Self-organisation of molecular nanostructures triggered by atomic force microscopy

M. Cavallini,[1] F. Biscarini[2]

[1]*Consiglio Nazionale delle Ricerche - Istituto per lo Studio dei Materiali Nanostrutturati (CNR-ISMN), Bologna, Italy*
[2]*Dipartimento Scienze della Vita, Università di Modena e Reggio Emilia, Modena, Italy*

Corresponding author: Massimiliano Cavallini, Consiglio Nazionale delle Ricerche - Istituto per lo Studio dei Materiali Nanostrutturati (CNR-ISMN), via P. Gobetti 101, 40129 Bologna, Italy
Tel. +39.051.6398516 - Fax: +39.051.6398540.
E-mail: m.cavallini@bo.ismn.cnr.it - fabio.biscarini@unimore.it

Summary
Scanning probe microscopy are an extraordinary tools for surfaces characterization at nano and atomic scale and also for nanofabrication whose major limitation depends on the serial nature of the related techniques. Here we propose an interesting approach applied to a supramolecular system (rotaxane) that contributes to overcome this limitation.
When a local mechanical perturbation is applied to the surface of a thin film of a rotaxane, the molecules self-organize into periodic arrays of discrete dots or lines. The dimensionality of the nanostructures depends on whether the mechanical stimulus acts along a 1D line or over a 2D area. The size and periodicity of the patterns are controlled solely by the film thickness. The phenomenon can be exploited as a new bottom-up nanofabrication method.

Key words: atomic force microscopy, patterning, rotaxane.

Introduction

Ordered arrays of nanometric-sized dots and stripes, fabricated on metals and semiconductors, are largely used to exploit magnetic (Cavallini *et al.*, 2003), optical, (Alivisatos *et al.*, 1996) or electrical (Greco *et al.*, 2008) properties of functional materials. This approach, generally called patterning, exploits the most important characteristic of nanotechnology that is the ability to tailor by Euclidean dimensionality the physical-chemical properties of systems. Thanks to this property, patterning techniques have been successfully applied in several fields of science and technology, the most important being nanoelectronics (Tian *et al.*, 2007), information storage (Cavallini *et al.*, 2005), catalysis (Pandelov and Stimming, 2007) and sensing (Wolfbeis, 2005).

The establishment of the field of nanotechnology requires the development of novel, low-cost and user-friendly nano-patterning approaches. The demand of new patterning techniques was born in order to overcome the restrictions of conventional fabrication techniques, such as photo- and electron-beam lithography that limited in spatial resolution or require complex infrastructures, respectively. With this purpose in mind, several new lithographic methods (Gates *et al.*, 2004) have been developed in the last 20 years, among them methods based on Scanning Probe Microscopy such as Scanning Probe Lithography (Garcia *et al.*, 2006), nanostencil lithography (Luthi *et al.*, 1999), dip-pen nanolithography (Ginger *et al.*, 2004), play a very important role due to their simplicity an the fact that often do not require any particular infrastructure nor complex instrumentation except the SPM-self.

Nowadays, SPMs and related fabrication techniques are largely diffused in most part of research laboratories. SPLs have many important advantages including: (i) the exploitation of a variety of local tip-surface interactions, such as mechanical (Sumomogi *et al.*, 1995), electrical (Garcia *et al.*, 2006) and optical (Moyer *et al.*, 1995); (ii) the possibility to make direct patterning of materials with a resolution down to the nanometer scale in stan-

dard operating conditions without the use of masks or stamps; (iii) usually, SPLs do not require special infrastructures, such as clean rooms, vacuum, or aggressive atmospheres.

On the other hand, major drawbacks of SPLs are due to the printable area, which is limited by piezoelectric actuators, and long processing time, which is related to serial nature of these techniques (*i.e.* the nanostructures are fabricated one-by-one). Despite the increase of the throughput has been pursued by means of self-actuating/self-sensing cantilever arrays, two-dimensional large parallel arrays of probes (Vettiger *et al.*, 2002), or inducing collective transformations (Cavallini *et al.*, 2003, Biscarini *et al.*, 2006), SPLs are often limited to a tool for proof-of-concept experiments.

