes), has received much less attention.[6] Alkoxysilane precursors are essentially used to form self-assembled monolayers on hydroxylated silica surfaces, in the presence of an adsorbed water layer.[8]

Nevertheless, alkoxysilanes do react with Si(001)-2 × 1 and Si(111)-7 × 7 at room temperature, enabling the grafting of hydrocarbon fragments on these surfaces.[9] The molecules examined so far were essentially precursors used in the deposition of silicon dioxide, such as tetraethoxysilane ($[CH_3CH_2O]_4Si$, TEOS)[9,10] and diethyldiethoxysilane ($[CH_3CH_2]_2Si[OCH_2CH_3]_2$, DEDEOS).[11]

The present paper examines specifically the reactivity of *n*-propyltriethoxysilane ($CH_3CH_2CH_2Si[OCH_2CH_3]_3$, PTES) at room temperature with a clean, reconstructed Si(001)-2 × 1 surface, using synchrotron radiation X-ray photoemission spectroscopy (XPS). As PTES presents Si−O−C and Si−C bonds, the previous studies on TEOS and DEDEOS may provide hints on the possible dissociation mechanisms on the surface. After exposure of the Si(111)-7 × 7 surface to TEOS, the C 1s XPS spectrum exhibits a multiplet of components attributed to C−Si bonds, C−O bonds, and aliphatic carbons neither bonded to silicon nor to oxygen.[9,10] The authors of a couple of studies[9,10] suggest the rupture of the C−O bonds, leading to the attachment of ethoxysiloxane and ethyl moieties. The evolution of the C 1s spectral shape indicates that the extent of C−O cleavage depends on the coverage: TEOS adsorbs by scission of two C−O bonds at low coverage, while at larger exposures a single C−O bond breaks, leading to a mixture of di- and triethoxysiloxane species. The breaking of the Si−O bond is also envisaged as a minority channel at high coverage,[10] "despite the high Si−O bond energy of ∼430 kJ mol^{-1} compared to 270−280 kJ mol^{-1} for C−O". Note that the information obtained for the clean Si(111) surface is useful for the discussion of the reaction of PTES with clean Si(001). Indeed, because of the zwitterionic nature of the main reactive sites on both surfaces, the adatom−restatom pairs on Si(111)-7 × 7 and the dangling bond pairs of the dimerized Si(001)-2 × 1 surface mechanisms and reactions available on one surface can often be simply transferred to the other substrate.[6] For DEDEOS deposited on Si(001)-2 × 1 at room temperature, an infrared spectroscopy study shows the presence of surface ethyl and ethoxy groups.[11] Remarkably no silicon hydride and dihydride modes are observed at this temperature. However the dissociation mechanism is not discussed in ref 11.

Therefore the nature of bond breaking in the ethoxy moiety (Si−O or C−O) remains largely elusive in the case of TEOS and DEDEOS. For PTES adsorbed on bare silicon, the determination of the formal oxidation states of silicon (Si^{n+}, where n ranges from 1 to 3 is the number of oxygen ligands around the atom) should greatly help refining the picture. As shown in Figure 1, the C−O bond breaking, as suggested in ref 9, leads exclusively to PTES adducts in a formal Si^{3+} oxidation state, plus a variable number (equal to the number of broken C−O bonds) of adsorbed ethyl groups, denoted $Si^*{-}C_2H_5$, where Si* is a substrate silicon atom.

On the other hand, Si−O bond scission leads to Si^{2+}, Si^{1+}, and Si^0 oxidation states, plus a variable number (equal to the number of broken Si−O bonds) of adsorbed ethoxy groups. In this context, Si 2p core-level XPS is the only spectroscopy able to determine unambiguously the oxidation states of silicon.[12−16] Naturally, for species with an areal density of about one monolayer, this determination requires a high surface sensitivity, which is not attained with a conventional Mg Kα X-ray source ($h\nu = 1253.6$ eV), the one used in refs 9 and 10, as the Si 2p photoelectron escape depth λ is in the 13−23 Å range.[17] We show here that synchrotron radiation XPS sheds more light on this issue. Thanks to the photon energy tunability, Si 2p spectra can be recorded in highly surface sensitive conditions ($\lambda \approx 4$

