

Electronic Supplementary Information for

“Nanoscale Condensation of Water on Self-Assembled Monolayers”

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Methods

Assembly of ω -functionalized monolayer surfaces SAM-1 – SAM-7

Unless otherwise noted, hydride-terminated surfaces were cleaned and functionalised via hydrosilylation of 1-alkene samples (**1–5**) according to the following process (manuscript, Scheme 1). Si(111) wafers were heated in xylene (130 °C for 40 minutes), before being rinsed thoroughly with ethanol and Milli-Q™ water. Wafers were then cleaned using “piranha” solution (concentrated sulfuric acid / 30% hydrogen peroxide, 3:1 v/v) at 90 °C for 1 hour and rinsed again thoroughly with Milli-Q™ water. Si(111) surfaces were hydrogen-terminated by immersion into deoxygenated 40% ammonium fluoride aqueous solutions for 20 minutes. Wafers were dried with nitrogen gas and transferred without any rinsing to a pre-dried schlenk flask under inert atmosphere.

The desired 1-alkene species (**1–5**) was either used neat (*ca.* 3 mL) or dissolved in dry mesitylene; degassed using five freeze–pump–thaw cycles and transferred under nitrogen to the schlenk flask containing the freshly hydrogen-terminated silicon wafer. The flask was immersed in an oil bath at 100 °C. After 16–18 hours the flask was cooled to room temperature, opened to atmosphere and the sample cleaned by rinsing several times with hot dichloromethane, anhydrous ethyl acetate and ethanol. Following cleaning, samples were stored under dry argon or nitrogen. Si–(CH₂)₁₅–CH₃ (**SAM-1**) was generated using the above procedure reacting 1-hexadecene **1**, Si–(CH₂)₁₁–Cl (**SAM-2**) was generated from 11-chloro-1-undecene **2**, and Si–(CH₂)₁₀–COOH (**SAM-5**) was prepared from 10-undecenoic acid **4**. Following functionalization **SAM-5** was washed with hot acetic acid, which removed any physisorbed acid **4**. This surface was then cleaned as per usual.

Si-(CH₂)₁₁-phthalimide (**SAM-3a**) was generated by placing a freshly hydrogen-terminated silicon wafer in a schlenk flask fitted with a refluxing condenser and loaded with 4 mL of a degassed and filtered solution of *N*-(ω-undecylenyl)-phthalimide **3** in mesitylene (5 % v/v). The flask was immersed in an oil bath at 150 °C for 18 hours under a nitrogen atmosphere. The sample was then removed from the solution and cleaned as per usual. Si-(CH₂)₁₁-NH₂ (**SAM-3**) was then derived from the phthalimide-terminated monolayer (**SAM-3a**) by reacting with *ca.* 5 mL of a 5 % solution (v/v) of hydrazine monohydrate in dry ethanol at room temperature under nitrogen for 4 days.

Si-(CH₂)₇-CH=CH₂ (**SAM-4**), an alkene-terminated surface, was prepared on a Si(100) substrate. Wafers were cleaned using “piranha” solution before being transferred first to an aqueous fluoride solution (2.5% hydrofluoric acid) for 1½ minutes. The samples were then transferred, taking care to exclude air from the reaction vessel, to a degassed sample (*ca.* 1 mL) of 1,8-nonadiene **5**. The reaction mixture was kept under argon and heated at 135 °C for 1½ hours. After cooling to room temperature the modified silicon wafers were then removed from the reaction flask and rinsed with copious amounts of ethyl acetate and dichloromethane before being analyzed.

Assembly of the acetylene-terminated monolayer (Si-CH=CH(CH₂)₅C≡CH, **SAM-6**) and the mixed monolayer (Si-(1-nonyne-8ene), **SAM-7**) by covalent attachment of terminal alkynes **6** and **7** is depicted in the manuscript Scheme 1 and were prepared by following procedures reported previously.¹⁻³ Si(100) wafers were cleaned and etched with fluoride solutions as described for **SAM-4**.

