

Supplementary information to:

Morphological and mechanical properties of alkanethiol self-assembled monolayers investigated via BiModal Atomic Force Microscopy

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1. BiModal Atomic Force Microscopy (BM-AFM) The experiments were carried out in air with a hybrid atomic force microscope that includes commercial components (Smena, NT-MDT, Russia) and a home-built bimodal excitation/detection unit (bimodal unit), developed within the FORCETOOL European project (NMP4, 013684). The bimodal unit allows us to perform both the multi-frequency excitation and the analysis of the cantilever oscillation signals. The unit provides four DC signals as outputs. These are the amplitudes and phase shifts of the first and second flexural modes (A_1 , A_2 , ϕ_1 , ϕ_2). These signals can be introduced as external inputs to the Atomic Force Microscopy (AFM) imaging software.

BM-AFM works in amplitude modulation (viz. Tapping Mode® technique) where the photodiode signal of the amplitude of the first mode is fed back to the microscopy control unit to perform the tip-sample distance control (like the standard Amplitude Modulation – AFM). The phase shift ϕ_1 existing between the excitation and cantilever's response at the first mode is directly related to energy dissipation into the sample¹ but it does not reveal changes in conservative tip-surface interactions. Such information comes from the phase shift at the second mode ϕ_2 because the force sensitivity to mechanical, magnetic or electric interactions is increased.² This is possible in reason of the second mode ability to probes tip-surface interactions at larger tip-surface average distances by applying maximum forces below 100 pN. The force sensitivity under bimodal excitation can be estimated by calculating the smallest force change that produces a phase shift variation above the noise level. In this way we obtain a value of 0.2 pN.² On alkanethiol SAMs we have measured changes in the

Van der Waals forces. They are defined as $F_{\text{vdw}} = -HR/6d^2$ where H , R , and d are the Hamaker constant, tip's radius, and tip-surface instantaneous distance, respectively. In particular, H depends on the tip-sample system thus it is expected to change for increasing alkanethiol chain length.³

2. Flame annealing process of Au films Vacuum-deposited Au films on evaporated Cr (3nm)/glass slides were purchased from Arrandee (www.arrandee.com). The film's annealing was performed in darkness, as described for flame-annealing of single crystals,⁴ then it roughly cooled in a stream of N gas.⁵ The film's structure changes from polycrystalline grains (diameter ~ 40 nm) to micrometer-sized crystals. In particular, the crystal surface appears smooth and constituted of Au(111) triangular terraces with ~ 300 nm of lateral size. Au step edges have an averaged height of (4 ± 2) Å, as measured from cross-section profiles on 900×900 nm² AFM topographic images. The crystals surface of bare Au has root mean square roughness $\sigma = (4.5 \pm 1.2)$ Å whereupon it is suitable to investigate the morphological and mechanical properties of alkanethiols SAMs at the micrometer scale length.

3. *n*-alkanethiols surface coverage Electrochemical techniques are extremely useful to quantify the alkanethiol SAM coverage onto Au(111) surface.⁶ In particular, the reductive desorption in basic solution shows a complete surface coverage of $(7.8 \pm 0.6) \times 10^{-10}$ mol/cm², regardless to the alkanethiol chain length n . As a consequence, as wrote in the text, SAMs which leave partially uncovered terraces ($n=5, 6, 8, 9, 10$) are really covered by flat-lying or bended alkanethiols chains.⁷ In the BM-AFM topographic imaging, the tip-surface force is about 20nN which is strong enough to compress such disordered alknethiols chains. Conversely, the well-ordered structures are not (or less) compressible. Accordingly, the height of the alkanethiols chains is measured from the difference between the height of disordered areas and the height of well-ordered structures. The contributions of the alkanethiols compression to the height are included in the observational error. Uncovered terraces are also observed in the BM-AFM phase images where is applied a force of 100pN at most (Figure 1SI). By comparing the non-cumulative phase distributions measured from conventional phase image (dashed line) and the BM-AFM one (continuous line), it is clear that a second Gaussian peak appear in the BM-AFM phase. Those peaks

suggesting two different alkanethiols organization which have phase values well below the bare Au phase value (prior cantilevers normalization).

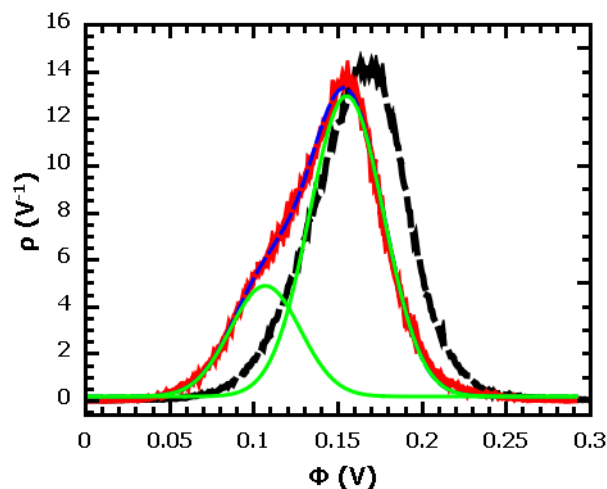


Figure 1SI: Non-cumulative phase distributions for $n = 5$ SAM

4. NEXAFS The measurements have been taken at the Aloisa beamline (Elettra synchrotron in Trieste, Italy). The sample was mounted on a variable temperature (120-1200 K) manipulator (CTPO with Omniax translator, by VG) with six degrees of freedom (precision of 0.01° for the three rotations). The manipulator is mounted coaxial to the photon beam, that impinges on the surface at grazing incidence (grazing angle R variable from 0 to 20°). The grazing angle is determined by measuring the specularly reflected photon beam either by collimated photodiodes placed behind the electron spectrometer lenses or by a TV camera coupled to a phosphor screen placed downstream the manipulator. The NEXAFS absorption spectra were taken in partial electron yield by means of a channeltron detector with a retarding grid electrode to filter out low energy secondary electrons. NEXAFS spectra measured at the C K-edges have been calibrated with a precision of 0.05eV by simultaneous acquisition of the $1s \rightarrow \pi^*$ gas phase transitions of CO at $h\nu = 287.40\text{eV}$. The rotation of the sample surface around the incident beam axis allowed the change of the surface orientation with respect to the linearly polarized X-ray electric field, while keeping the grazing angle fixed at 7° . Complementary XPS measurements have been performed *in situ* at Aloisa to ensure

about the surface quality and the absence of contaminants due to brief air exposition prior of the insertion of the SAM/Au systems into the UHV experimental chamber.

Bibliography

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