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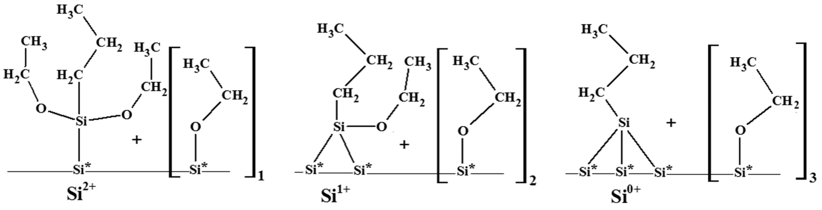
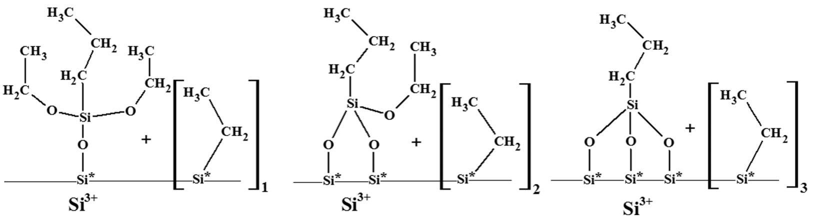


(a) C–O bond breaking (Si^{3+} and Si^{*1+})



(b) Si–O bond breaking (Si^{n+} {n=0,1,2} and Si^{*1+})

Figure 1. Possible products formed by dissociative adsorption of PTES on Si(001)-2 × 1 surface (a) after C−O bond breaking and (b) Si−O bond breaking. Si* designates a substrate silicon.

Å) at photon energies around 150 eV.[17,18] The spectral decomposition of the high resolution C 1s spectrum and the determination of the formal Si oxidation state (substrate and adsorbate) allow us to conclude that PTES bonds to the clean Si(001) via Si−O bond breaking. We also discuss why this reaction may be facile.

Experimental Section

Si(001)-2 × 1 surfaces were produced in the preparation chamber of the TEMPO beamline end-station at SOLEIL synchrotron facility. Highly doped (phosphorus) n^+-type Si(001) wafers (resistivity 0.003 Ω × cm, $N_D \sim 2 \times 10^{19}$ cm^{-3}) are cleaned from their native oxide by flash annealing (Joule effect) at 1100 °C after prolonged degassing at 600 °C in ultrahigh vacuum (10^{-10} mbar base pressure). The silicon surface is then exposed to PTES (commercial product Sigma-Aldrich, purum 98%) by dosing at room temperature under a pressure in the 10^{-8} mbar range (ion gauge uncorrected reading). Doses are expressed in Langmuirs (1 L = 10^{-6} Torr × s, where 0.75 Torr = 1 mbar).

Details on the TEMPO beamline and end-station can be found elsewhere.[19] The X-ray spot (normally focused in a spot 45 μm long in the horizontal direction by 10 μm wide in the vertical dimension) is defocused on purpose, to a spot of dimensions 1 mm × 2 mm, to eliminate beam damage, without losing photoelectron count rate. Photoelectrons are detected at 0° from the sample surface normal and at 46° from the polarization vector **E**. The C 1s core-level spectra are recorded at $h\nu = 350$ eV with an overall experimental resolution better than 100 meV (other C 1s spectra are recorded at $h\nu = 390$ eV together with the Si LVV Auger for normalization purposes, see below). Surface sensitive Si 2p spectra are measured at $h\nu = 150$ eV, with an overall experimental resolution better than 80 meV. To ease the determination of the various components contributing to the Si 2p spectra, the $j = {}^1/_2$ component of the Si $2p_{1/2,\,3/2}$ doublet is numerically stripped[17] after a Shirley background subtraction, assuming a $2p_{1/2}$:$2p_{3/2}$ ratio of 0.5 and a spin−orbit splitting of 0.602 eV.[20,21] The zero binding energy (BE) (i.e., the Fermi level) is taken at the leading edge of a clean molybdenum foil in electrical contact with the silicon crystal. The Si $2p_{3/2}$ BE is found at 99.35 and 99.40 eV for the clean and PTES-reacted Si(001)-2 × 1 surfaces, respectively.

The core-level spectra are fitted by sums of Voigt curves, i.e., the convolution of a Gaussian (of fullwidth at half-maximum GW) by a Lorentzian (of full-width at half-maximum LW). For Si 2p and C 1s, the chosen LW are 45[22] and 80 meV,[23] respectively. The *total* full-width at half-maximum (fwhm) of the Voigt profile is calculated using the following formula[24]

$$\mathrm{fwhm} \approx 0.5346 \times \mathrm{LW} + \sqrt{0.2169 \times \mathrm{LW}^2 + \mathrm{GW}^2}$$

