Functional Monolayers on Oxide-Free Silicon Surfaces via Thiol-Ene Click Chemistry

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Electronic Supplementary Information

Table of Contents

1. General Information

All materials were obtained from Aldrich and used as received, unless otherwise noted. Fmoc-protected cysteine (99.6%) was purchased from Chem-Impex International. Diethyl ether and dichloromethane were distilled before use. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded on a Bruker Avance III 400 MHz spectrometer at room temperature. Chemical shifts are reported in parts per million (δ) relative to $CHCl_3$ (7.26 ppm for ^{1}H and 77.2 ppm for ^{13}C) as internal reference.

Static water contact angles were measured with an automated Krüss DSA 100 goniometer under ambient conditions. Small droplets of 3.0 μL deionized water (18.3 MΩ cm resistivity) were dispensed with a micro syringe. The error in the contact angles is ±1°. XPS measurements were performed on a Jeol JPS-9200 system using a standard Al K_α source with an X-ray power of 300 W, an analyzer pass energy of 10 eV, and energy resolution of <0.65 eV. All C_{1s} (C-C) and Si_{2p} peaks were calibrated to binding energies of 285.0 and 100.0 eV, respectively. ATR-IR spectra were collected with a Bruker spectrometer (model Tensor 27) equipped with a Harrick ATR accessory and MCT-detector. A

Harrick grid polarizer was placed in front of the sample for measuring spectra with p-polarized (parallel) light. Double side polished n-Si(111) wafers (5 × 1cm) with 45° bevels (± 100 internal reflections) were obtained from Siltronix (France). The spectra were taken at a resolution of 4 cm^{-1} with 2048 scans (constant flow of dry N_2) and were referenced to a clean native oxide-covered ATR crystal. Atomic force microscopy (AFM) images were obtained using a scanning probe microscope in AC-mode (AC-AFM) in air (JSPM-5400, JEOL Japan). The imaging was performed using silicon cantilevers NSC35/AIBS from MikroMasch using a scan rate of 1 Hz per line.

2. Synthesis of 1,13-Tetradecadiene

This compound was prepared according to the procedure reported by Wilkinson.[1] The Grignard reagent was prepared from Mg turnings (2.6 g, 108 mmol) and 11-bromo-1-undecene (12.7 g, 54 mmol) in dry diethyl ether (150 mL). The resulting solution was filtered and allyl bromide added dropwise (13.0 g, 102 mmol). The mixture was refluxed overnight. The organic solvent was removed and subsequently the mixture was washed with water. The organic phase was extracted with diethyl ether and washed with water three times. The organic phase was then dried with anhydrous $MgSO_4$, filtered and the solution was concentrated by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (eluted with hexanes). The desired compound was isolated as a colorless oil in 90 % yield (2.72 g, 50.4 mmol) and a purity of 99.7% (GC-MS).

^1H NMR ($CDCl_3$, 400 MHz) δ 5.77-5.86 (m, 2H, C-H), 4.92-5.03 (dd, 4H, CH_2=CH), 2.02-2.08 (q, 4H, CH-CH_2), 1.37-1.41 (m, 6H, CH_2), 1.24-1.28 (m, 8H, CH_2).

^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.19 (CH_2=CH), 114.36 (CH_2=CH), 33.80 (CH-CH_2), 29.50 (CH_2), 29.14, 29.07 (CH_2).

3. Monolayer Preparation

Monolayers were prepared according to the procedures reported previously by our group.[2] Samples of single-polished Si(111) (n-type, 475-550 μm thick, resistivity 1.0-5.0 Ω cm, Siltronix, France) were washed first with acetone (semiconductor grade) and then sonicated for 5 min in acetone. The samples were cleaned using piranha acid (H_2SO_4 : H_2O_2, 3:1) for 0.5 h. **Caution: Piranha solution reacts**

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[1] Wilkinson, R. *J. Chem. Soc.* **1931**, 3057-3062.

violently with organic materials and should be handled carefully! After rinsing with copious amounts of deionized water (18.3 MΩ cm resistivity) and dried with a stream of dry Argon, the Si(111) substrates were etched in an Argon saturated 40% aqueous NH_4F (semiconductor grade) solution for 15 min under Argon. The substrates were rinsed with deionized water and dried with a stream of Argon. Neat 1,13-tetradecadiene (1.0 g) was poured in a small three-neck flask equipped with a capillary (for the Ar inlet) and a reflux condenser (connected to a vacuum pump). The flask was immersed in an oil bath at 75 °C. The solution was degassed for 0.5 h by bubbling Argon through the capillary; subsequently the pressure of the flask was reduced to approximately 4 mbar. The freshly etched Si(111) substrate was added to the flask under Argon at atmospheric pressure. After addition of the substrate, pressure was reduced, and the capillary was moved away from the solution to avoid disturbance of the forming monolayer. The reaction flask was kept at 75 °C for 16 h under vacuum (4 mbar) with a small Argon flow and ambient light (i.e., standard fluorescent lamps in the fume hood were on). After cooling the reaction flask to room temperature, the vacuum was released with Argon and the silicon wafer was removed from the diene. The silicon wafer was rinsed with hexanes, ethanol and dichloromethane and dried with a stream of Argon. The functionalized silicon wafers were characterized by water contact angle measurements, X-ray photoelectron spectroscopy (XPS) and attenuated total reflectance infrared (ATR-IR) spectroscopy. Static water contact angle: 96°.

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[2] Scheres, L.; Arafat, A.; Zuilhof, H. *Langmuir* **2007**, 23, 8343-8346.

