

Experimental Details

Reaction of Si(111)-H with ethyl undecylenate. Shards of Si(111) were first cleaned in a mixture of 30 percent hydrogen peroxide and concentrated sulfuric acid (clean room grade, 1:3 v/v) at 100°C for 20 minutes. After copious rinsing with MilliQ water the shards were placed in a previously deoxygenated solution of 40 percent ammonium fluoride (Olin, 10 ppb) for 15 minutes. The shard was carefully removed and transferred under argon, into a Schlenk tube containing 3ml of deoxygenated ethyl undecylenate, and irradiated in a Rayonet reactor for 3 hours. The functionalized substrate was rinsed with THF, MilliQ water and trichloroethane.

Ester hydrolysis. The ester functionalized surface was placed in a teflon vial containing 10ml of 2.4N HCl and warmed to 70°C for 2 hours. The vial was cooled down to room temperature and the substrate was rinsed with MilliQ water, THF and trichloroethane.

Reaction with glycine methylester. In a Schlenk tube, were placed 0.5g (4 mmoles) of glycine methylester hydrochloride, 1.7 ml (12 mmoles) of triethylamine, 2 ml (12.8 mmoles) of 1,3-diisopropylcarbodiimide and 12 ml of CHCl₃. The acid-terminated surface was immersed in the solution and warmed for 18 hours at 50°C. The silicon substrate was then rinsed at room temperature with ethanol, tetrahydrofuran and trichloroethane.

Preparation of the alcohol-terminated surface. The ester-modified surface (prepared as above) was transferred under argon in a Schlenk tube containing 9ml of sodium borohydride 0.5M in methoxyether and warmed to 85°C for 4 hours. The substrate was then rinsed with ethanol, MilliQ water, tetrahydrofuran and trichloroethane.

Reaction of the alcohol-modified surface with acetyl chloride. The alcohol-terminated substrate was transferred under argon into teflon vial containing 10 ml of acetyl chloride, and allowed to react at 50°C for 14 hours. The excess of acetyl chloride was removed by rinsing, at room temperature, with ethanol, tetrahydrofuran and trichloroethane.

Reaction of the ester-modified surface with decyl magnesium bromide. The ester-functionalized surface was transferred into a Schlenk tube under argon. A solution of decyl magnesium bromide 1.0 M in diethyl ether was added until the substrate was fully covered. After 24 hours at 90°C, the substrate was rinsed, at room temperature, with 1% CF₃COOH solution in THF, MilliQ water, THF and trichloroethane to yield a surface terminated with an alcohol function. The tertiary alcohol was esterified with acetyl chloride using the procedure outlined above.

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectra (XPS) were recorded on a Kratos Axis Instrument, using monochromated AlK α (1486 eV) radiation with detection on the surface normal. The pressure during analysis was about 5×10^{-8} Torr. The XP survey spectrum for the amide modified surface is shown in Figure 1S. The high resolution spectra for Si_{2p}, O_{1s}, N_{1s} and C_{1s} are shown in Figure 2S. Estimated atomic percentages of the elements are given in Table 1S.

Atomic Force Microscopy

Atomic force microscopy was carried out using a Molecular Imaging PicoSPM equipped with an environmental chamber and a Nanoscope IIIa controller (Digital Instruments). The sample was kept in an Argon environment for all measurements. AFM images were acquired at 1 Hz in contact mode using silicon nitride sharpened tips (Digital Instruments, 0.12 N m^{-1}) at a constant force of 1 to 2 nN. Images are leveled but otherwise unfiltered. An AFM image of the ester modified surface is shown in Figure 3S.

Table 1S. XP Intensity data for the $\text{Si}(111)\text{-C}_{10}\text{H}_{20}\text{C}(\text{O})\text{NHCH}_2\text{CO}_2\text{Me}$ surface.