To quantify the amount of deposited carbon, the C 1s kinetic energy (KE) is chosen ($h\nu = 390$ eV, KE ≈ 105 eV) close to that of the Si LVV Auger peak (∼90−98 eV range). The C 1s photoemission peak integrals are normalized with respect to an equal Si LVV height. Then neglecting any photoelectron diffraction effect, absolute carbon surface quantities are given after comparison with the cyclopentene-saturated Si(001) surface (10^{-8} mbar for 15 min, 6.7 L) for which an average carbon surface density of ∼4 carbon atoms per dimer can be deduced from the scanning tunneling images of ref 25: all cyclopentene molecules are di-σ bonded to the Si−Si dimer,[25,26] but full coverage is not reached as STM shows vacant sites (about 20% of the dimers), even after a 300 L exposure, due to possible steric interactions between molecules. This estimation from C 1s XPS can be cross-checked by measurement of O 1s intensities ($h\nu = 635$ eV, KE ≈ 105 eV), also normalized with respect to the Si LVV height. Comparison was made with the water-saturated Si(001) surface, where the oxygen areal density is one O per dimer.[27]

Results

The clean Si(001) surface was exposed to 2.2 L of PTES (300 s × 10^{-8} mbar) at room temperature. The normalized C 1s and O 1s intensities enable us to estimate the molecular coverage (see Table 1 and the experimental section here above for details on the procedure). It results that about 0.4 molecules per silicon dimer are present on the surface, i.e., on the average one molecule occupies 2.5 dimers.

The C 1s spectrum ($h\nu = 350$ eV) of the surface exposed to 2.2 L of PTES is reported in Figure 2. We recall that schemes of conceivable adducts have been already presented in Figure 1. To facilitate the discussion, carbon atoms attributed to a

TABLE 1: Normalized C 1s and O 1s Peak Intensities of PTES-Covered Si(001)-2 × 1 (2.2 L) Measured at $h\nu = 390$ and 635 eV, Respectively[a]

molecule	normalized C 1s intensity KE ≈ 105 eV range	normalized O 1s intensity KE ≈ 105−120 eV range	C atoms per dimer	O atoms per dimer	C/O ratio	no. PTES molecule per dimer
cyclopentene-saturated Si(001) surface	1		~4			
water-saturated Si(001) surface		1		1		
PTES	0.93	1.2	~3.7	1.2	3.1	~0.41

[a] Comparison is made with the normalized C 1s peak intensity of cyclopentene-saturated Si(001)-2 × 1 surface measured at $h\nu = 390$ eV and with the normalized O 1s peak intensity of water-saturated Si(001)-2 × 1 measured at $h\nu = 650$ eV. The stoichiometric C/O ratio is 3.

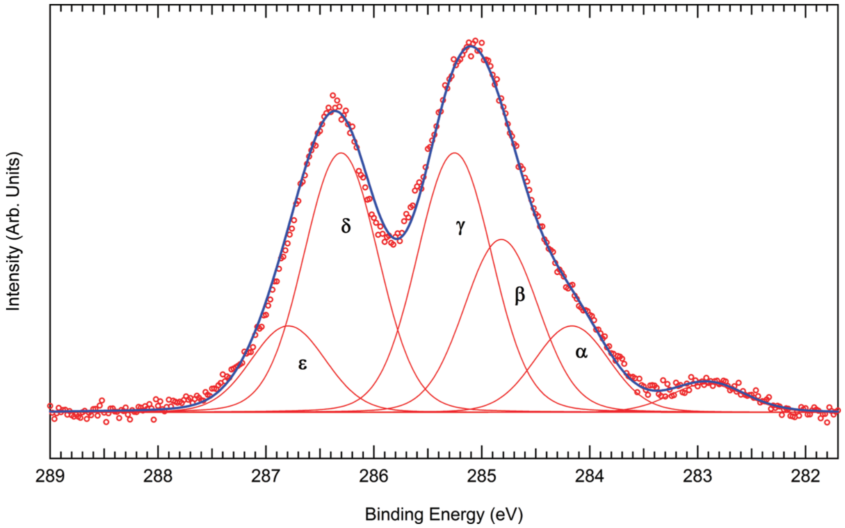


Figure 2. C 1s spectrum (red dots) of the Si(001)-2 × 1 surface exposed to 2.2 L of PTES at room temperature ($h\nu = 350$ eV). A Shirley background was subtracted. The energy reference is the position of the Si $2p_{3/2}$ spectrum at 99.40 eV. The spectrum is fitted with a sum (blue solid line) of five components (red solid line) $\alpha, \beta, \gamma, \delta, \varepsilon$ of fwhm 0.81 eV, plus a weak component at 282.80 eV, attributed to silicon carbide contamination. The BE, spectral weights, and attributions of the different components are reported in Table 2.

