Hydrosilylation of Styrene on Water-saturated Si(001)–2×1 at Room Temperature

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Contents: C 1s shake up spectrum and Si 2p spectrum of the clean Si(001)–2×1 surface exposed to 6.7 L of styrene at room temperature.

S1. Direct adsorption of styrene on clean Si(001)-2×1 at room temperature

The clean surface preparation is described in the experimental section of the paper. After cleaning, the surface was exposed to a styrene dose of 6.7 L (900 s under a pressure of 0.75×10^{-8} Torr) at room temperature.

S.2 Wide C 1s spectrum of the styrene terminated Si(001)-2×1 surface

The wide C 1s spectrum (hν = 390 eV) of the styrene-terminated Si(001)–2×1 surface is presented in figure S1 after background subtraction. One observes shake up structures at lower kinetic energy than the main C 1s peak. The shake ups are fitted using two broad Gaussians at –6.1 eV (*FWHM* = 3 eV) and –9.2 eV (*FWHM* = 4 eV), representing 8% of the whole spectral intensity. Note that in gas phase benzene well resolved π→π* shake ups transition energies are observed at –5.9 eV ($^1(2b_1 \rightarrow 3b_1)$), ☐7.0 eV ($^1(1a_2 \rightarrow 2a_2)$), –8.3 eV ($^1(1b_1 \rightarrow 3b_1)$) and –10.7 eV ($^1(1b_1 \rightarrow 4b_1)$), amounting to 10% of the whole spectrum.[1] The π→π* transition energies in benzene match with the observed (broad) structures of styrene on Si(001), suggesting that the aromatic ring is intact after adsorption.
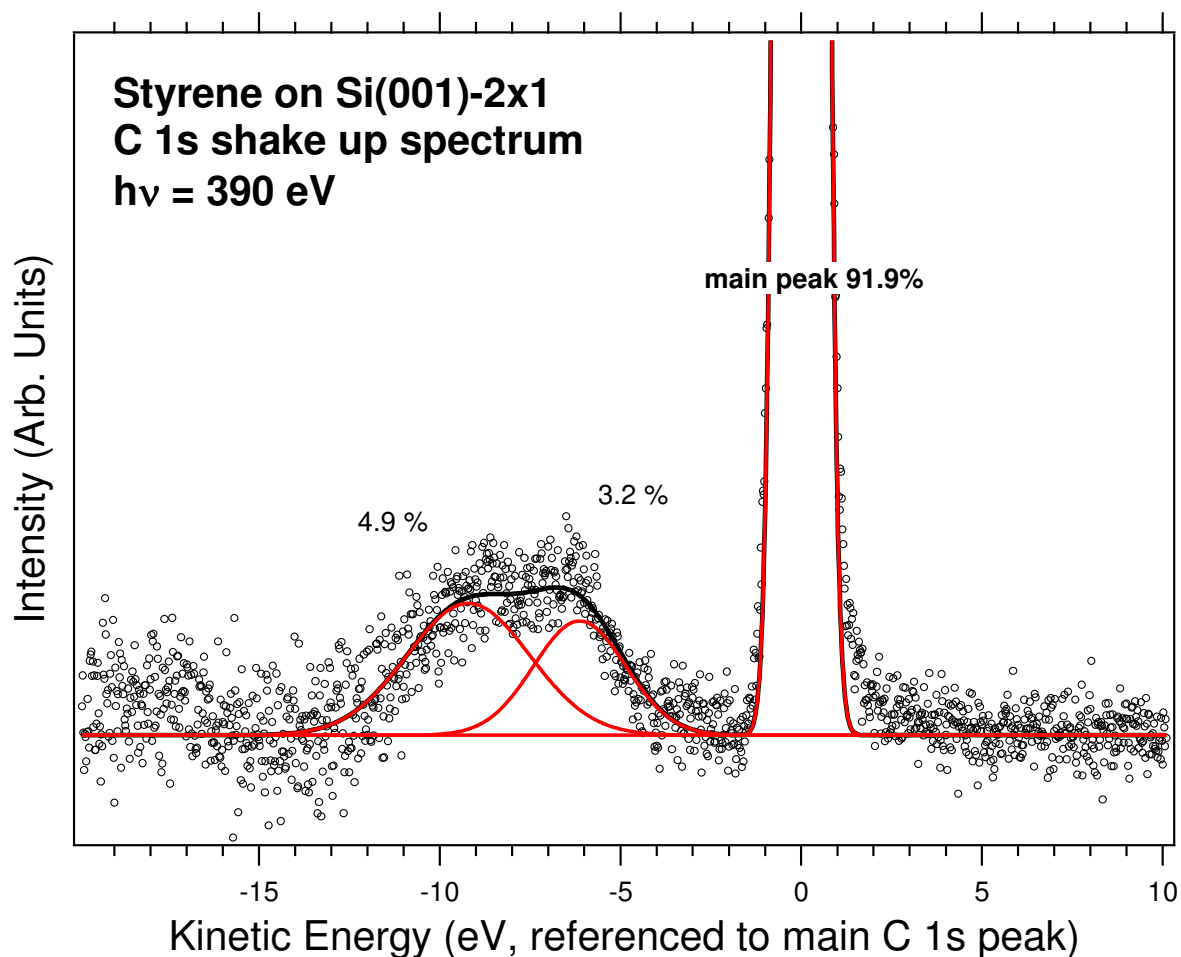
Figure S1. Wide XPS C 1s spectrum (dots) of the clean Si(001)–2×1 exposed to 6.7 L of styrene after subtraction of the background. The photon energy is 390 eV. The $\pi\rightarrow\pi^*$ shake ups are fitted (black solid line) with two Gaussian components (red solid line), at –6.1 eV (*FWHM* = 3 eV and –9.2 eV (*FWHM* = 4 eV). The takeoff angle of the electrons, with respect to the surface normal, is 45°.

