

## Surface characterization.

### (a) Contact angle measurements.

A Digidrop-GBX contact angle meter G1 goniometer was used to determine the chemical properties of the surfaces (such as hydrophobic character). The measurements were performed by using HPLC water (Acros organics). About 6 drops were deposited onto the surface using a microsyringe, and the reading was taken 6 s after deposition; the temperature was held at 25 °C.

### (b) Ellipsometric measurements.

The measurements were made on a Plasmos SD 2300 ellipsometer with a rotating analyzer as modulating element. The laser source was a helium/neon laser with a wavelength of 632.8 nm. The angle of incidence is 70° and the spot size was about 2 mm. The substrate was silica which had grown on silicon. The refractive index was 1.46 for silica and 3.83 for silicon. A refractive index of 1.45 was used for the silane layers.

### (c) *In situ* ATR Measurements.

ATR infrared spectra were recorded on a FTIR Perkin-Elmer 2000 spectrometer equipped with narrow band liquid nitrogen cooled MCT detector and a thermoregulated ATR flow cell. The sample compartment was purged with dry air. All the spectra were recorded at a resolution of 1  $\text{cm}^{-1}$ , and 128 scans were accumulated. The flow cell containing the IRE was placed and aligned in the dry air purged sample compartment of the spectrophotometer and thermoregulated at the convenient temperature of the reaction. A peristaltic pump was used to pump the solutions through the cell. First, the cell was filled with pure solvent to collect background spectra and then solutions of reactive materials were pumped and spectra recorded.

### (d) Atomic Force Microscopy.

The atomic force microscope used for these experiments was a commercial optical deflection microscope (stand-alone configuration for a large sample, Dimension 3100 with a nanoscope IIIa, Digital Instruments) operated in ambient conditions. For roughness analysis, measurements were performed in the tapping mode, and commercial silicon cantilever probes with a nominal radius of 5 – 10 nm and a spring constant in the range of 20 – 70 N/m were used. Data are acquired on 1  $\mu\text{m}$  x 1  $\mu\text{m}$  frames having 512 x 512 data points. The images were flattened and no other filtering was done before the roughness is analyzed.

### (e) XPS measurements.

We used a monochromatic Al K $\alpha$  X-ray source and an analyzer pass energy of 12 eV. Under these conditions, the overall resolution as measured from the FWHM of the Ag 3d5/2 line

wass 0.55 eV. The binding energy scale was calibrating using the Au 4f7/2 line at 0.84 eV. The acceptance angle of the analyzer is set to 14° and the angle between the incident X-rays and the analyzer was 90°. The detection angle of the photoelectron is 25°, as referenced to the sample surface. The intensity of the various XPS core levels (CLs) were measured as the peak area after standard background subtraction according to the Shirley procedure. For the CL decomposition, we used Voigt functions and at least-square minimization procedure. The different components were modeled with the same parameters, i.e. the Gaussian and Lorentzian broadenings were kept fixed for each component of a given CL.

Preparation of 10-isocyanatodecyltrichlorosilane:

To a solution of 5.10 g of 9-decenylisocyanate in 5.60 ml trichlorosilane was added drop-wise, under inert atmosphere 300 µl of Karstedt's catalyst while stirring. The reaction was exothermic and the mixture turns yellows. After 2 hours excess trichlorosilane was evaporated, and the residue was distillated under vacuum.

8.4 g (94% yield) of 10-isocyanatodecyltrichlorosilane were obtained.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) : 1.34-1.47 (m, 14H) ; 1.54-1.71- (m, 4H) ; 3.31 (t, <sup>3</sup>J = 6.5 Hz, 2H). <sup>13</sup>CNMR (50 MHz, CDCl<sub>3</sub>) : 22.29 (t, 1C, CH<sub>2</sub>) ; 24.70 (t, 1C, CH<sub>2</sub>) ; 26.82 (t, 1C, CH<sub>2</sub>) ; 29.31 (t, 1C, CH<sub>2</sub>) ; 29.36 (t, 1C, CH<sub>2</sub>) ; 29.62 (t, 1C, CH<sub>2</sub>) ; 29.79 (t, 1C, CH<sub>2</sub>) ; 31.70 (t, 1C, CH<sub>2</sub>) ; 32.17 (t, 1C, CH<sub>2</sub>) ; 43.38 (t, 1C, CH<sub>2</sub>) ; 122.36 (s, 1C, N=C=O). IR (CH<sub>2</sub>Cl<sub>2</sub>) : 2930 (v CH), 2856 (v CH), 2225 (v N=C=O), 1488, 1466, 1056. High Resolution Mass : (M+HCl)<sup>+</sup> : C<sub>11</sub>H<sub>22</sub>O N Cl<sub>4</sub>Si : calc : 352.0225, found 352.0275