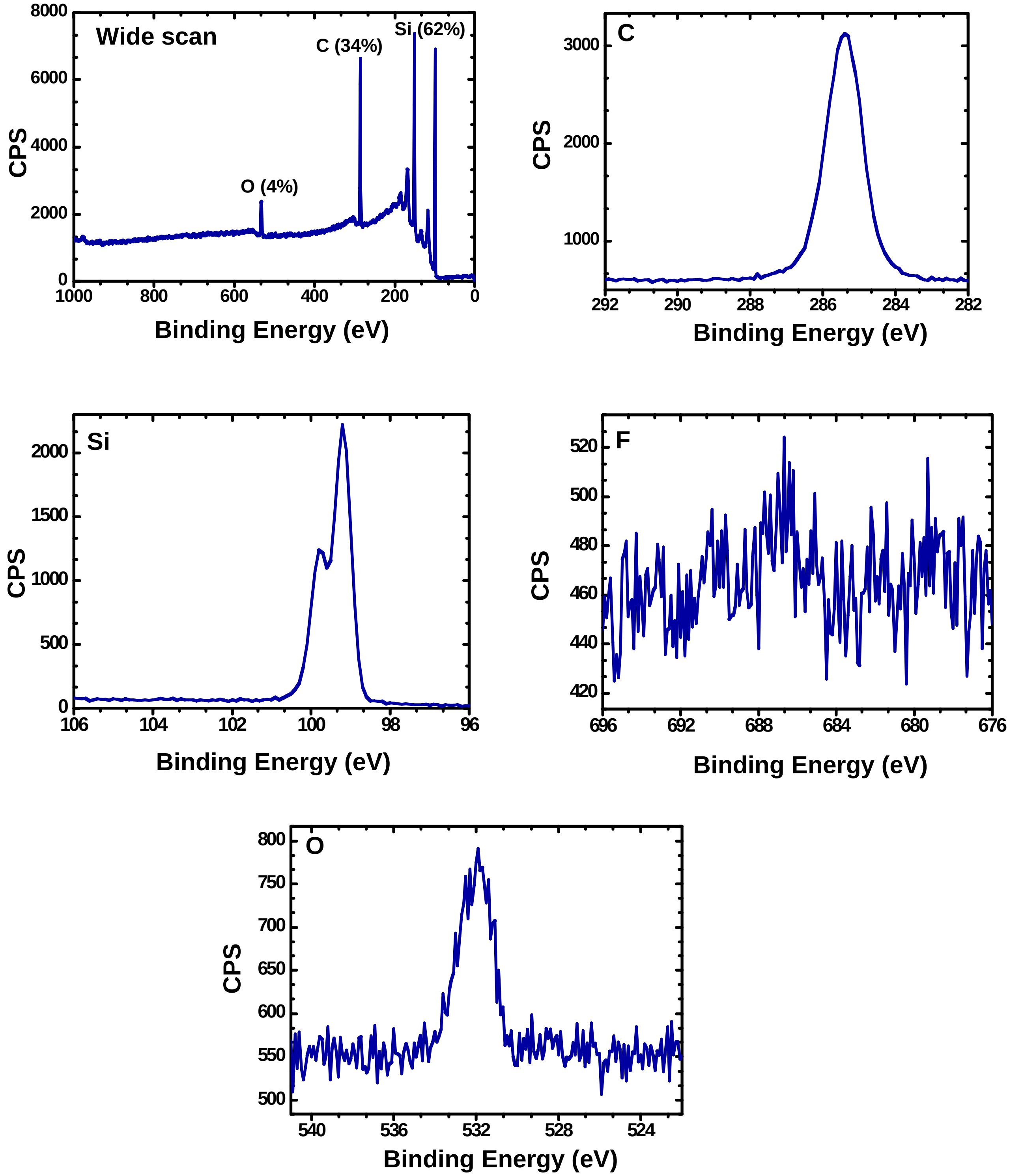


Figure S1. XPS spectra of the alkene-terminated silicon monolayer.

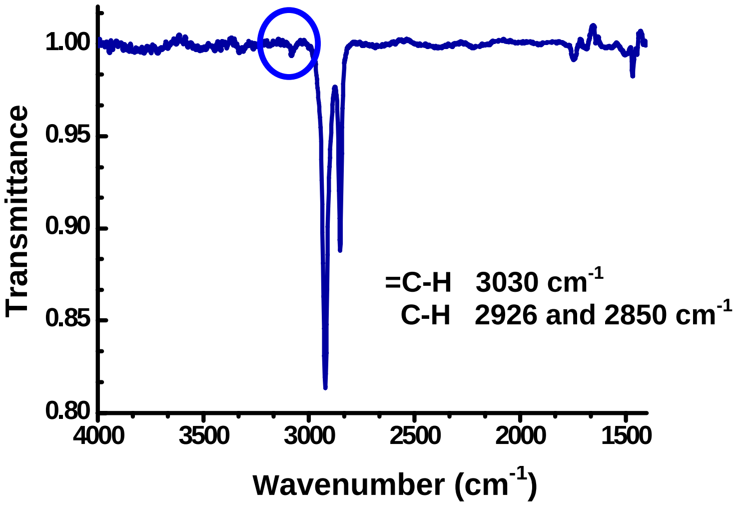


Figure S2. ATR-IR spectrum of the alkene-terminated silicon monolayer.

4. Thiol-Ene Chemistry

In a vial, 1 equiv. of corresponding thiol and 0.2 equiv. of DMPA (2,2-dimethoxy-2-phenylacetophenone) were dissolved in the minimal amount of chlorobenzene or a mixture of chlorobenzene : DMF (1:1) in order to solubilize all components. The solution was stirred before the alkene-terminated silicon wafer was covered with the solution. The solution was irradiated with a UV lamp (365 nm) for 1.5 h under ambient conditions without deoxygenation. After the reaction, the silicon wafer was washed several times with chlorobenzene, n-hexane and dichloromethane and dried with a stream of Argon. The silicon wafers were characterized by water angle contact measurements and XPS.

4.1 Thioglycolic acid

Amounts employed: 0.5 mL (665 mg, 7.22 mmol) thioglycolic acid, (370 mg, 1.44 mmol) DMPA in 1 mL chlorobenzene. Static water contact angle of resulting monolayer: 56°.

