Poster

Molecular structure and surface modification of monolayer organic films

C. Munuera, E. Barrena and C. Ocal

Instituto de Ciencia de Materiales de Madrid Cantoblanco 28049- Madrid e-mail: carmenocal@icmm.csic.es

Surface functionalization and its potential application in different fields of science and technology make monolayer organic films attractive candidates as linkages between an underlying substrate and other molecular species. By now, self-assembled monolayers (SAMs) [1,2] generated from either alkanethiols (RSH) or disulfides (RSSR) ($R=C_nH_{2n+1}$), have become a practical tool for *homogeneous* surface modification. Functionalization due to a characteristic surface energy can be tailored by choosing the desired specificity of the exposed end groups.

Since SAMs are nanometer-sized elements in one dimension (perpendicular to the surface plane), *local* modifications or patterning of SAMs have an important role as the first step in the fabrication of novel nanostructured organic materials. Different techniques compete in terms of lateral resolution (LR) versus range of patterned area (PA). Scanning probe lithography (LR=10nm, PA= 10^{-8} cm²) or e-beam lithography (LR=10nm, PA= 10^{-8} cm²) have been offered as alternatives to techniques as microcontact printing or UV lithography, both with LR=500nm, PA= 50 cm² [3].

Local surface modification by scanning probe lithography, has been successfully used in a variety of inorganic systems. In the case of organic films, local surface modification basically consists in the mechanical manipulation with the tip of the local probe.

It is well established that on single crystalline substrates such as Au(111), alkanethiols self-assemble into large, structurally well defined, domains [2]. The full-coverage phase corresponds to a monolayer of closely packed molecules with the chains tilted around 30-35° from the surface normal but, for a wide range of coverage below the monolayer completion, the organization of alkanethiols on Au(111) substrates induces different ordered molecular structures. Under non-equilibrium conditions and depending on the balance between existing interactions, differently tilted configurations (figure 1) do appear (from near-flat to upright phases) and films with different thickness can be obtained [4].

Modifications in SAMs by methods as nanoshaving [5] and nanographting [6] are based on the adsorption energy competition between two molecules with different chain lengths. The final film locally presents two distinct thickness due to the length difference. Our approach, however, consists in obtaining similar patterned films, i.e. with different local thickness but using monomolecular films. We are able to locally induce transitions between configurations by tip perturbation. In such a way, chain length dependent film properties are avoided but an understanding of the role of the fundamental interactions determining the self assembled structure of each configuration, is crucial to control the patterning process and to obtain durable modifications.

We have addressed this study for molecules (RSH and RSSR) of different chain lengths, the formation of. The high spatial resolution of the local probe has been used to determine the molecular order within the organic films (figure 1) but also to induce structural changes (durable marks) in the molecular configurations (figure 2). The results are analysed within a simple model, which provides un understanding of the role of the competing interactions in the energetic balance of the self-assembling process (figure 3).

References

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FIGURES