**Example of Preparation of semicarbazide-terminated Si(100) surfaces.**

(a) Preparation of oxidized silicon Si(100) surface.

First, the native oxide layer was removed by immersion in aqueous HF solution (40 %) until total dewetting of the surface (about 10 s). The substrates were cleaned by rinsing with HPLC water (Acros Organics). The substrates were then exposed in a home-built UV-ozone chamber. This technique is well-known to eliminate all organic impurities from a surface but was also used to oxidize silicon and obtain a hydrated flat silica surface free from organic pollution. The wafers were placed at a maximum distance of 5 mm from a two-wavelength low-pressure mercury lamp ( $\lambda$  = 185 and 254 nm) under an O<sub>2</sub> stream. After 30 min of exposition, a hydrophilic silica surface (contact angle  $\theta$  < 10°) was obtained. Its thickness, measured by ellipsometry, was about 1.8 – 2.0 nm and its roughness, measured by tapping mode atomic force microscopy, was about 0.15 nm.

(b) Grafting of 10-isocyanatodecyltrichlorosilane on oxidized silicon surface.

The oxidized silicon wafer was placed into a Schlenk tube under nitrogen atmosphere. The grafting solution containing 10-isocyanatodecyltrichlorosilane ( $10^{-2}$  M), diisopropylethylamine ( $10^{-1}$  M) in trichloroethylene was introduced into the tube. trichloroethylene was freshly distilled before use. The wafer was let into the solution for 45 min, at  $0^{\circ}\text{C}$ , under nitrogen atmosphere, without stirring. After this time, the solution was removed and the wafer was washed with trichloroethylene, THF and trichloroethylene.

(c) Reaction of the immobilized isocyanate with the Boc-hydrazine.

Immediately after the washing of the surface, a solution containing Boc-hydrazine ( $10^{-1}$  M) in trichloroethylene was introduced. The wafer was let into the solution for 2 h, at  $0^{\circ}\text{C}$ , under a nitrogen atmosphere, without stirring. After this time, the solution was removed and the wafer was rinsed in trichloroethylene (5 min), then in chloroform (5 min) in an ultrasonic bath, dipped in absolute ethanol (5 min), in trichloroethylene (1 min) and dried under a flow of nitrogen.

(d) Reaction of the immobilized isocyanate with the Fmoc-hydrazine.

Immediately after the washing of the surface, a solution containing Fmoc-hydrazine ( $10^{-1}$  M) in DMF was introduced. The wafer was let into the solution for 2 h, at  $0^{\circ}\text{C}$ , under a nitrogen atmosphere, without stirring. After this time, the solution was removed and the wafer was rinsed in DMF (5 min), then in chloroform (5 min) in an ultrasonic bath, dipped in absolute ethanol (5 min), in trichloroethylene (1 min) and dried under a flow of nitrogen.

(e) Removal of the Boc group and deprotection of the semicarbazide function.