TABLE 2: BE and Weight of the Components Resulting for the C 1s Spectral Decomposition of the Si(001) Surface Exposed to 2.2 L of PTES[a]

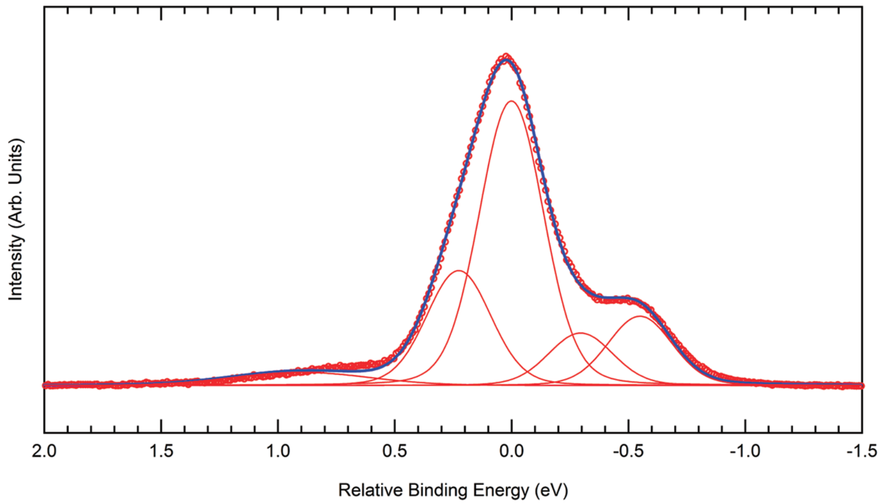
component	BE (eV)	attribution	weight (%)
α	284.16	$\mathrm{Si{-}\underline{C}H_2{-}CH_2{-}CH_3}$ $\mathrm{Si^*{-}\underline{C}H_2{-}CH_3}$	10
β	284.82	$\mathrm{Si{-}CH_2{-}\underline{C}H_2{-}\underline{C}H_3}$ $\mathrm{Si^*{-}CH_2{-}\underline{C}H_3}$	20
γ	285.25	$\mathrm{Si{-}O{-}CH_2{-}\underline{C}H_3}$ $\mathrm{Si^*{-}O{-}CH_2{-}\underline{C}H_3}$	30
δ	286.30	$\mathrm{Si^*{-}O{-}\underline{C}H_2{-}CH_3}$	30
ε	286.79	$\mathrm{Si{-}O{-}\underline{C}H_2{-}CH_3}$	10
$\alpha + \beta + \gamma$			60
$\delta + \varepsilon$			40

[a] The common energy reference is the Si $2p_{3/2}$ bulk component at 99.40 eV of the covered surface. The attributions are given in the framework of the Si−O bond cleavage model, which leads to a theoretical $(\delta + \varepsilon)/(\alpha + \beta + \gamma)$ ratio of 0.5. Experimentally we find a ratio of 0.66. Si* denotes a substrate silicon atom.

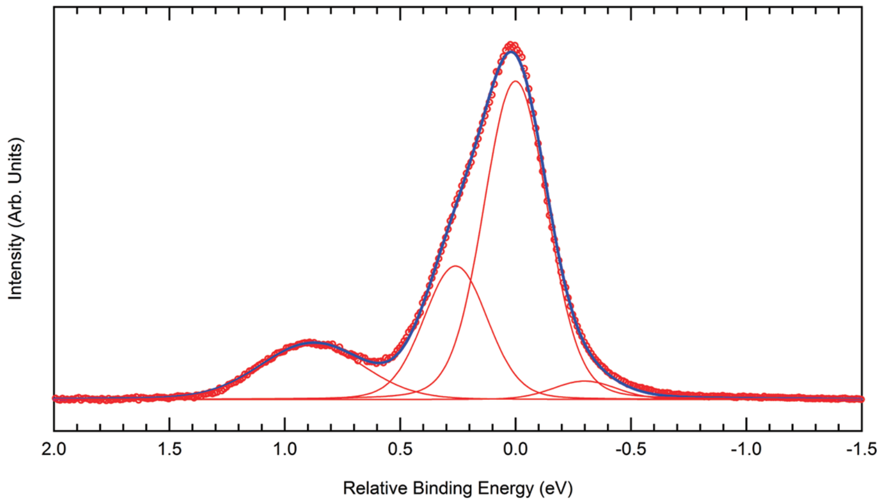
specific component are underlined (for instance $\mathrm{O{-}\underline{C}H_2{-}CH_3}$ denotes an ethoxy group carbon bonded to the oxygen). The C 1s photoemission spectrum is fitted by a sum of six Voigt components (fwhm = 0.81 eV). The peak at lower BE (~282.80 eV, 2.3% of the whole spectral weight) is ascribed to a silicon carbide contamination.[28] The attribution of the BE of the five remaining components is based on straightforward initial state considerations. Because Si (Pauling electronegativity = 1.90) is less electronegative than hydrogen (Pauling electronegativity = 2.20), the C atoms bonded to Si and Si* atoms are expected to be slightly more charged than aliphatic carbons not bonded to silicon in ethyl and propyl groups; therefore they are expected at lower BE. On the other hand the bonding of an aliphatic carbon atom with the more electronegative O atom (Pauling electronegativity = 3.44) leads to a charge loss and to an increased BE. To give an example, in gas-phase ethanol, the BE of $\mathrm{CH_3{-}\underline{C}H_2{-}OH}$ is shifted up by 1.4 eV with respect to that of $\mathrm{\underline{C}H_3{-}CH_2{-}OH}$.[29]

