Aligning and positioning molecular matter on pre-patterned surfaces

ABSCHLUSSBERICHT
Über die gesamte Forderperiode (01.07.06-30.06.08)

Max Buchner Forschungsstiftung

Dr. Marga Cornelia Lensen, Prof. Dr. Martin Möller

Aachen, Februar 2009

Aligning and positioning molecular matter on pre-patterned surfaces

Incentives

The aim is to make functional patterns that will direct the specific and controlled positioning and alignment of (supra)molecular material. Because of the dimensions of supramolecular assemblies and macromolecules, i.e. nanometer-sized, the challenge is to apply functional patterning on surfaces with nanoscopic precision. We have worked on the development of micro- and nano-patterning techniques using novel, elastomeric materials with desired properties (e.g. chemical inertness). We use two approaches; separately and in combination. The first method, which results in topographic patterns (i.e. a relief) is nanoreplication molding, a patterning technique derived from nanoimprint lithography (NIL). The (supra- or macro-)molecular material is positioned and aligned by the confinement in the surface structures. The second technique is denoted block copolymer micelle nanolithography. With this patterning technique gold dots can be deposited on a surface in periodic and aperiodic patterns by applying (photo)lithography on self-assembled films of block copolymer micelles that bear a gold salt load. The resulting gold nanoparticles serve as specific anchoring sites for the binding of (bio)functionalities and enables us to make chemical patterns with nanoscopic periodicities. The combination of the topographic and chemical patterning (for instance by using the pre-patterned substrates to deposit the block copolymer micelles or by replication of a template decorated with gold nanoparticles) should yield nano-patterned surfaces on which molecular material is positioned and aligned with nanoscopic precision and control.

Toolbox

Preparation of anchoring sites; gold nanoparticles

For the anchoring of the molecular material, e.g. supramolecular assemblies, macromolecules, biomolecules or small ligand molecules, we take advantage of metal-ligand coordination chemistry. More specifically, the molecules are connected directly or via a linker molecule to gold dots. In order to position the material at specific and desired locations on the surface it is crucial to have control of the positioning of the gold dots in the first place. For this we rely on our vast experience with metal nanoparticles, and with the creation of regular patterns of these nanoparticles. The so-called block copolymer micelle nanolithography method is depicted in Figure 1.

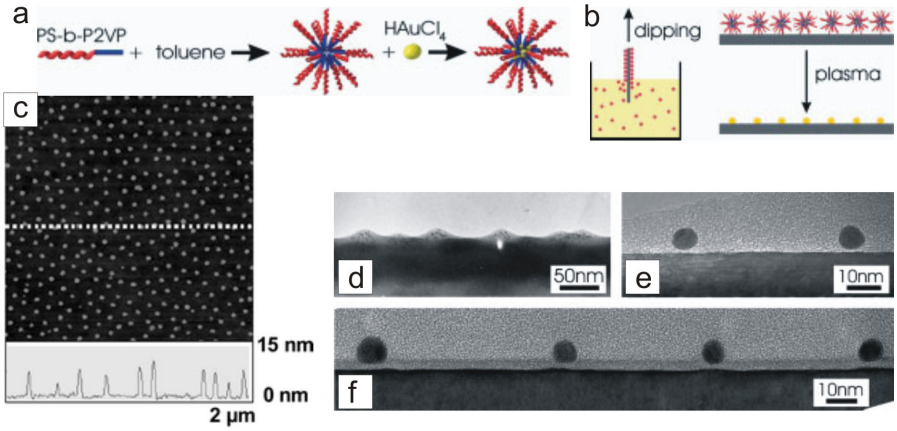

Figure 1 a) Schematic representation of the preparation of block copolymer micelles loaded with a metal (gold) precursor and (b) of the formation of monolayers of the micelles and the consequent plasma etching which removes the polymer material and converts the load into gold nanoclusters; c) AFM image of the periodic pattern of gold nanoparticles prepared according to the strategy depicted in a) and b); d-f) TEM cross-section image of gold salt loaded micelles on a carbon-coated copper grid (d) and of the final array of gold nanoparticles on top of a sapphire substrate (e) as well as on silicon (f).

Besides the hexagonal pattern as shown in Figure 1c, aperiodic patterns can be made by applying additional patterning techniques, such as photo- or electron beam lithography (EBL) on the block copolymer micelle film (before the final plasma treatment). This process is depicted in Figure 2c and d). Another approach to create patterns of higher complexity - hence higher functionality - is to deposit the micelles on pre-patterned surfaces. This was shown to be feasible in the case of a silicon substrate that was patterned with grooves by EBL (Figure 2a and b).