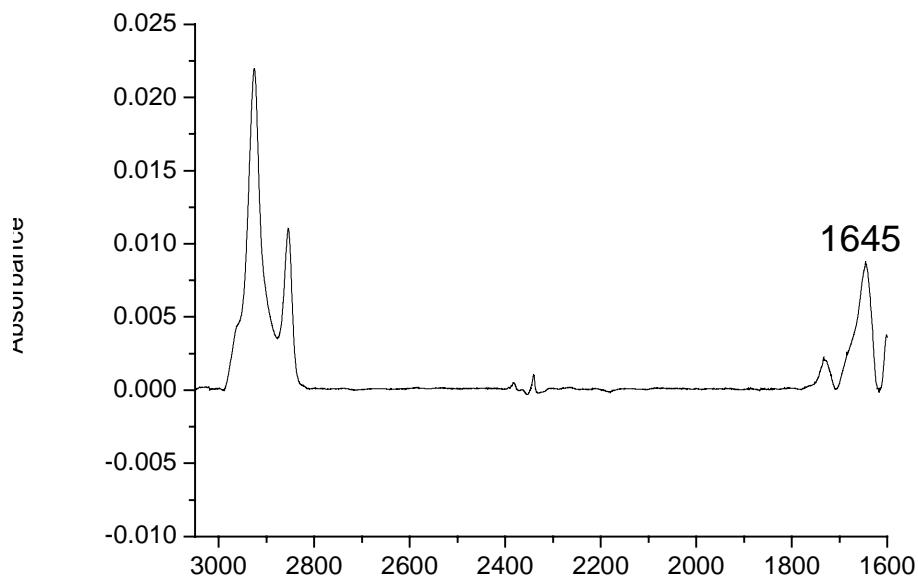
The Boc removal was performed by dipping the protected semicarbazide-terminated surface in a trifluoroacetic acid (TFA)/dichloromethane (6/4) solution for 4 hours. Then the sample was rinsed in an ultrasonic bath in dichloromethane (5 min) and dipped in absolute ethanol (5 min), then dried under a nitrogen flow.

(f) Removal of the Fmoc group and deprotection of the semicarbazide function.

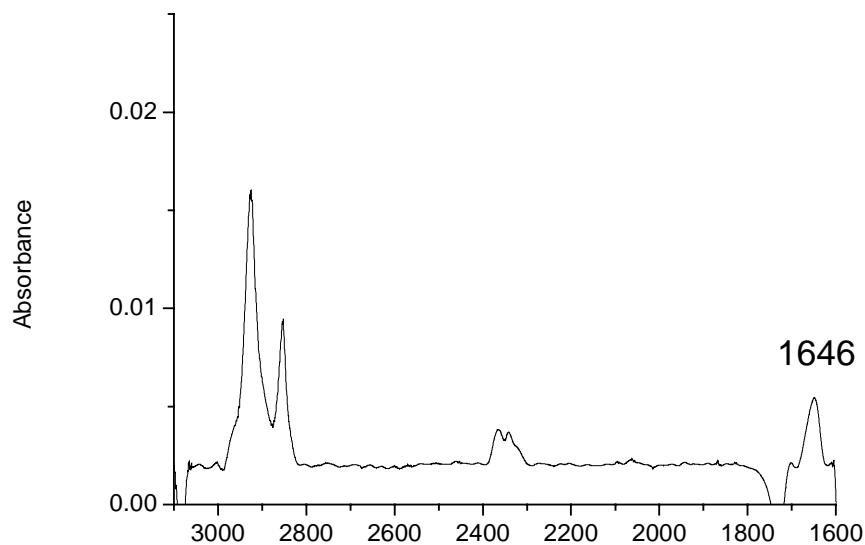
The Fmoc removal was performed by dipping the protected semicarbazide-terminated surface in a solution containing piperidine ( $10^{-1}$  M) in DMF for 4 hours. Then the sample was rinsed in DMF (5 min), then rinsed in an ultrasonic bath in dichloromethane (5 min) and dipped in absolute ethanol (5 min), then dried under a nitrogen flow.

