Disclosing fine frictional details dependent on the supramolecular order of polymorphic self-assembled monolayer

Markos Paradinas,[a] Carmen Munuera,[a‡] Christophe Silien,[b§] Manfred Buck[b] and Carmen Ocal[a]

[a] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), 08193-Bellaterra, Spain
[b]EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, KY169ST, UK
[‡]present address: Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Cantoblanco 28049 Madrid, Spain
[§]present address: Department of Physics and Energy, and Materials and Surface Science, University of Limerick, Ireland

mparadinas@icmab.es

Abstract

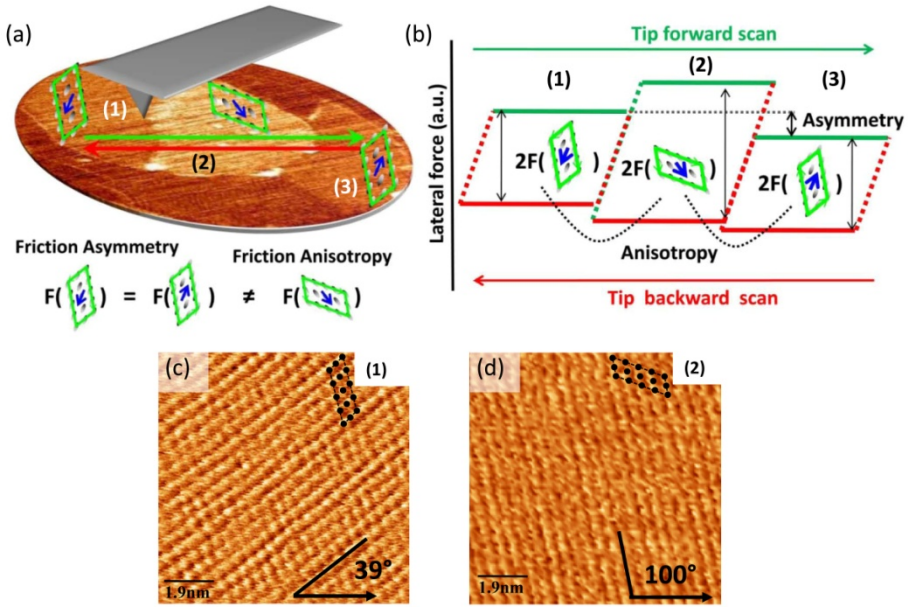
Micro-/nanoelectromechanical systems demand robust ultrathin films or lubrication. As they can drastically modify the frictional properties of surfaces, few nanometers thick self-assembled monolayers (SAMs) constitute accepted candidates as boundary lubricants. Their high stability and easy preparation make them attractive also for low cost applications. Given their high order, organosulfur SAMs have been archetypal systems for structural investigations, but few efforts have been devoted to analyze the influence of lateral inhomogeneities on their surface properties. In this work, the impact on the frictional response of the surface due to the existence of crystalline domains with lateral dimension in the sub-micrometer range is considered.

To this end, two polymorphic structures of SAMs of ω-(4'-methylbiphenyl-4-yl) butane-1-thiol (BP4) coexisting on Au(111) are investigated by friction force microscopy technique (FFM). FFM is ideally suited for non-invasive friction studies since forces can be measured with high sensitivity and different types (e.g. local normal force and lateral force) can be monitored simultaneously. However, FFM measurements can provide even more detailed information, for example, on non-isotropic packing of molecules or molecular tilt in the SAMs. Described by rectangular $5\sqrt{3} \times 3$ (α-phase) and oblique $6\sqrt{3} \times 2\sqrt{3}$ (β-phase) unit cells, the two polymorphic structures of the BP4 SAM exhibit pronouncedly different frictional responses. The lateral nano-tribological heterogeneity of the surface is further influenced by the azimuthal orientation dependence of friction for each phase. These details can be revealed by friction anisotropy and friction asymmetry both of which are related to the dependence of the mechanical response on the sliding direction. In particular, this phenomenon is exploited in the less densely packed β-phase for which the separate analysis of forward and backward lateral force scans is used to differentiate domains rotated 180º. The results presented in this work demonstrate the level of structural control required in the design of SAMs for nano-tribology applications.

References

[1] M. Paradinas, C. Munuera, C. Silien, M. Buck, C. Ocal, *Phys. Chem. Chem. Phys.* **15** (2013) 1302.

Figures



In figure (a) the tip forward and backward scan over different BP4 β-phase crystalline domains is represented and superimposed to the experimental friction map. The friction (F) is defined as the half of the difference between lateral force forward and backward signals. The corresponding lateral force signals are schematically represented in (b). While $F(1) \neq F(2)$ is a clear signature of friction anisotropy related to molecular domains with different azimuthal orientation (proved by the corresponding molecular periodicity images (c and d) obtained in each location), there are also regions which exhibit the same friction values (i.e., $F(1) = F(3)$) but a shift in the lateral force signals, indicating the same tip-surface sliding relationship, in other words (1) and (3) are domains rotated by 180°.