Materials and methods

Among the proposed methods an original approach to patterning of arrays of nanostructures was pioneered by our group a few years ago (Cavallini *et al.*, 2003) with the aim to transform SPL in a quasi-parallel technique inducing a collective transformation of a continuous thin film by a mechanical perturbation. The approach described here exploits the spatial confinement of a collective molecular reorganisation in a thin film triggered by an AFM probe. Figure 1 shows a scheme of the process.

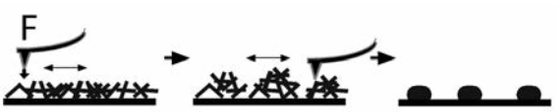

Figure 1. Schematic drawing of the patterning mechanism of rotaxane thin films upon the mechanical perturbation of an AFM tip.

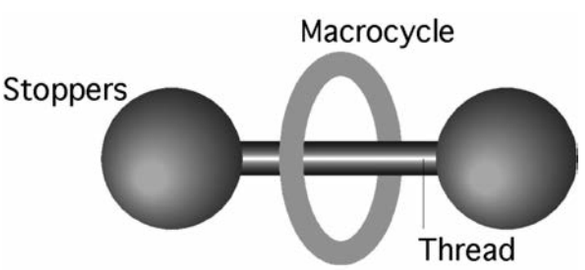

Figure 2. Schematic structure of rotaxanes.

The peculiarity of this approach is that the molecules self-organise themselves into nanostructures whose size and positions emerge as characteristic length scales of the transformation. The SPM probe does not write the nanostructures one-by-one, it simply supplies the energy for the transformation to a local region of the thin films. This self-organization mechanism has been explored and then controlled on thin films made of benzylic amide rotaxanes. Rotaxanes are bistable molecules where a macrocycle is mechanically interlocked on a 'thread'. Two bulky 'stoppers' prevent the macrocycle from sliding away the thread (Figure 2). The bistability arises from two or more (quasi) degenerate co-conformations that correspond to energy minima in the intramolecular hydrogen bonds formed between the macrocyle and the thread.

Results

Rotaxanes have been used to devise switchable surfaces (Cavallini *et al.*, 2003), because the interconversion in the solid state changes the intermolecular interactions and the interactions with the surface. The modified interaction can trigger an instability that propagates across length scales (*e.g.* wetting/dewetting transition).

The reorganization phenomenon occurs when the AFM tip scans the thin film just above a threshold force of about 2nN. Rotaxane thin films (3-35 nm thickness) were grown by drop casting on graphite or mica. The films were imaged by AFM in contact mode using a setpoint force below the threshold value. The films exhibit a homogeneous morphology over a cm^2 area and are stable over a period of months. As the tip is scanned at a load force just above the 2nN threshold, a string of regularly spaced dots appears collectively along the line. The dots emerge upon repeating the linescan a number of times (between 4 and 20) depending on the scan rate (typically 1-2 Hz). The schematics process is shown in Figure 1. Scanning a series of lines results in a regular array of dots of uniform width, height and pitch (Figure 3).

The number of dots is proportional to the length of each scan-line, so any predetermined number of dots can be reliably fabricated on the surface. As example Figure 4 shows a sequence of dots representing different numbers. The film thickness controls dot size and spacing, and hence the density of dots per unit line; the thinner the film, the denser

and smaller are the dots. The transformation can be induced over a large area also across surface steps and terraces. The linear dependence on the scan length allows one to write information as strings of bits (Figure 4).

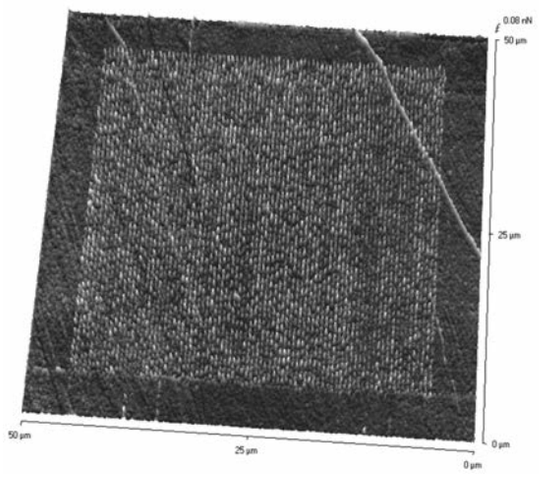

Figure 3. Array of dots fabricated by individual line scans of the AFM tip on a 20 nm-thick film deposited on highly oriented pyrolitic graphite (HOPG).