Results

X-ray Photoelectron Spectroscopy

The composition and quality of the self-assembled monolayers (**SAM-1**–**SAM-6**) were examined using X-ray photoelectron spectroscopy. High-resolution spectra confirm the presence of high quality monolayer surfaces with the appropriate molecular functionality. The amount of Si detected from all of these surfaces was also consistent with the film thickness derived from X-ray reflectometry. In most cases little detectable photoemission in the 102–104 eV region was observed, indicating negligible oxidation of the underlying silicon substrate. Notable exceptions, showing evidence of substrate oxidation, were the phthalimide-terminated monolayer (**SAM-3a**) and the subsequently derived amino-terminated monolayer (**SAM-3**), which correlates with the relatively poor degree of molecular packing observed by X-ray reflectometry. The N 1s core level spectrum for this latter surface (Figure S3(d)) showed 3 peaks, indicating incomplete conversion of the phthalimide groups to the amino functionality.

Si-(CH₂)₁₅-CH₃ (SAM-1)

XPS spectra obtained from a methyl-terminated Si-(CH₂)₁₅-CH₃ self-assembled monolayer surface (SAM-1) are shown in Figure S1. Only Si, C and O are detected on the surface, as revealed by the survey scan (Figure S1(a)). The C 1s core level spectrum (Figure S1(b)) shows a single peak centred around 285.0 eV is attributed to carbons in the alkyl chain. The Si 2p region (Figure S1(c)) consists of the Si 2p_{3/2} and Si 2p_{1/2} peaks (FWHM ~ 0.6 eV) due to spin-orbit splitting; the position of the peaks (99.2 and 99.8 eV respectively) confirms the chemical state of Si as Si⁰. The absence of any appreciable amount of photoelectron emission around 102-104 eV in the Si 2p spectrum, where signals from SiO_x would be expected, indicates that the amount of substrate oxidation is minimal (< 3%).

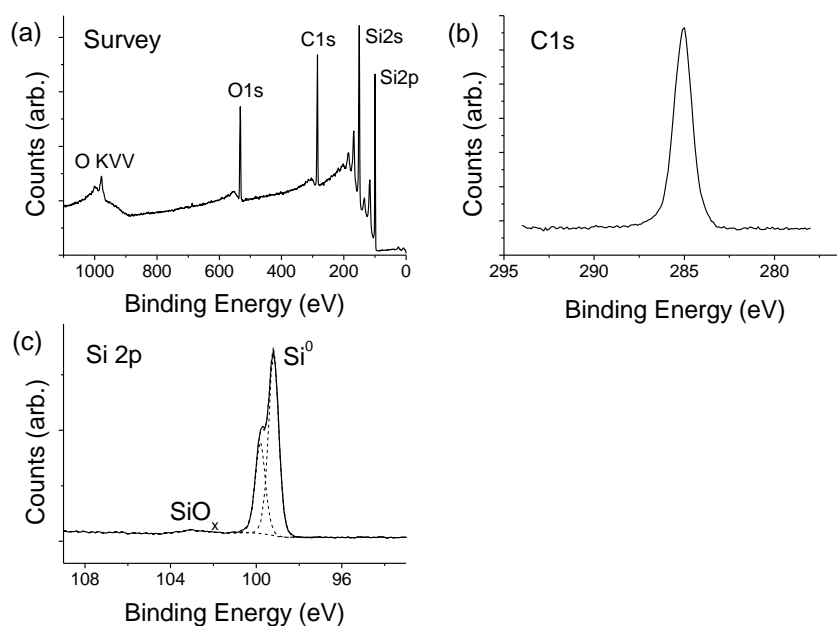


Figure S1. XPS spectra obtained from monolayers of -(CH₂)₁₅CH₃ on a Si (111) (SAM-1) (a) Survey spectrum, (b) C 1s core level spectrum, (c) Si 2p core level spectrum.

Si-(CH₂)₁₁Cl (SAM-2)

XPS survey spectra obtained from a chloro-terminated Si-(CH₂)₁₁-Cl self-assembled monolayer surface (SAM-2) indicate Si, C, Cl and O (Figure S2(a)); as well as a very small amount of F impurity is detected on the surface due to adventitious fluoride ions. The C 1s core level spectrum (Figure S2(b)) shows a main peak at 285.0 eV due to C-C and C-H bonds, as well as a small peak centred around 286.8 eV corresponding to C-Cl bonds and oxidised carbon. The Si 2p region (Figure S2(c)) also confirms that the amount of substrate oxidation is very small (~3% oxidation). The Cl 2p spectrum is shown in Figure S2(d); the high background is due to the Si plasmon loss features.