**ATR-FTIR spectra of the NuH-substituted isocyanate surfaces.**

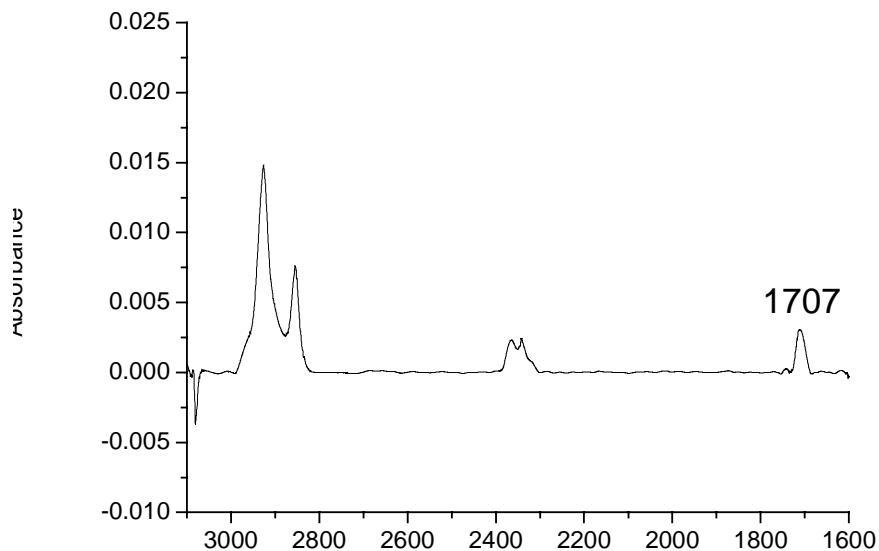
p-Toluidine



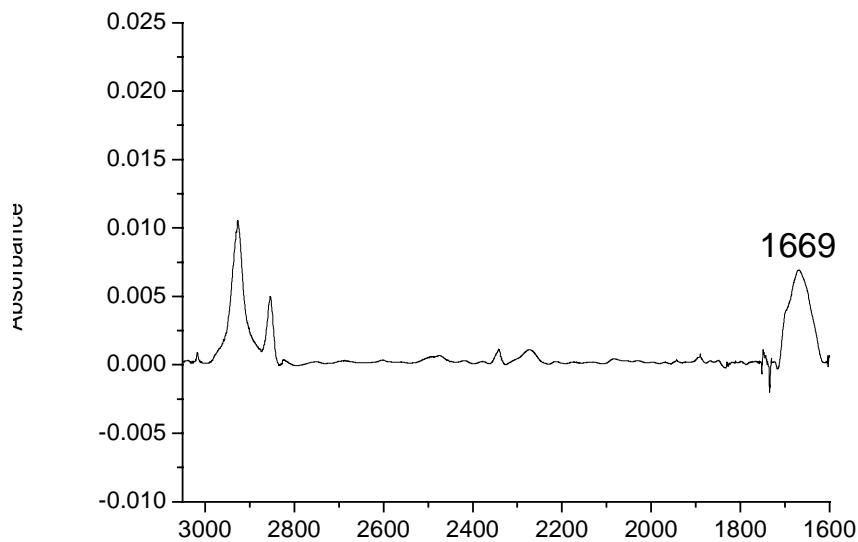
p-Anisidine



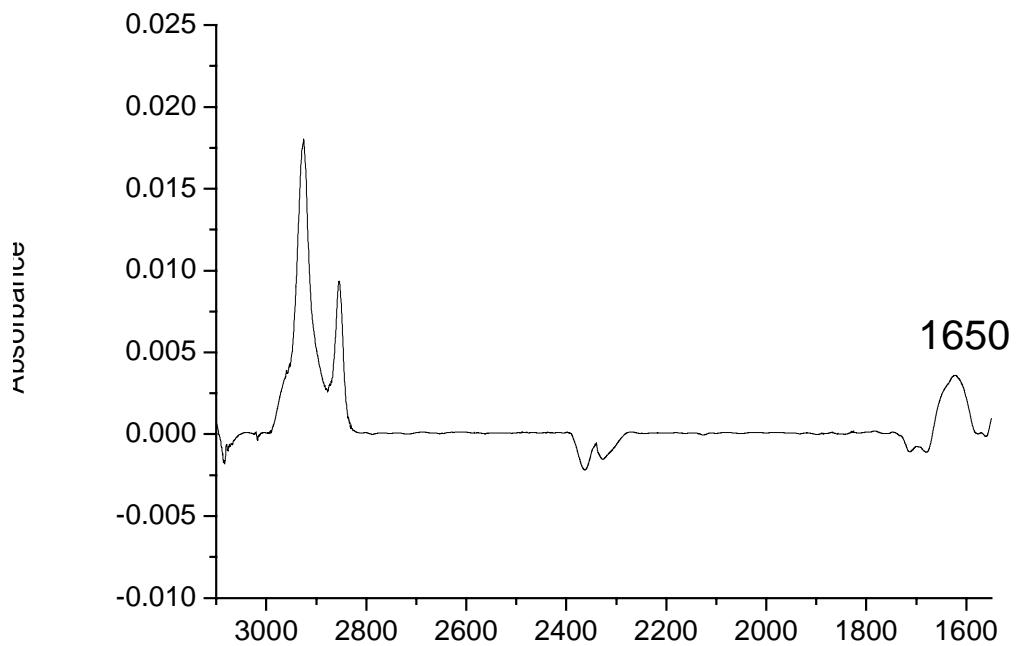
p-Methoxyphenol



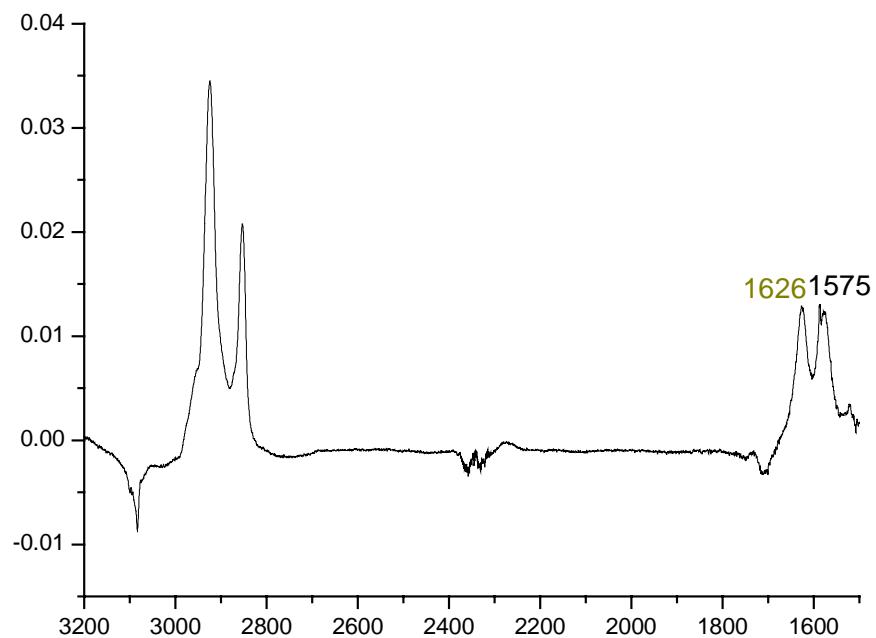