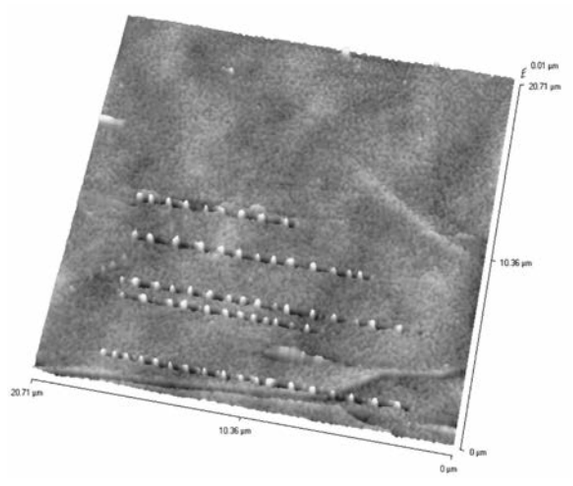

Figure 4. For a given thickness (here 20 nm) the number of dots is linearly proportional to the scan length. The number of dots can be determined with an accuracy of at least 2%. Film thickness controls the characteristic size. Proof-of-concept for information storage writing a different numbers of dots by changing the length of the linear scan.

Discussion

Different rotaxanes have been tested, giving similar responses, while no effect was observed when scanning thin films made of the thread or the macrocycle alone. However similar behaviour was observed in polymers able to reorganize at surfaces upon an external perturbation (Napolitano *et al.*, 2012).

The effect of the mechanical perturbation on the film appears as a roughening of the topographical profile, with the position of the dots fixed at early stages. Peculiarly, the transformation can be interrupted and restarted by turning off and on the perturbation. No sign of scraping or wear of the film is observed, ruling out trivial ploughing with the AFM tip, which instead occurs as the setpoint force exceeds 3-4 nN.

The collective fabrication of dots arises from coupled nucleation and re-crystallization favored by the ease of intercomponent mobility in the solid state. The scanning AFM tip gives the energy to the molecules along the line to reorganize into nuclei. As nuclei coarsen by ripening, a characteristic distance emerges and stable nuclei grown are due to the incorporation of mobile molecules on the surface. Extending this reorganization process on a two dimensional region, the final result is a pattern of lines (Figure 5) that does not change its

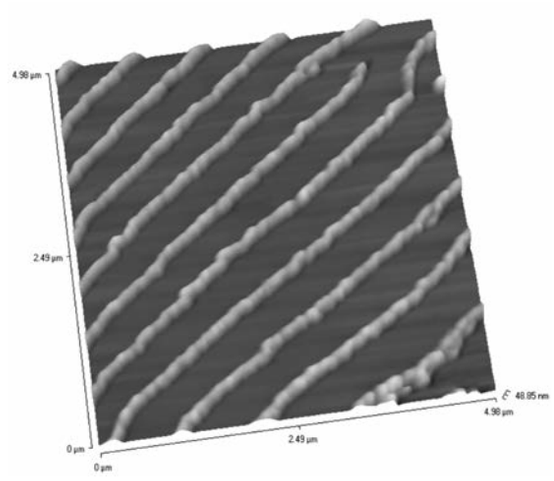

Figure 5. AFM image after the action of the external mechanical perturbation obtained by 2D AFM scanning applying a loading force higher than the threshold (here 4 nN). The surface transforms into stripes with characteristic thickness, distance, and height.

morphology also upon further mechanical perturbations. The detailed mechanism is described in an extensive study (Biscarini *et al.*, 2005).

Conclusions

In conclusions, we have shown that self-organization of supramolecules can be triggered and spatially controlled with an SPM to create a pattern of either nanostructured dots or lines across micrometer wide areas. The method represents an example of bottom-up nanopatterning induced by an SPM.

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