The α peak at 284.16 eV is attributed to C atoms bonded to silicon atoms in ethyl ($\mathrm{Si^*{-}\underline{C}H_2{-}CH_3}$) and propyl ($\mathrm{Si{-}\underline{C}H_2{-}CH_2{-}CH_3}$) groups; in agreement with previous observations[9,26,30] the β peak at 284.82 eV is attributed to C atoms not linked to Si in ethyl and propyl groups (i.e., $\mathrm{Si^*{-}CH_2{-}\underline{C}H_3}$, $\mathrm{Si{-}CH_2{-}\underline{C}H_2{-}\underline{C}H_3}$); the γ peak at 285.25 eV to terminal C atoms of the ethoxy moieties not linked to O atom ($\mathrm{Si{-}O{-}CH_2{-}\underline{C}H_3}$, $\mathrm{Si^*{-}O{-}CH_2{-}\underline{C}H_3}$), shifted to higher BE than the β component due to the presence of an oxygen as a second neighbor; and finally the δ peak at 286.30 eV, and its companion ε at 286.79 eV, to C atoms linked to O atom in ethoxy moieties. The ε component may be related to $\mathrm{Si{-}O{-}\underline{C}H_2{-}CH_3}$ whose BE would be larger (by ~0.5 eV) than that of $\mathrm{Si^*{-}O{-}\underline{C}H_2{-}CH_3}$, due to the reduced relaxation energy (a final state effect) associated with a greater distance from the substrate. (If we consider the peak corresponding to the C−O bonds ($\delta + \varepsilon$) as a single peak, its asymmetry may be due to vibrational progressions.) The BE difference between the ethoxy components δ and γ is 1.05 eV. This value is in good agreement with the BE distance of 1.2 eV found between the two carbons in the ethoxy species ($\mathrm{Si^*{-}O{-}CH_2{-}CH_3}$) bonded to the silicon surface after reaction of ethanol with Si(001)-2 × 1.[31] The BE position and spectral weights are collected in Table 2.

The theoretical distribution of the five ($\alpha{-}\varepsilon$) components depends strongly on reaction products, issued either from C−O or Si−O cleavage reaction paths. If we consider the C−O



(a) Si $2p_{3/2}$ Clean Surface



(b) Si $2p_{3/2}$ 2.2 L Covered Surface

Figure 3. Si $2p_{3/2}$ spectra (red dots) of the clean (a) and PTES-dosed (b) Si(001)-2 × 1 surface (room temperature, 2.2 L). The BE reference is that of the bulk (plus down atoms) component (B + SS). The spectra are fitted by sum (blue solid line) of Voigt components (red solid lines) whose BE, fwhm and weights are reported in Table 3.

scission products (see Figure 1a), the $(\delta + \varepsilon)/(\alpha + \beta + \gamma)$ spectral ratio is 2:7 (0.285) for Si*−O−Si$(OC_2H_5)_2(C_3H_7)$ (plus Si*−C_2H_5), 1:8 (0.225) for (Si*O)$_2$Si$(OC_2H_5)(C_3H_7)$ (plus two Si*−C_2H_5), and 0 for (Si*O)$_3$Si(C_3H_7) (plus three Si*−C_2H_5). Now if the Si−O bond breaks, the $(\delta + \varepsilon)/(\alpha + \beta + \gamma)$ spectral ratio is 0.5, whatever the number of cleaved bonds, as shown in Figure 1b. Experimentally the $(\delta + \varepsilon)/(\alpha + \beta + \gamma)$ ratio is equal to 0.66 (Table 2), which is a strong argument in favor of the Si−O bond scission model.

We show in Figure 3 the Si $2p_{3/2}$ spectra of the clean (Figure 3a) and PTES-exposed (Figure 3b) Si(001)-2 × 1, measured in surface sensitive conditions at $h\nu = 150$ eV.