p-Bromothiophenol



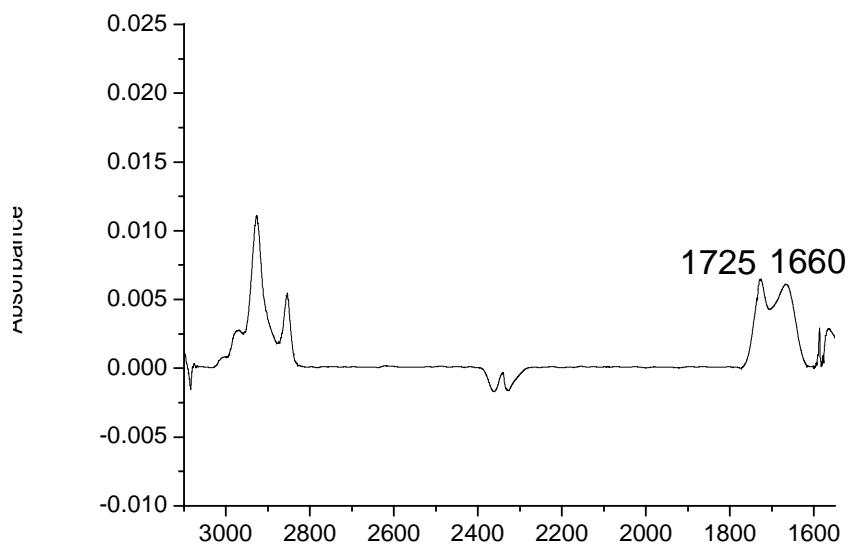
Dodecanethiol



Dodecylamine



Boc hydrazine



**XPS spectra of the Fmoc $\text{NHNH}_2$ -substituted isocyanate surfaces before and after treatment by DMF-piperidine ( 10% of deprotection occurred)**

