Shaking molecules: detection of defects in SAMs of aliphatic amines with jumping mode AFM

José A. Heredia-Guerrero[1], *Miquel Salmerón*[2], *Jesús J. Benítez*[1]
[1]*Instituto de Ciencia de Materiales de Sevilla. Centro Mixto CSIC-Universidad de Sevilla. Centro de Investigaciones Científicas Isla de la Cartuja. Avda. Americo Vespuccio 49, 41092 (Sevilla). Spain.*
[2]*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, USA, and Materials Science and Engineering Department, University of California, Berkeley, USA*
alejandrohg@cartuja.csic.es

The alkylamine SAM formation on mica has been described as a two stage process [1]. The first one is relatively fast and comprises molecular adsorption on the substrate through an acid-base reaction, a process that is exclusively conditioned by the direct interaction between the amino end group and the adsorption sites on mica. The second stage is slow and consists in the diffusion and aggregation of scattered adsorbed molecules into self-assembled island takes place. This second stage is dominated by the attractive van der Waals interactions between alkyl chains and, consequently, is faster for longer chain alkylamines. In humid environments this accretion stage is followed by another very slow process characterized by molecular tilting within the islands. This was modeled by the penetration of water that from the environment, which protonates the amino groups and gives rise to an electrostatic repulsion.

In the present study, we have studied the effect of mechanical energy transfer from the tip of an Atomic Force Microscope (AFM) on the dynamics of self-assembly of a monolayer film of octadecylamine on mica, usin jumping mode AFM [2]. The formation of the self-assembled film proceeds in two successive stages, the first being the fast adsorption from solution, which can be described by a Langmuir isotherm. This is followed by a second stage of slow aggregation and island growth. The dynamics of the second process can be altered by the addition of mechanical energy into the system through controlled tip-surface interactions. This leads to either the creation of pinholes as a consequence of vacancy concentration in defect-rich regions, as well as to the opposite phenomenon, the assembly of residual scattered molecules into more compact islands.

References:

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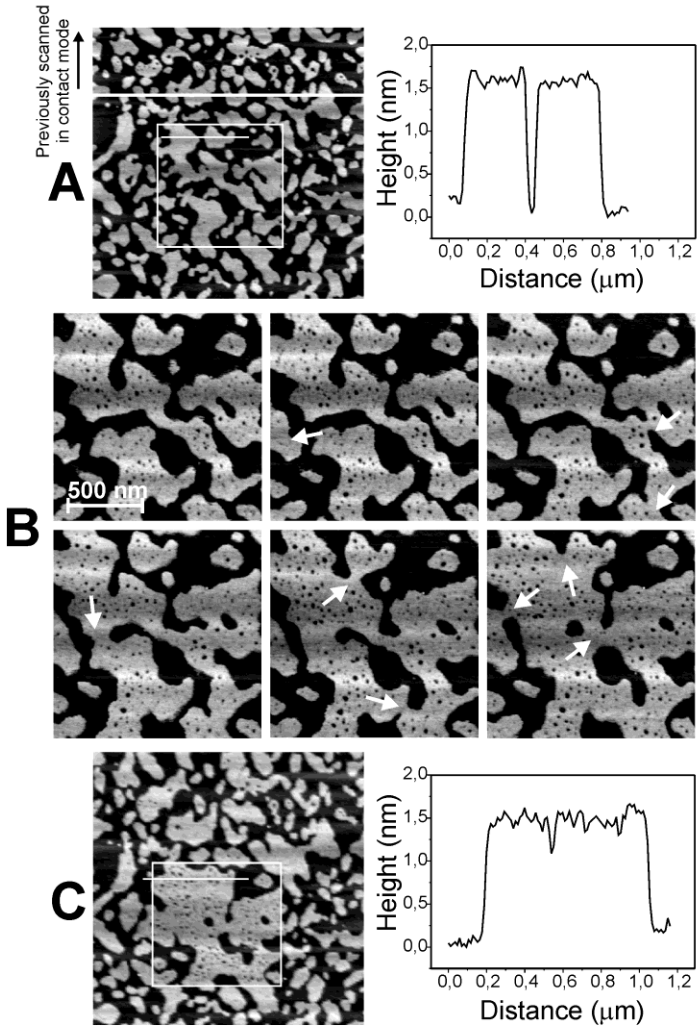

Figure. Topographic AFM image obtained in jumping mode over octadeylamine SAM islands on mica previously and partially scanned in contact mode by applying a positive 0.5nN force. The white horizontal line is the limit between the contact (upper part) and the contact preserved sides (lower part). Contact mode imaging causes island damage that is not observed when switching to jumping mode with identical set point. The image shows the initial stages of island aggregation. When the area marked by the white square is successively scanned in jumping mode (by increasing the set point to 2nN), pinholes and aggregation points (marked by arrows) are created (B). Images corresponds to 11, 15, 19, 21, 27 and 33 accumulated scans respectively (in each scans, every point is sampled four times). When the repetitive cycle ends, a larger range scan (jumping, set point 0.5nN) allows to distinguish the induced island aggregation at the repeatedly scanned area. Line profiles indicate no modification of island height along the experiment. The sample is prepared from an octadecylamine 15 mM solution and ripened for 48 hours.