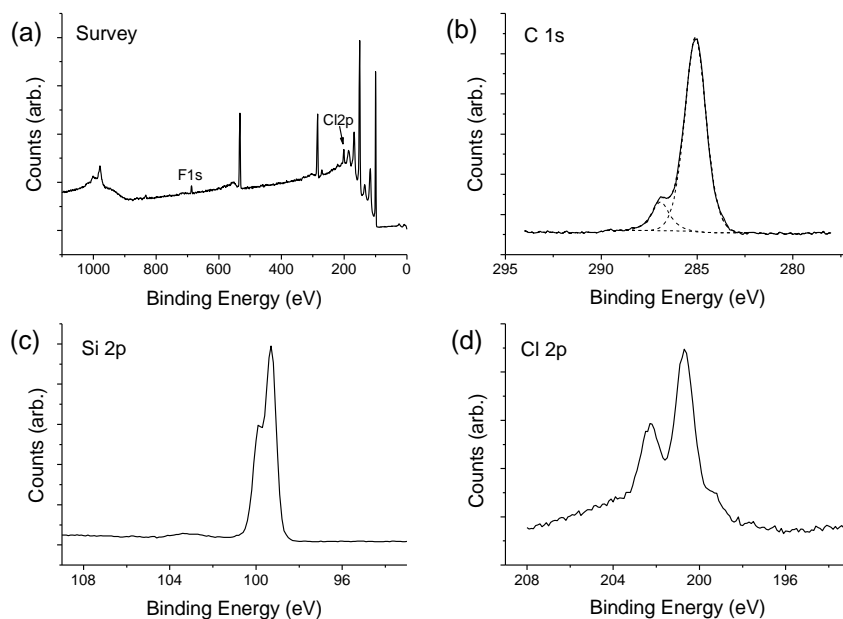


Figure S2. XPS spectra obtained from monolayers of -(CH₂)₁₁Cl prepared on a freshly etched Si (111) surface (SAM-2) (a) Survey spectrum, (b) C 1s core level spectrum, (c) Si 2p core level spectrum, (d) Cl 2p core level spectrum.

Si-(CH₂)₁₁NH₂ (SAM-3)

XPS spectra obtained from amino-terminated surface (SAM-3) are shown in Figure S3. Only Si, C, N and O are detected on the surface as revealed by the survey scan (Figure S3(a)). In addition to the predominant C peak located at 285.0 eV (C-C) there are also two small peaks centred around 286.6 eV (C-N) and 288.5 eV (C=O) (Figure S3(b)), with the latter indicating unreacted phthalimide groups. The amount of Si substrate oxidation was found to increase (Figure S3(c)) following this reaction. The N 1s core level spectrum (Figure S3(d)) shows a main peak centred around 400.6 eV, as well as two weaker peaks at 398.3 and 402.6 eV, suggesting that the reaction from SAM-3a to SAM-3 was incomplete.