Peak	Position (eV) ^a	Raw Area	Sensitivity Factor	Atomic Conc. (%)	Normalized Atomic Conc. (%) ^a
Si_{2p}	99.34	4319	0.27	55.2	-
	99.95	2954			
O_{1s}	532.09	2455	0.66	9.33	3.7 (3)
	534.15	546			
N_{1s}	400.13	503	0.42	2.46	1 (1)
C_{1s}	284.86	3004	0.25	32.98	13.4 (14)
	286.65	440			
	288.20	345			
	289.58	231			

^aThe peak positions and intensities were determined using a standard deconvolution procedure.

^bThe expected atomic concentration is in parentheses.

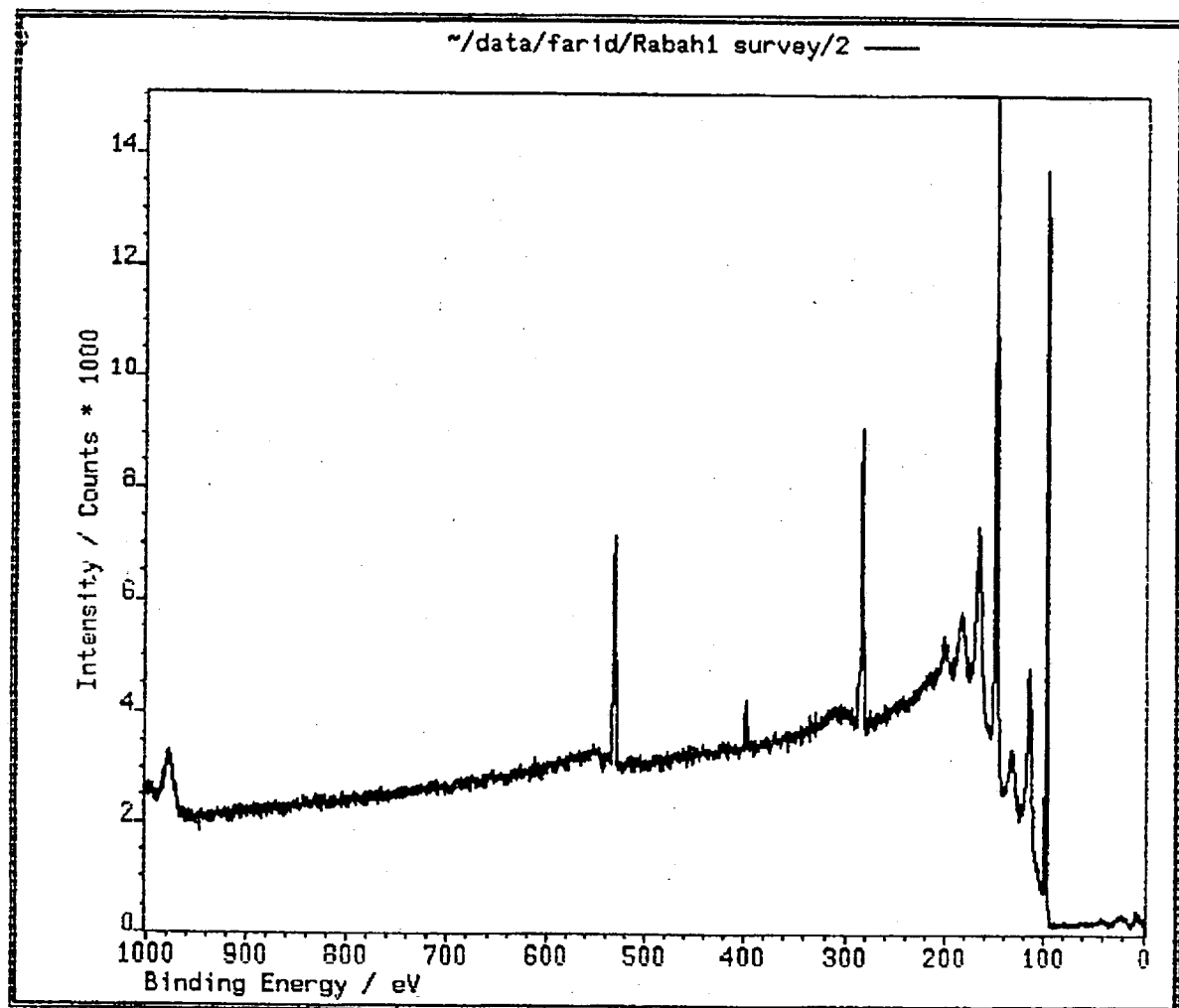


Figure 1S. XP survey spectrum of a Si(111)-C₁₀H₂₀C(O)NHCH₂CO₂Me surface.