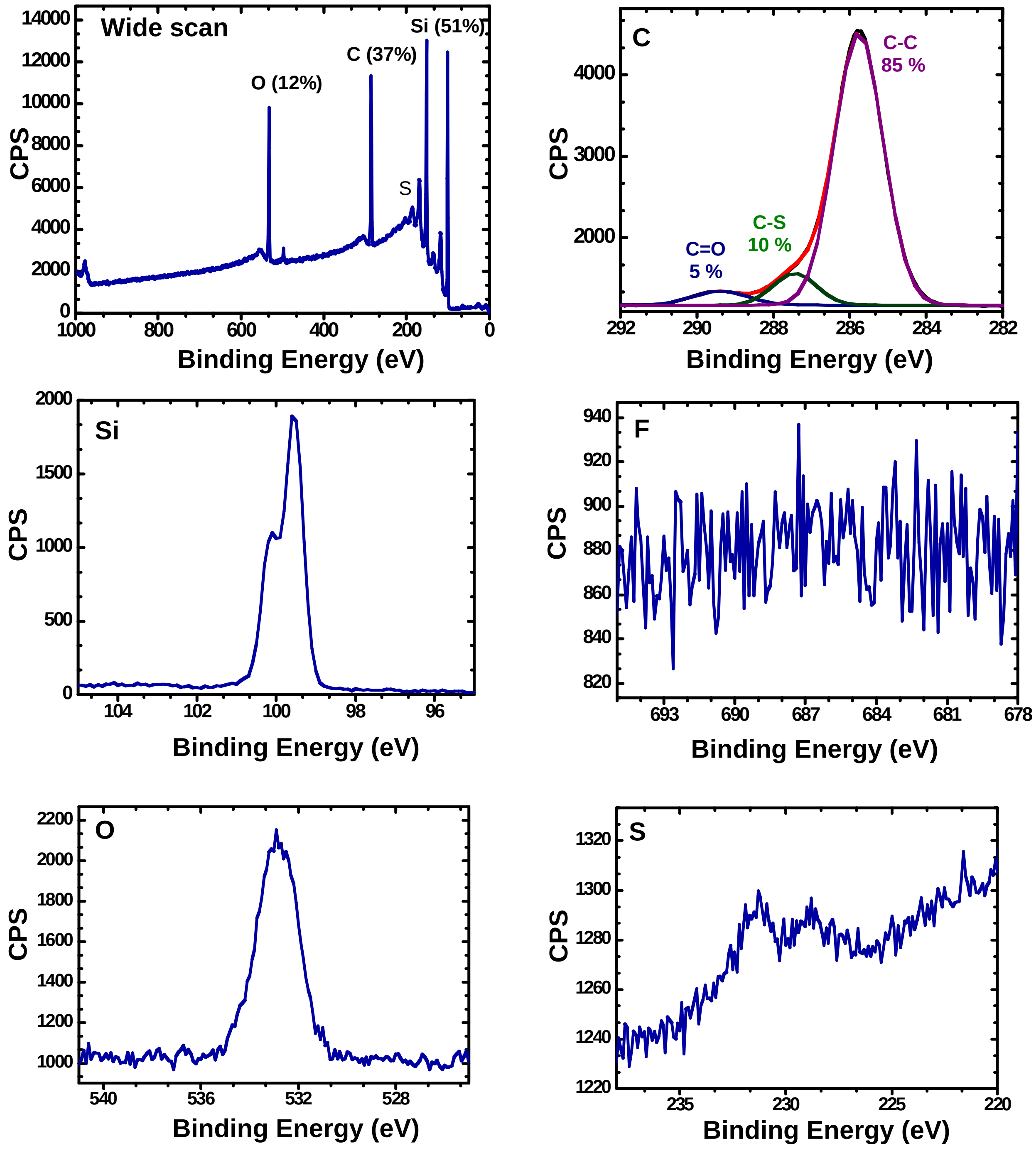


Figure S3. XPS spectra of the acid-terminated silicon monolayer.

4.2 Thiolacetic acid

Amounts employed: 0.25 mL (264 mg, 3.47 mmol) thiolacetic acid, (177 mg, 0.70 mmol) DMPA in 0.5 mL chlorobenzene. Static water contact angle of resulting monolayer: 82°