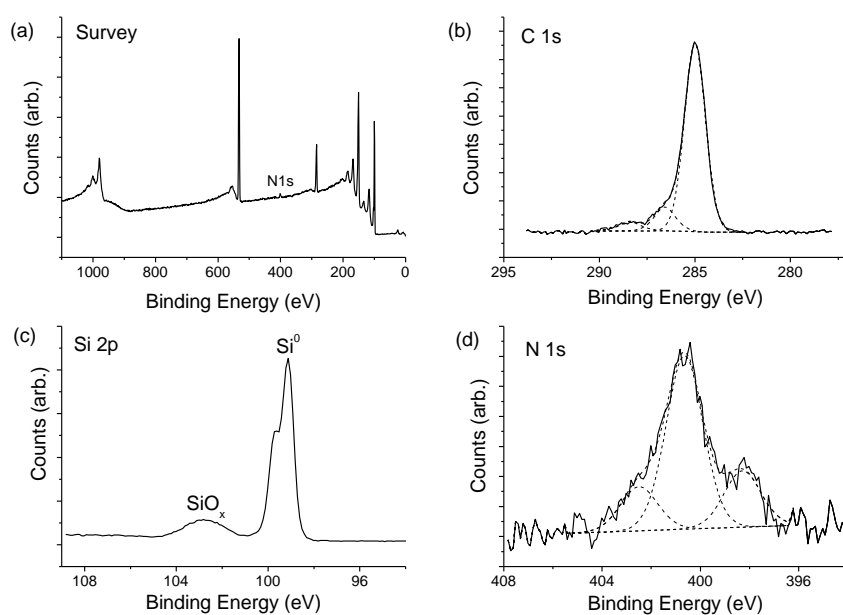


Figure S3. XPS spectra obtained from monolayers of $-(\text{CH}_2)_{11}\text{NH}_2$ prepared on a freshly etched Si (111) (SAM-3) (a) Survey spectrum, (b) C 1s core level spectrum, (c) Si 2p core level spectrum, (d) N 1s core level spectrum.

Si-CH₂-CH(CH₂)₅CH=CH₂ (SAM-4)

XPS spectra acquired on SAM-4 are found in Figure S4. Figure S4(a) shows a representative survey spectrum that indicates the presence of Si, C and O only. The high resolution scan of the C 1s region (Figure S4(b)) shows evidence of oxidized carbonaceous material (286.5 eV) and a narrow signal with a mean binding energy of 285.0 eV associated with aliphatic carbon-bound carbons (C-C). The high resolution Si 2p spectra (Figure S4(c)) afforded information on the monolayer quality with regard to its ability to prevent oxidation of the underlying Si substrate, with the lack of a detectable photoemission in the 102–104 eV region indicating negligible substrate oxidation.

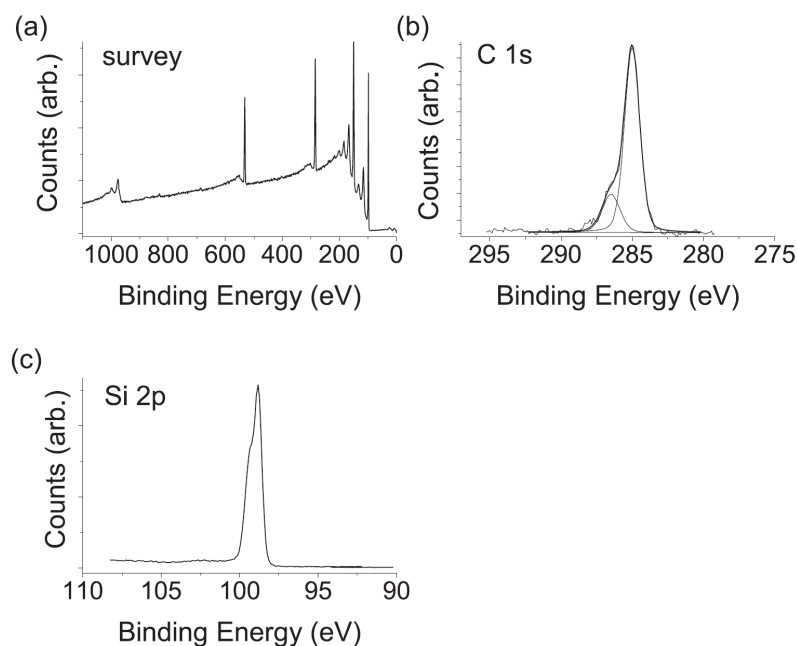


Figure S4. XPS spectra of monolayers assembled from the 1,8-nonadiene **5** on a hydrogen-terminated Si(100) sample (SAM-4) (a) Survey spectrum, (b) Narrow scan of the C 1s region, (c) High-resolution scan for the Si 2p region.