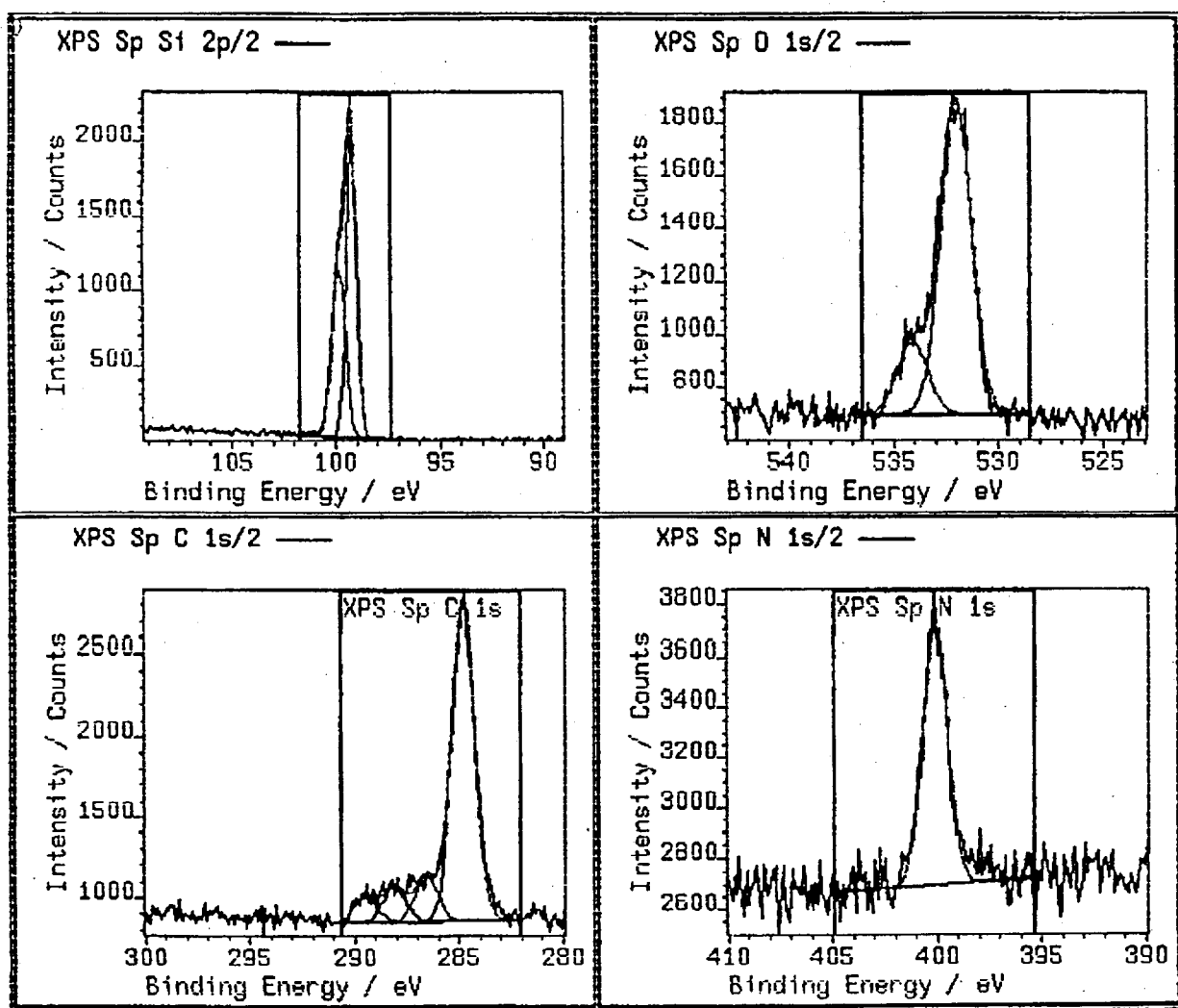


Figure 2S. High resolution XP spectra of the Si_{2p}, O_{1s}, C_{1s} and N_{1s} peaks. Deconvolution was carried out with the assumption that the line widths are invariant for a given element.