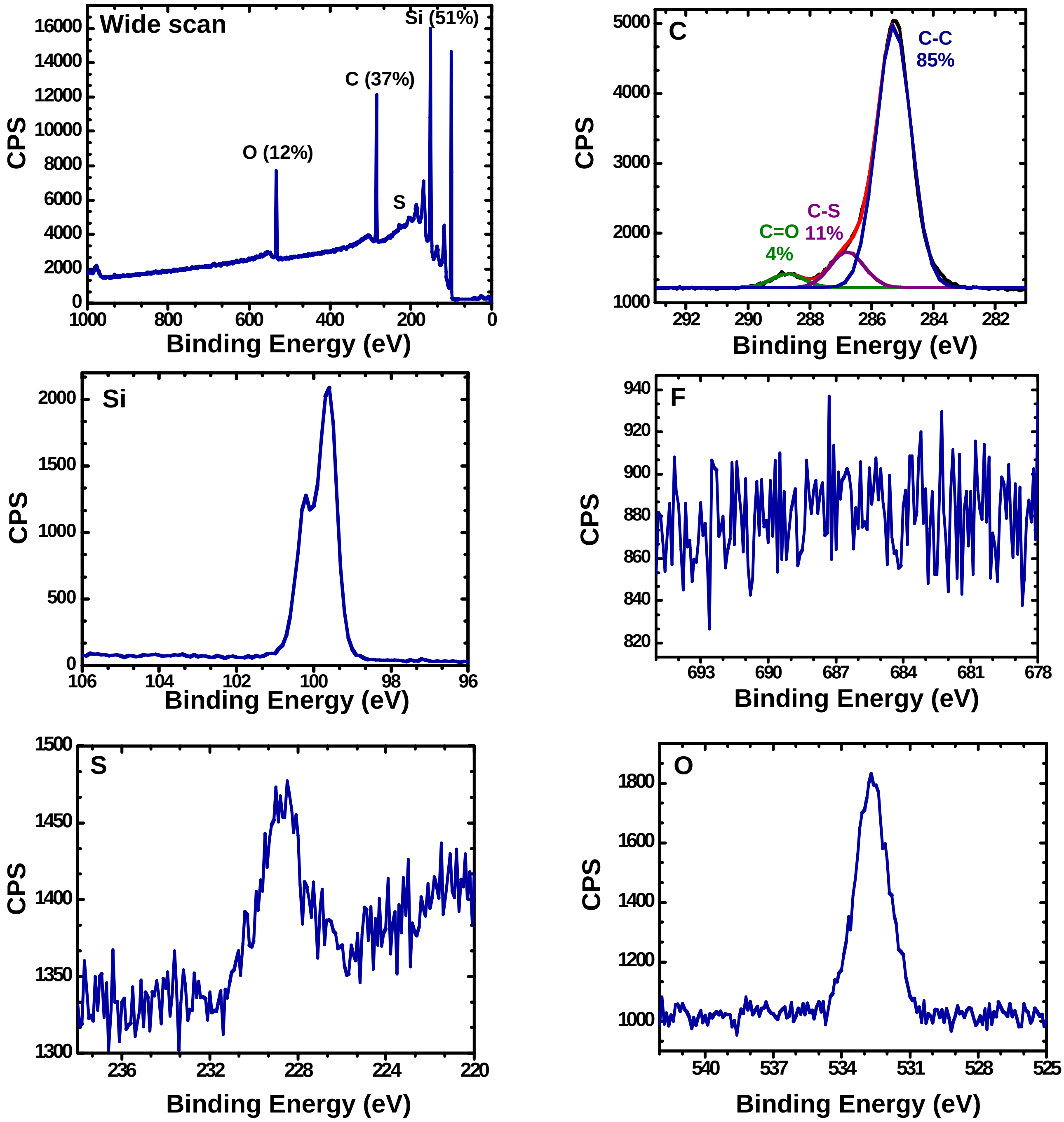


Figure S4. XPS spectra of the thioester-terminated silicon monolayer.

4.3 Thioglycerol

Amounts employed: 0.25 mL (311 mg, 2.86 mmol) thioglycerol, (147 mg, 0.57 mmol) DMPA in 0.5 mL chlorobenzene. Static water contact angle of resulting monolayer: 55°.

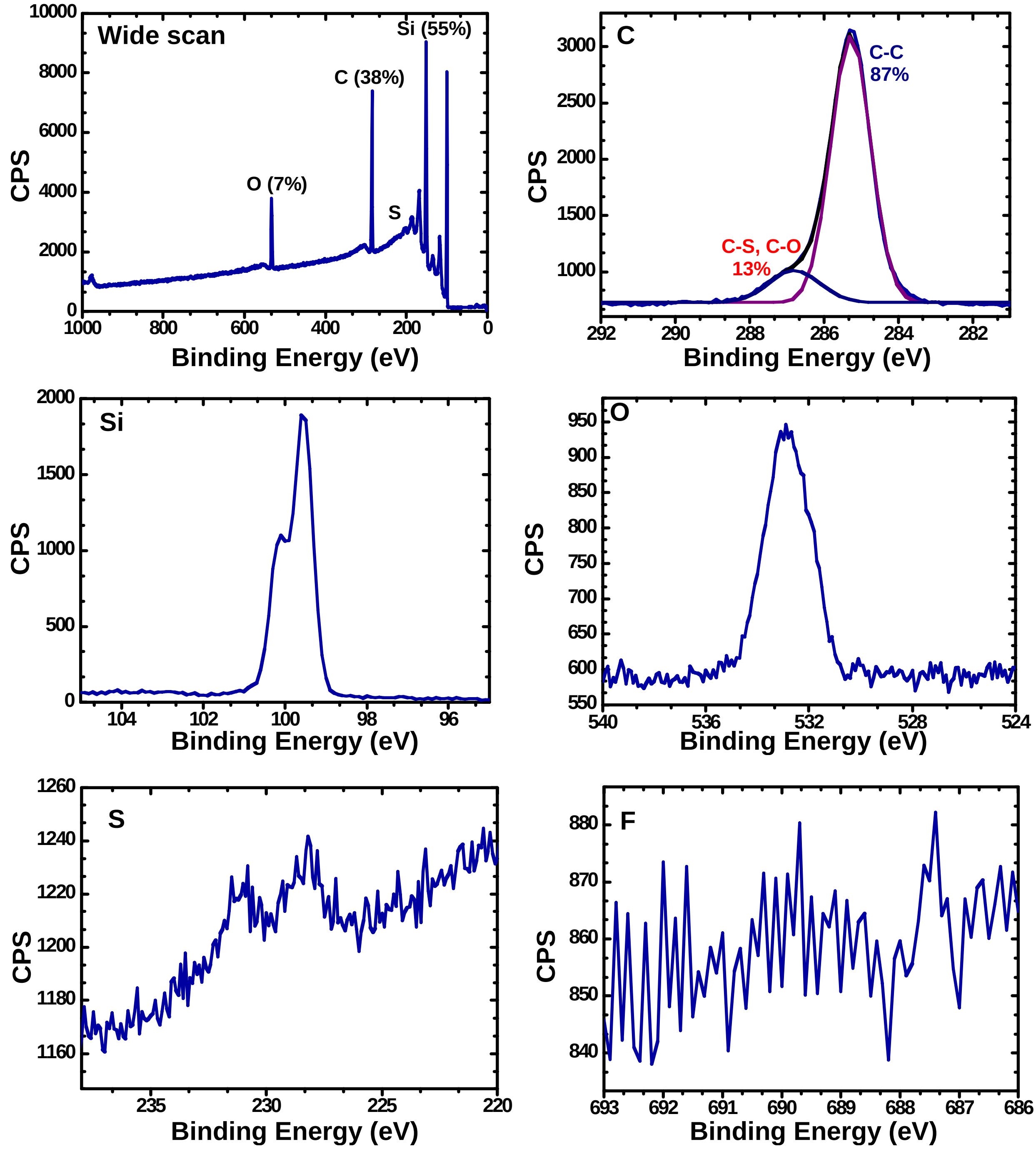


Figure S5. XPS spectra of the alcohol-terminated silicon monolayer.