Si-(CH₂)₁₀(COOH) (SAM-5)

XPS spectra obtained from a carboxylic acid-terminated Si-(CH₂)₁₀COOH monolayer (SAM-5) are shown in Figure S5. In addition to Si, C and O, a small amount of F and Na impurities were detected on the surface (Figure S5(a)). The C 1s core level spectrum consists of three peaks: the main peak located at 285.0 eV (C-C) as well as two small peaks centered around 286.6 eV (due to oxidized carbon) and 289.3 eV (due to carboxylic groups O=C-OH), as shown in Figure S5(b). The amount of Si substrate oxidation is relatively small (~4%) (Figure S5(c)).

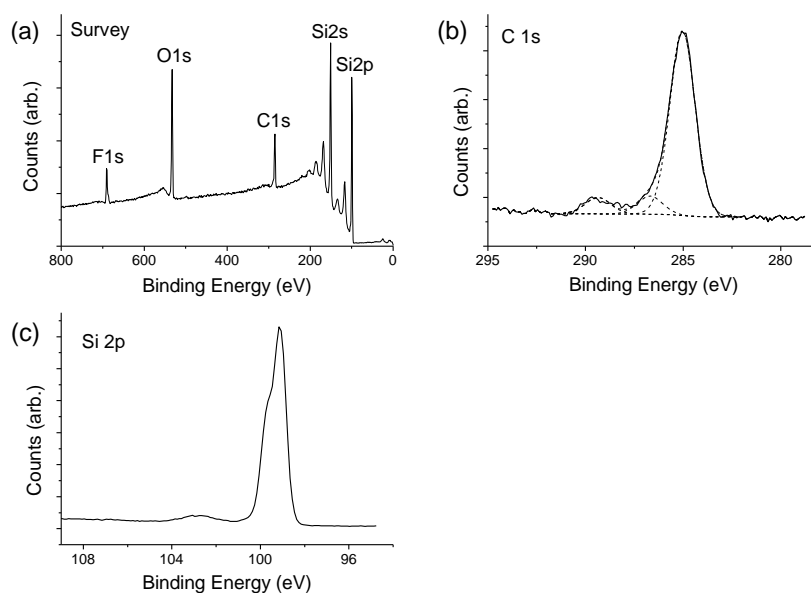


Figure S5. XPS spectra obtained from monolayers of C₁₀H₂₀(COOH) on a Si (111) (SAM-5) (a) Survey spectrum, (b) C 1s core level spectrum, (c) Si 2p core level spectrum.

Si-CH=CH(CH₂)₅C≡CH (SAM-6)

XPS spectra acquired on the acetylene-terminated monolayer (SAM-6) prepared from the diyne **6** are shown in Figure S6 and all the refined spectral features (*i.e.* C 1s and Si 2p emissions) agree with previous reports.¹⁻³ The high-resolution Si 2p scan reveals relevant information about the monolayer quality and its ability to prevent appreciable oxidation of the underlying Si substrate. In the Si 2p region (Figure S6(c)) obtained for SAM-6, the silicon oxide content was below the spectrometer detection limit (*ca.* 0.06 SiO_x monolayers) in the 102–104 eV region.