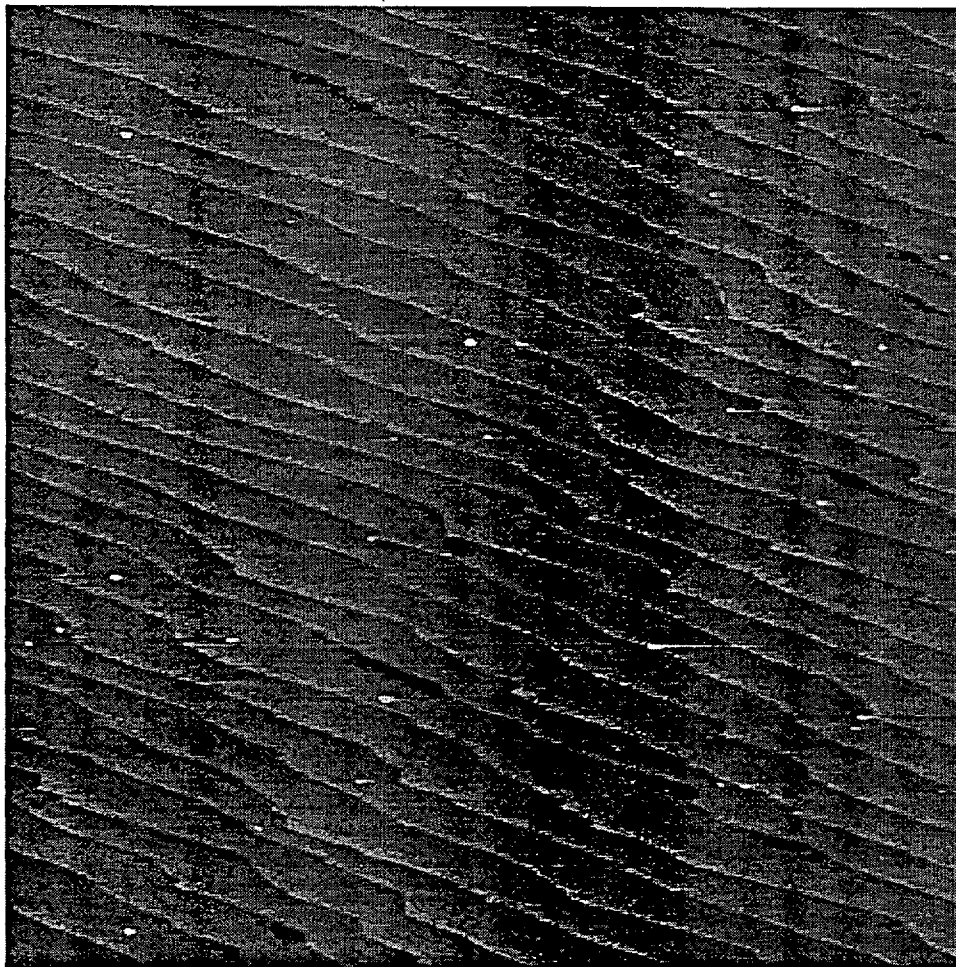


Figure 3S. Contact mode AFM image ($5 \times 5 \mu\text{m}^2$) of the ester modified surface, Si(111)- $\text{C}_{10}\text{H}_{20}\text{CO}_2\text{H}$. The image has been flattened but not leveled in order to be able to view all of the terraces. The step height as measured by AFM is $0.31 \pm 0.02 \text{ nm}$. This and other images demonstrate that the surfaces are atomically flat on the tens of micron scale.