4.4 1-Thio-β-D-glucose Tetraacetate

Amounts employed: 50 mg (1.14 mmol) thioglucose, (7.02 mg, 0.027 mmol) DMPA in 0.5 mL DMF. Static water contact angle of resulting monolayer: 65°.

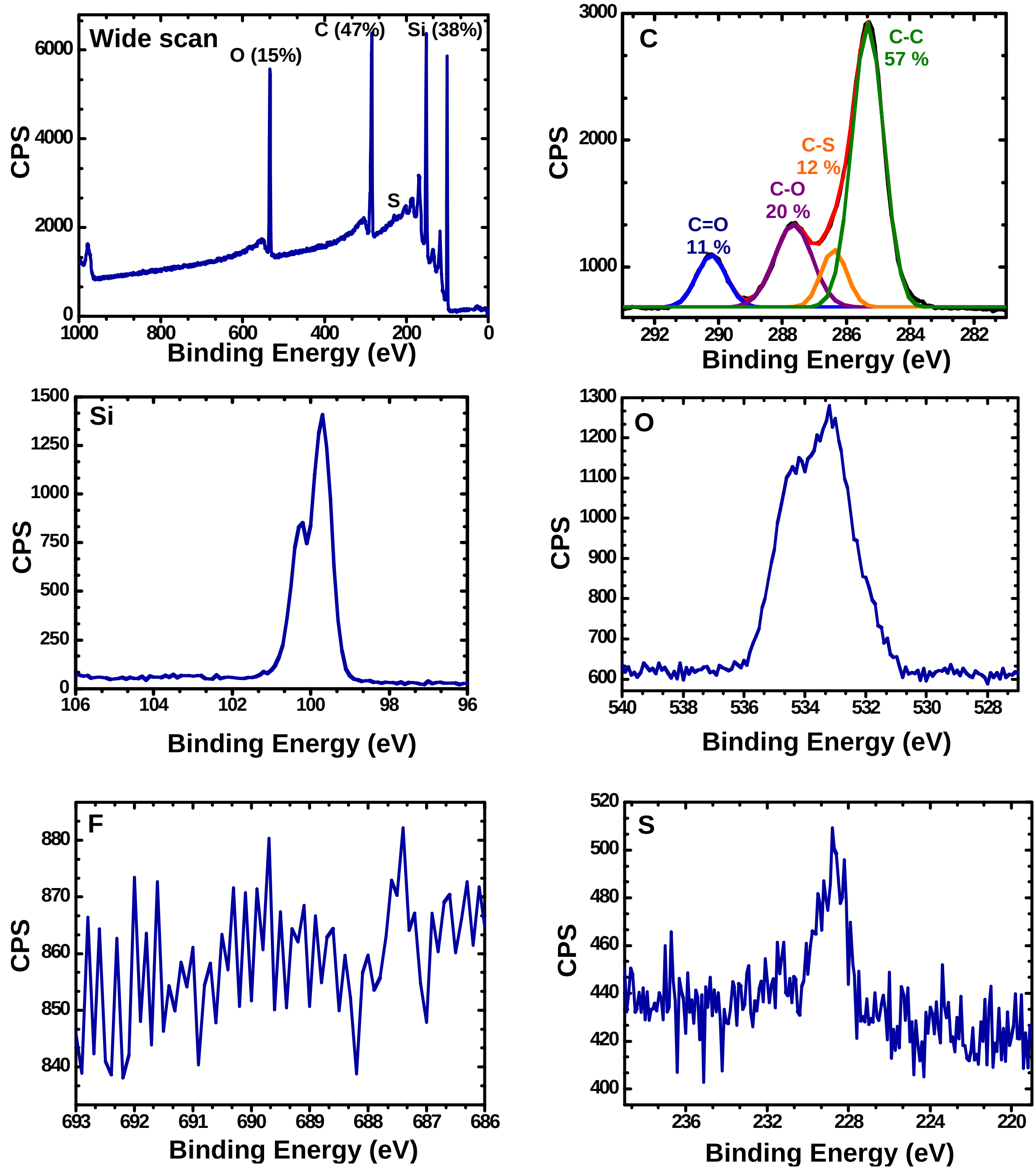
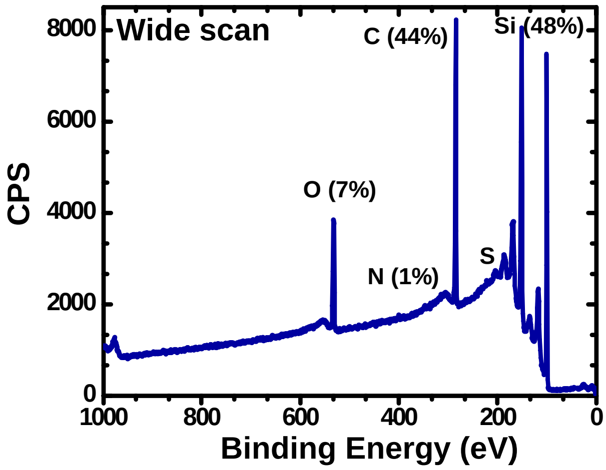
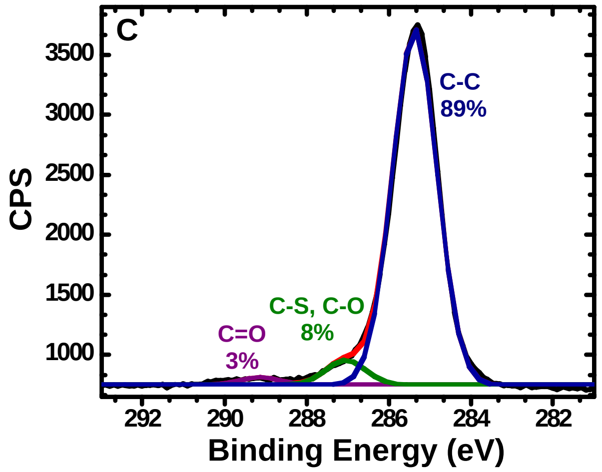