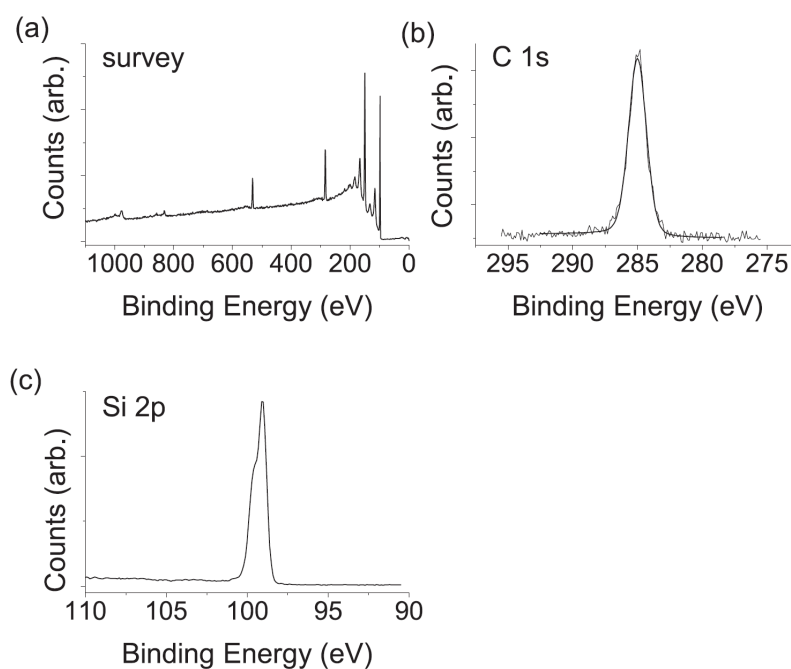


Figure S6. XPS spectra of monolayers assembled from the diyne **6** on a hydrogen-terminated Si(100) sample (SAM-6) (a) Survey spectrum, (b) Narrow scan of the C 1s region, (c) High-resolution scan for the Si 2p region.

X-ray Reflectometry

Si-H terminated Surface: Oxidation and Adsorption of Water

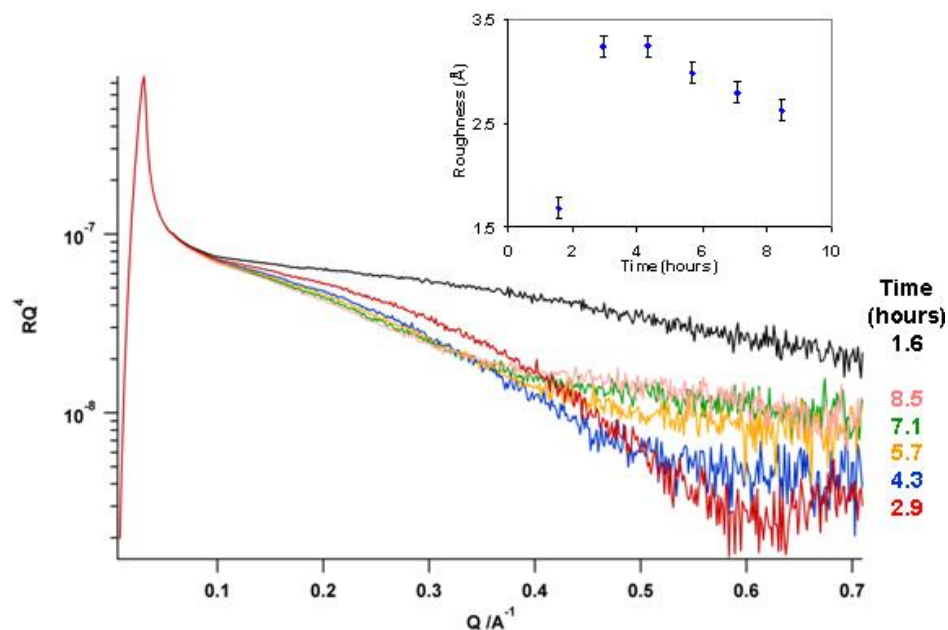


Figure S7. X-ray reflectivity (RQ^4 vs Q) of an H-terminated silicon wafer versus time showing the initial oxidation of the surface. The inset shows the variation in the refined surface roughness with time.

Figure S7 shows the variation in X-ray reflectivity data for a freshly etched and hydrogen-terminated Si(111)-H wafer over the first 8½ hours after exposure to air (with data plotted as RQ^4 vs Q for clarity). The surface is initially very smooth with a RMS roughness of 1.7(1) Å (black curve). Over the next 1½ hours the surface reveals a marked increase in roughness (3.2(1) Å, red curve), associated with the oxidation of the hydride surface. The following 5 hours shows a progression in the oxidation of the surface (inset, Figure S7), with the oxide layer becoming increasingly smooth

(2.6(1) Å, pink curve); although never as smooth as the original hydride-terminated surface.

Reflectivity data after the first 8½ hours (Figure S8) show a different phenomenon taking place at the surface. Preliminary modelling of these data suggested that the surface was becoming rougher; however this was not the case. The appearance of a clear minimum associated with a Kiessig fringe at $Q \sim 0.6 \text{ \AA}^{-1}$ after 15½ hours, and its movement to lower Q values with time indicated the presence of an adsorbed water layer on this surface. The increase in thickness of the adsorbed water layer on this surface is given in the manuscript Figure 3.