The Si $2p_{3/2}$ line shapes are reconstructed by sum of Voigt curves, whose BE are referenced to the elemental silicon bulk BE (99.35 eV for the clean surface, 99.40 eV for the 2.2 L dosed surface). The fitting parameters are collected in Table 3. The attribution (and notation) of the various components is based on the work of Landemark and co-workers:[20] a main structure labeled B + SS at 0 eV, encompassing both the bulk component B and the positively charged down silicon dimer atom SS (a surface core-level shift (SCLS) of +0.06 eV from the bulk component[31]); a peak labeled S with a SCLS of −0.55 eV (13% of the spectral weight), related to the negatively charged up silicon dimer atom; a structure labeled C with a SCLS of −0.30 eV (8.8% of the spectral weight), ascribed by Landemark et al.[20] to subsurface silicons (3rd layer); finally the S′ peak with a SCLS of +0.22 eV from B + SS (21% of the spectral weight), attributed to the silicon second plane. The broad structure at

TABLE 3: SCLS, fwhm, and Spectral Weights of the Voigt Components Used to fit the Si $2p_{3/2}$ Spectra of the Clean and PTES-Covered (2.2 L) Si(001) Surface on Figure 3

	SCLS (eV)	fwhm (eV)	weight (%)
	0 L		
B+SS	0	0.32	52.2
S	−0.55	0.32	13
S′	+0.22	0.32	21
C	−0.30	0.32	8.8
energy losses/contamination	+0.90	0.80	5
	2.2 L		
B	0	0.32	57.4
S′+C−Si bond	+0.26	0.32	23.9
C	−0.30	0.32	3.2
OS	+0.88	0.52	15.5