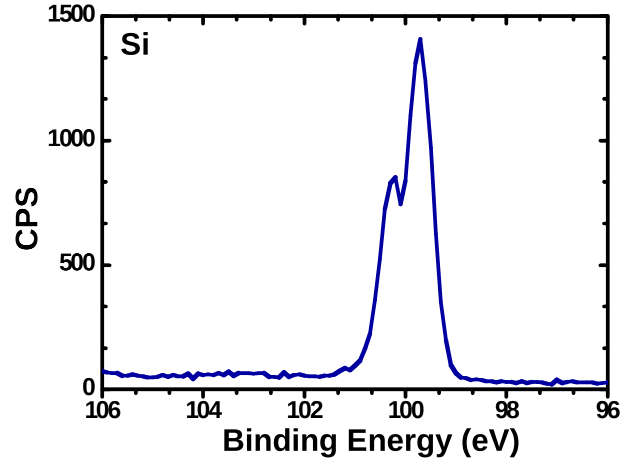
Figure S6. XPS spectra of the thioglucose-terminated silicon monolayer.

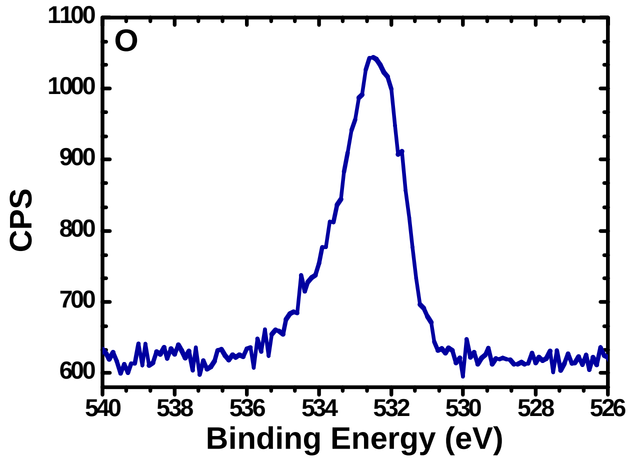
4.5 Fmoc-Cysteine

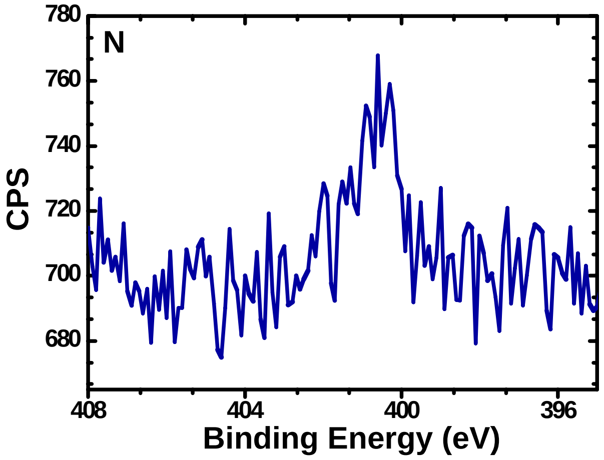
Amounts employed: 25 mg (0.072 mmol) Fmoc-Cys, (3.73 mg, 0.014 mmol) DMPA in 0.5 mL DMF-chlorobenzene (1:1). Static water contact angle of resulting monolayer: 70°.











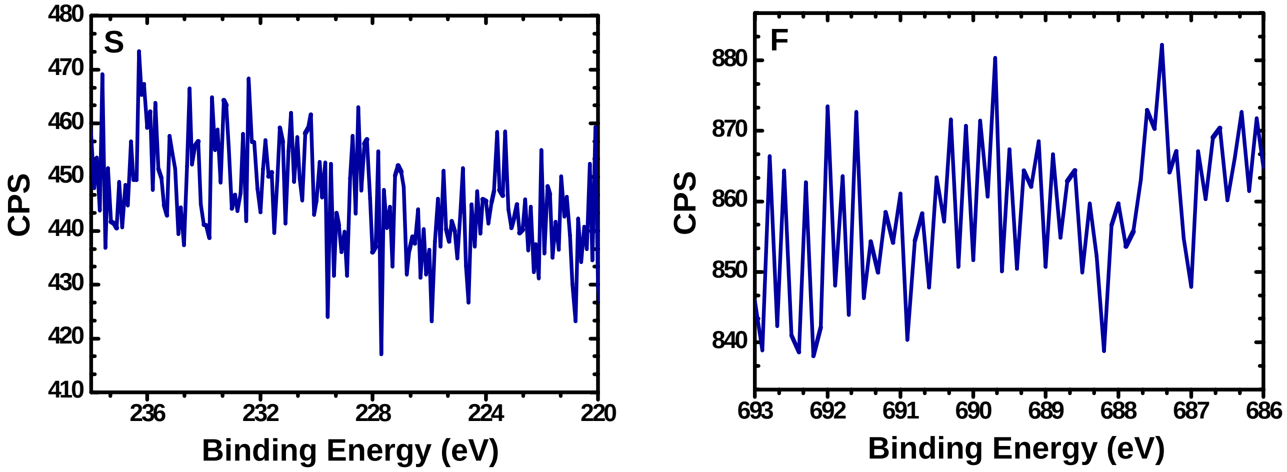


Figure S7. XPS spectra of the Fmoc-cysteine-terminated silicon monolayer.