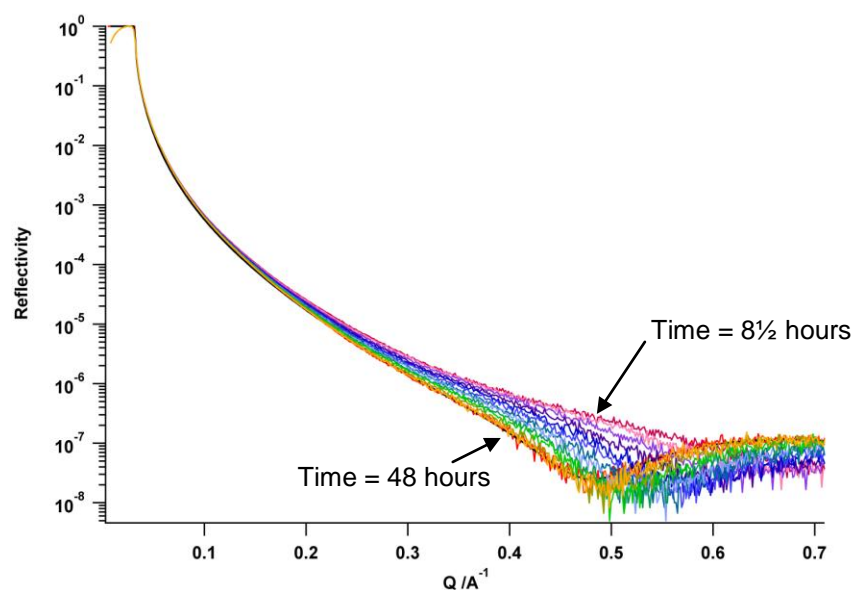


Figure S8. X-ray reflectivity of the water uptake on an oxidized Si-H surface with time. Time period between each curve is 82 minutes/hours.

Effect of vacuum treatment

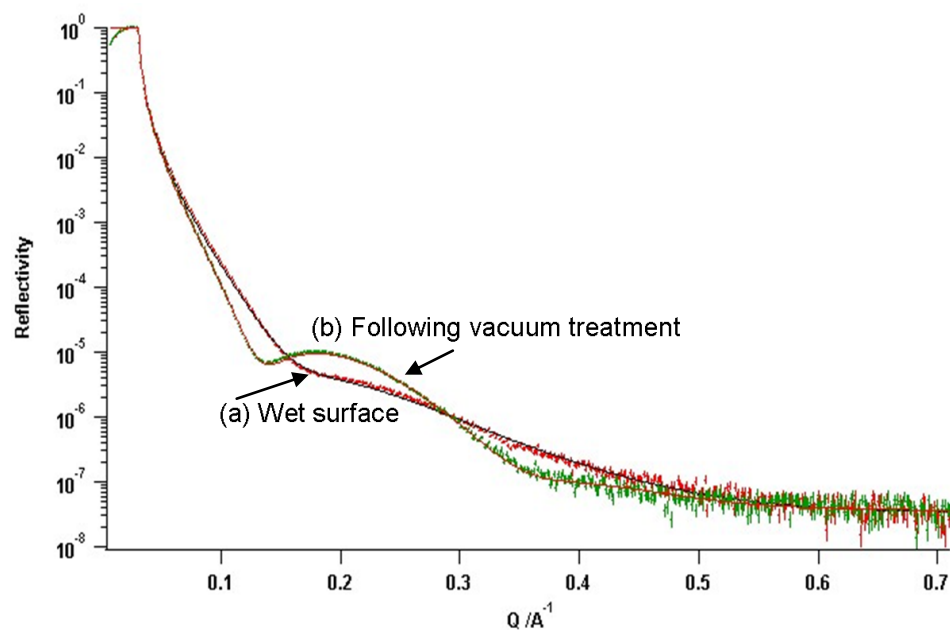


Figure S9. Observed (points) and fitted (solid lines) X-ray reflectivity data from: (a) SAM-6, wet after exposure to ambient conditions for several days (red data); (b) the same sample after storage under vacuum for 20 hours (green data).

References

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