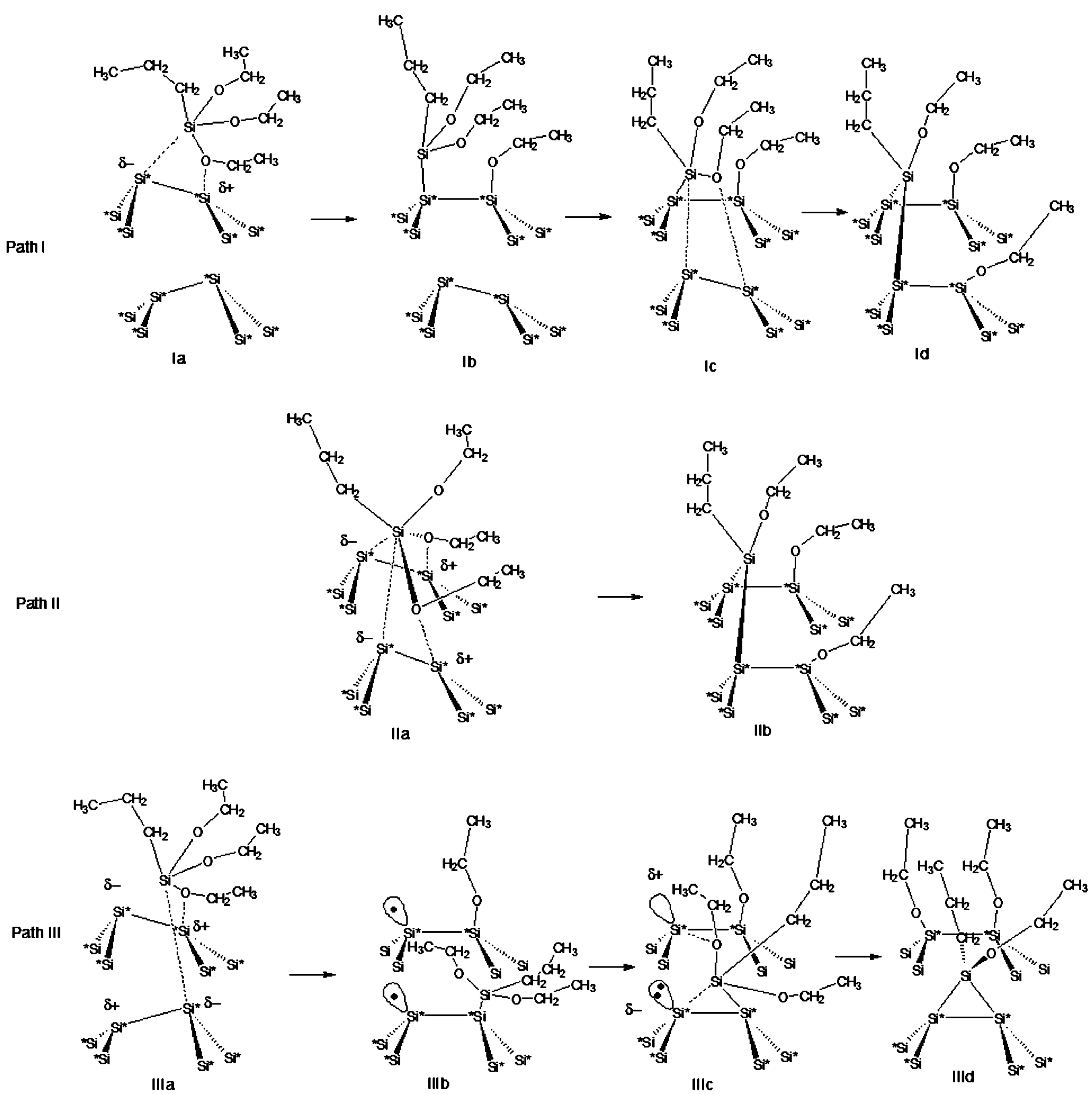


Figure 4. Schemes of PTES on Si(001)-2 × 1 reaction paths for a final states with two Si−O bonds broken: a datively bonded molecular adduct is first formed through O/down Si* dimer atom interaction (schemes Ia, IIa, and IIIa) followed by a nucleophilic attack of the PTES Si atom by the up silicon atom and final Si−O bond breaking. As only the first oxidation state is observed in the Si 2p spectrum, at least two Si−O bonds necessarily break in a concerted manner (path II) or sequentially (paths I and III). Paths I and II lead to an end-bridge (Id, IIb) geometry, while path III leads to an on-dimer configuration (IIId).

+0.90 eV from B + SS (5% of the spectral weight) can be ascribed to energy losses[32] or carbide contamination.[33] We note that peak S, related to the up silicon dimer atoms that account for half the surface atoms, represents about 13% of the spectral weight.

After the exposure to PTES, the S component has completely vanished, indicating that the molecule reacts with the surface dimers. Concomitantly we see the growth of a silicon oxidation state OS (with a SCLS of +0.88 eV and a spectral weight of 15.5%). Structure C weakens (3.2% of the spectral weight) but does not disappear. The presence of Si−C bonds, inferred from the decomposition of the C 1s spectra, does not appear clearly: the S′ component moves slightly toward higher BE (SCLS of +0.26 eV), and its spectral weight increases from 21% (clean surface) to 23.9%. The BE of Si−C bonds formed after π bonded hydrocarbon cycloaddition are in the +230 to +330 meV range from the bulk line[30] (except for the ethylene adduct which gives a component at lower BE), and therefore are hidden within the S′/B doublet.

The attribution of the OS component to a given surface oxidation state requires some discussion. Taking into account that the analysis of the C 1s photoemission spectrum points to the breaking of the Si−O bond in the triethoxysilane termination, when i Si−O bonds break (i from 1 to 3), i Si*−OC_2H_5 (with a Si^{*1+} oxidation state) moieties plus one $(Si^*)_iSi(OC_2H_5)_{(3-i)}(C_3H_7)$ moiety (with a $Si^{(3-i)+}$ oxidation state) are formed. The literature indicates that $Si^{*}{-}OC_2H_5$ species, formed after dissociation of ethanol on Si(001)-2 × 1, gives a component at +0.88 eV[31] from the bulk line.[34] By consideration of the present issue, we can first affirm that a formal Si^{*1+} state in a $Si^{*}{-}OC_2H_5$ species, resulting from PTES Si−O bond cleavage, can contribute to the OS peak. Second, a formal Si^{1+} state in a $(Si^{*})_2Si(OC_2H_5)(C_3H_7)$ moiety (resulting from the breaking of two Si−O bonds, see Figure 1b) could also contribute to OS, as it should be shifted by about +1 eV from elemental silicon, assuming the validity of chemical shift additivity and taking into account that Si−C bonding induces generally a small (below 0.33 eV) positive BE shift.[30] The SCLS of the second oxidation state Si^{2+} in a $(Si^{*})Si(OC_2H_5)_2(C_3H_7)$ moiety (resulting from the scission of only one Si−O bond) should be about +2 eV. As we do not observe any such state in the experimental spectrum, this possibility must be rejected. (Note that the nonobservation of the third oxidation state Si^{3+}, estimated SCLS in the +2.7−3.0 eV range, confirms that the C−O scission path, see Figure 1a, is not operative.) To sum up: the presence of only the first oxidation state in the Si 2p spectrum (attributable to Si^{*1+} and/or Si^{1+}) means that two or three Si−O bonds are broken in the adsorption process. Remembering that the OS state weight is about 15.5% of the spectral weight, compared to 13% for the S states of the clean surface (their areal density is equal to that of silicon dimers), the present Si 2p spectrum analysis leads to ∼1.2 Si−O bond *per* dimer, i.e., 0.4 PTES molecules per dimer, in excellent agreement with the coverage estimated via the analysis of the C 1*s* spectrum.