S.3 Si 2p spectra of the clean and styrene-terminated Si(001)–2×1 surface

We present the Si 2p spectra (hv = 150 eV) of the clean Si(001)–2×1 surface in figure S2. The surface directly exposed to 6.7 L of styrene is given in figure S2 (b). The attribution (and notation) of the various component is based on the work of Landmark and coworkers.[2] The fitting parameters are

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collected in table S1. The spectrum of the clean surface (figure S2 (b)) is fitted with: a main peak labeled *B+SS* at 99.35 eV, encompassing both the bulk component *B* and the positively charged *down* silicon dimer atom *SS* (SCLS of +0.06 eV); a peak labeled *S* at 98.78 eV (SCLS of –0.57 eV) related to the negatively charged *up* silicon dimer atom; a structure labeled *C* at 99.05 (SCLS of –0.3 eV from *B+SS*) ascribed to subsurface silicons (3rd layer); and finally the *S'* peak at 99.57 (SCLS of +0.22 eV) attributed to the silicon second plane.

After an exposure to 6.7 L of styrene (figure S2 (a)), the *S* component has completely vanished, indicating that the molecules reacts with the surface dimers. We see a component *S1* (SCLS of –0.3 eV, 3.95% of the spectral weight), that can be a remainder of the clean surface structure *C*. The formation of the SiC bond is manifested by the growth of structure *S2*, with an SCLS of +0.26 eV and a weight of 23.95% (*S2* may include the *S'* component of the clean surface). A small unidentified component at a SCLS of +1.2 eV is also seen and can be attributed to contamination (suboxides) or losses.