4.6 3-Mercaptopropyl Trimethoxysilane

Amounts employed: 0.25 mL (264 mg, 1.34 mmol) 3-mercaptopropyl trimethoxysilane (69 mg, 0.27 mmol) DMPA in 0.5 mL chlorobenzene. Static water contact angle of resulting monolayer: 60°.

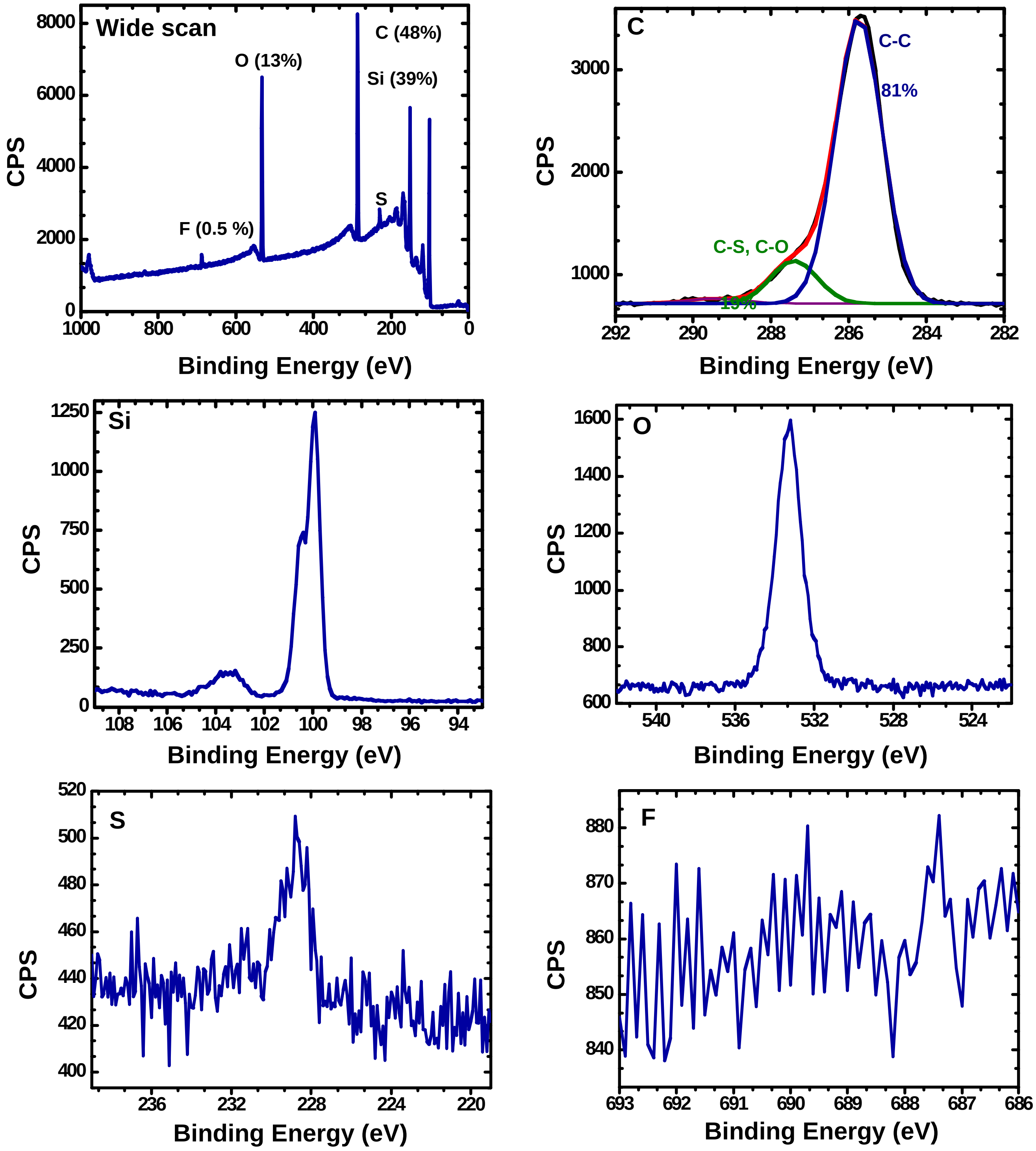


Figure S8. XPS spectra of the trimethoxysilane-terminated silicon monolayer.

5. Deprotection of the Thioester Group and Attachment of Gold Nanoparticles

The thioester-terminated silicon wafer obtained after thiol-ene chemistry with thiolacetic acid was dried with a stream of Argon before immersion into a solution of sodium methoxide (2 mL, 0.5 M in MeOH) under Argon for 0.5 h. The wafer was washed with ethanol and dichloromethane and dried with a stream of Argon. The surface was characterized by water contact angle measurements and XPS spectroscopy. Static water contact angle of resulting monolayer: 78°.