Possible Reaction Paths and Adsorption Geometries. The XPS results clearly indicate that PTES adsorbs on Si(001) by breaking at least two Si−O bonds of the triethoxysilane termination. Let us now examine the nature of the reactants. On the one hand, the buckled silicon dimer is zwitterionic (the up dimer atom is electron-rich while the down dimer atom is electron-poor).[4,35] On the other hand, the PTES molecule presents also one electron-rich center, the ethoxy oxygen with its two lone-pairs, and an electron-deficient center, the silicon atom. Therefore one can expect reactions driven by charges, i.e., the formation of nondissociated molecular adduct due to the attractive interaction between the O atoms and the down silicon dimer atoms, followed by a nucleophilic attack of the PTES Si atom by the up silicon dimer atom and then the breaking of the Si−O bond. An on-dimer reaction leading to the breaking of one Si−O bond is depicted in schemes Ia and Ib of Figure 4. Indeed the calculated reaction path of trimethoxysilane, a close analogue of PTES,[36] follows this scheme (the density functional theory approach is used and a single-dimer Si_9H_{12} cluster mimics the Si(001)-2 × 1 surface). In particular it is shown that an intermediate reaction state is formed (the $Si^{*}{-}O$ bond length is 1.94 Å, only about 0.30 Å larger than a normal Si−O bond length) stabilized by −0.60 eV with respect to the energy of the separated reactants. Then the Si−O bond breaks with a small activation barrier of only 0.15 eV from the molecular intermediate state energy. Apart from an on-dimer reaction leading to the breaking of only one Si−O bond (and therefore to the formation of Si^{2+} and Si^{*1+} surface states), one could also imagine a concerted reaction involving two ethoxy oxygens and two adjacent dimers in the same row, as shown in path II (schemes IIa and IIb of Figure 4). This leads to the simultaneous breaking of two Si−O bonds and the formation of Si^{1+} and Si^{*1+} states, as observed by photoemission. Path III presents an intrarow reaction involving two adjacent dimers leading to the scission of one Si−O bond. In the nonconcerted reaction paths I and III, the reaction can proceed to the scission of a second Si−O bond, so that Si^{1+} and Si^{*1+} states are produced.

As shown in Figure 4, reaction paths I and II lead to an end-bridge $(Si^{*})_2Si(OC_2H_5)(C_3H_7)$ species, while path III leads to an on-dimer configuration. The latter one should exhibit a strained three-membered Si_3 ring. Calculations of the on-dimer adsorbed SiH_2 fragment geometries on Si(001)-2 × 1[37] show that the ∠Si*SiSi* angle is only 63°, while it reaches 92° in the case of the end-bridge geometry. Bond lengths are 2.43 (2.40) and 2.32 (2.41) Å for the on-dimer (end-bridge) geometries. It is therefore plausible that in the PTES case the end-bridge geometry is more stable than the on-dimer configuration. Note that in the case of SiH_2 adsorption, the end-bridge geometry is the only one observed by scanning tunneling microscopy[38] (cross-trench geometries are also excluded).

All the $(Si^{*})_2Si(OC_2H_5)(C_3H_7)$ reaction products envisaged in Figure 4 for final states with two Si−O bonds broken, encompass two dimer sites in the same row corresponding to 0.5 molecules per dimer. The measured PTES coverage of 0.4 molecule per dimer may suggest that steric effects prevent some Si dimers to be used as adsorption sites. Alternatively, a third Si−O bond may break. In this case six silicon atoms of the substrate are needed to link the three ethoxy moieties and to form the trisilypropysilane $(Si^{*})_3Si(C_3H_7)$ (see Figure 1b). This can be envisaged if three dimers are involved in the adsorption process, resulting in a coverage of 0.33 molecule per dimer. Therefore to account for the observed coverage of 0.4 molecule per dimer a mixture of $(Si^{*})_2Si(OC_2H_5)(C_3H_7)$ and $(Si^{*})_3Si(C_3H_7)$ adducts could be present on the surface.

Conclusion

The adsorption of PTES on clean Si(001)-2 × 1 at room temperature is studied using synchrotron radiation photoemission spectroscopy. Both C 1s and surface sensitive Si 2p core-level spectroscopy reveal that PTES dissociatively adsorbs on the surface via Si−O bond scission, to produce $(Si^{*})_iSi(OC_2H_5)_{3-i}(C_3H_7)$ and $Si^{*}{-}OC_2H_5$ species, with *i* equal to 2 or 3. The coverage at a dose of 2.2 L attains ∼0.4 molecule per dimer. Despite the fact that the Si−O bond energy of the anchoring head is stronger than the C−O one, we argue that the Si−O bond breaking may be facile due to the formation of a nondissociated molecular intermediate state datively bonded to the surface via the interaction of one (or two) electron-rich oxygens with one (or two) acidic sites of the clean surface. We hope that the present work will stimulate further studies on the adsorption of multifunctional molecules bearing an ethoxysilane functionality as a potential anchoring unit, in view of their application in molecular layer deposition processes.[6,39]

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