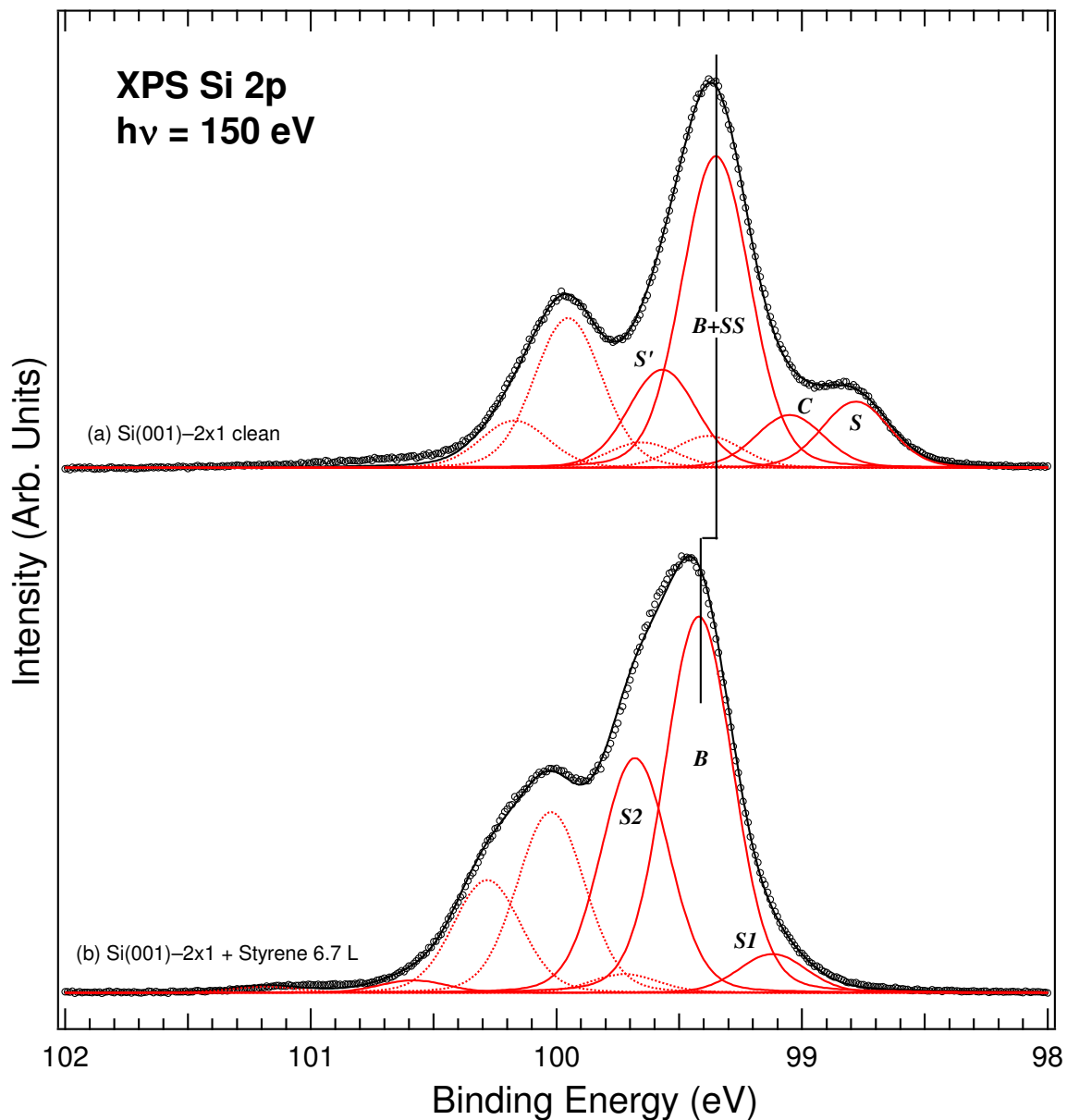
Figure S2. XPS Si 2p spectra (hν = 150 eV) of the n^{+}-doped Si(001)–2×1 surface (a) clean and (b) after exposure to 6.7 L of styrene at room temperature. The takeoff angle of the electrons, with respect to the surface normal, is 45°. The experimental curves (circles) are fitted with sums of Voigt components (dark solid lines). The Si $2p_{3/2}$ (Si $2p_{1/2}$) fitting components are the red solid (red dotted) lines. The Si $2p_{3/2}$ binding energy, the widths and the spectral weights of the various components are given in table S1. Note the small rigid binding energy shift of +0.07 eV, due to a band bending variation.

Surface	Component	Si 2p$_{3/2}$ Binding energy (eV)	SCLS (eV)	GW (eV)	*FWHM* (eV)	Weight (%)	Attribution
Clean	*S'*	99.57	+ 0.22	0.30	0.32	12.54	2nd plane
	B(+SS)	99.35	0	0.30	0.32	39.85	Bulk+ down atom
	C	99.05	–0.30	0.30	0.32	6.73	Subsurface
	S	98.78	–0.57	0.30	0.32	8.44	Up atom
6.7 L Styrene on Si(001)	*S3*	100.6	+ 1.2	0.30	0.32	1.27	Losses
	S2	99.68	+0.26	0.30	0.32	23.95	Si☐C and 2nd plane
	B	99.42	0	0.30	0.32	38.40	Bulk
	S1	99.12	–0.30	0.30	0.32	3.95	Subsurface (C)

Table S1. Binding energies (Si 2p$_{3/2}$), surface core level shifts (SCLS) referenced to the bulk component binding energy, Gaussian widths (GW), *FWHM* and spectral weights of the Voigt components used to fit the Si 2p experimental spectra shown in Figure S2. The Lorentzian width (LW) was 0.045 eV for all components.

References

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