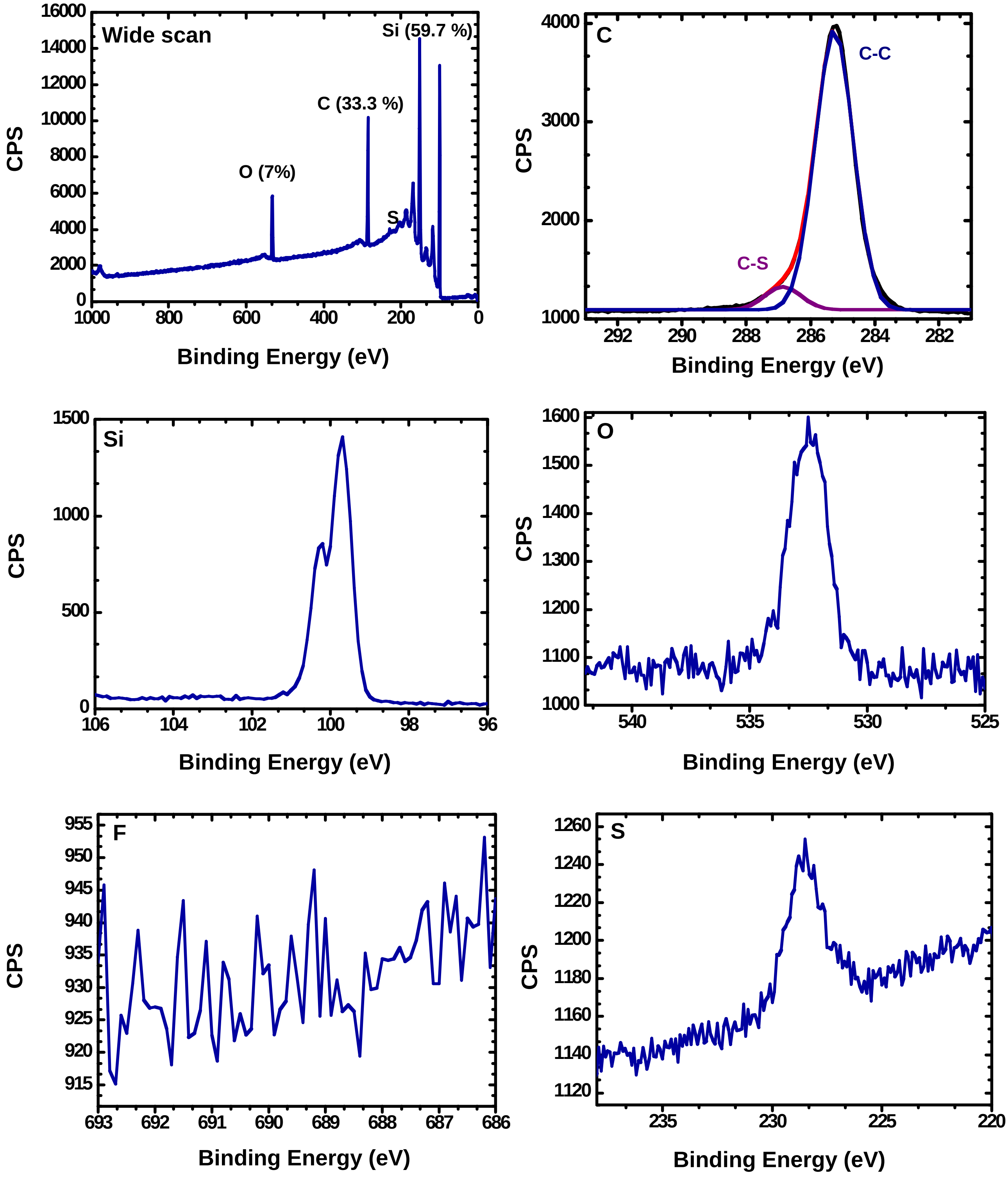
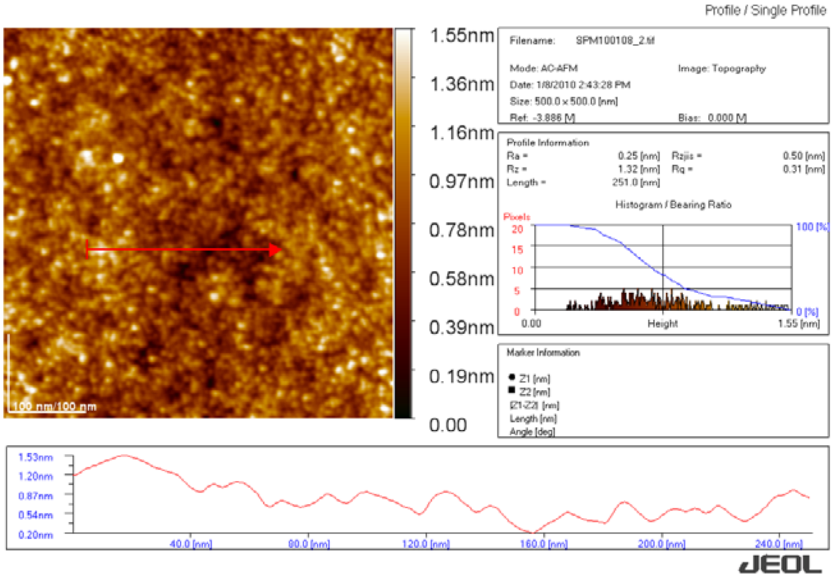


Figure S9. XPS spectra of the thiol-terminated silicon monolayer.

The thiol-terminated surface was then immersed in a solution containing gold nanoparticles (15 nm) for 10 minutes under Argon. The wafer was washed with ethanol and dichloromethane and dried with a stream of Argon. The surface was characterized by AFM in topographical tapping mode.



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Profile Information

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Length = 251.0 [nm]

Rzjis = 0.50 [nm]

Rq = 0.31 [nm]

Figure S10. AFM image of the thiol-terminated silicon monolayer

6. Microcontact Printing

PDMS stamps (flat and with pillar-like features of 10 μm) were prepared by casting a prepolymer of PDMS on a photolithographically patterned silicon master, cured for 20 h at 60 °C and released at 60 °C. Subsequently, the stamps were cleaned by extensive soxhlet extraction and ultrasonicated with EtOH and dried under a stream of N_2. A PDMS stamp was inked with a solution containing thioglycolic acid (1.0 mL) and DMPA (320 mg) in EtOH (0.3 mL), and subsequently dried in a stream of N_2. The stamp was brought in conformal contact with the alkene-terminated monolayer and the sample was irradiated through the stamp with a UV lamp (365 nm) for 5 minutes under ambient conditions. The stamp was released and the patterned monolayer was rinsed several times with EtOH and CH_2Cl_2. The silicon wafer was ultrasonicated with CH_2Cl_2 and dried with a stream of dry nitrogen.