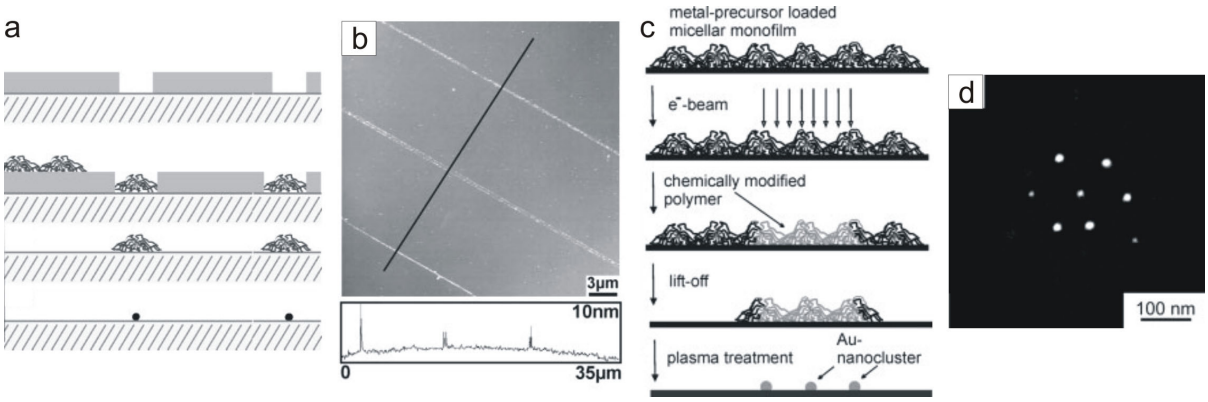

Figure 2 a) Schematic representation of the process by which gold nano-particles are precisely deposited on a substrate in a pattern of grooves created by e-beam lithography; b) AFM image of a silicon wafer after patterning the micelles in 200 µm long grooves and subsequent plasma etching as depicted in a); c) Schematic representation of the creation of aperiodic patterns of gold nanoclusters on a substrate by e-beam lithography; b) AFM image of the resulting aperiodic pattern of gold dots.

However, since EBL is a very costly, slow and serial technique, it is not feasible to apply this lithographic technique on a large scale. Thus, there is a need to have easy access to gold dot-patterned substrates of a large variety and which are more readily available. This allows the flexibility to investigate many parameters, such as patterns with different geometries, various spacings between the gold dots, and also different substrates, other than silicon. For this reason we have developed other lithographic techniques to make pre-patterned substrates for the selective and controlled positioning of the anchoring sites. Notably, we have worked with flexible, elastomeric materials besides hard substrates (e.g. silicon or glass). This enables to manipulate the pattern of anchoring sites and the eventual molecular material bound to them, and represents an additional tool to align, for instance, molecular wires.

UV-based imprinting

The cheap, fast and parallel lithographic technique I have been using as an alternative to EBL is nano-imprint lithography (NIL). Imprint lithography can also be denoted 'replica molding'. In the imprinting process, a mold is pressed into a soft material, which is cured (hardened) after which the mold is released, leaving a replica of the mold structure behind as an imprint. We have used a UV-based imprinting method, in which a soft pre-polymer mixture is cured upon illumination by UV-light (Figure 3). The curing chemistry relies on photoinitiated radical cross-linking reactions that take place between the pre-polymer macromolecules bearing reactive end-groups, in the presence of a photo-initiator.

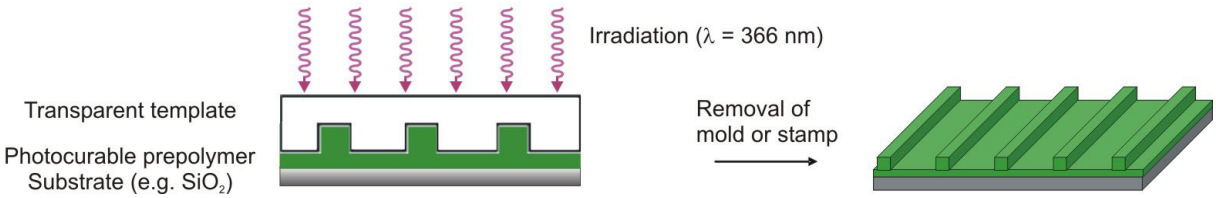

Figure 3. Schematic representation of UV-based imprinting.

Results

Preparation of pre-patterned surfaces

In our case, we have been using perfluorinated polyether pre-polymers, which bear methacrylate end-groups (PFPE DMA). The PFPE material has many desired properties, the most important one of which is the low surface energy. This makes it easy to remove the mold from the replica and also enables to replicate small features. The imprinted replica is peeled off as a self-supportive elastomeric film, which is stable, transparent and flexible. Figure 4 demonstrates the ability of the polymer to replicate micro- and nanostructured (silicon) masters.

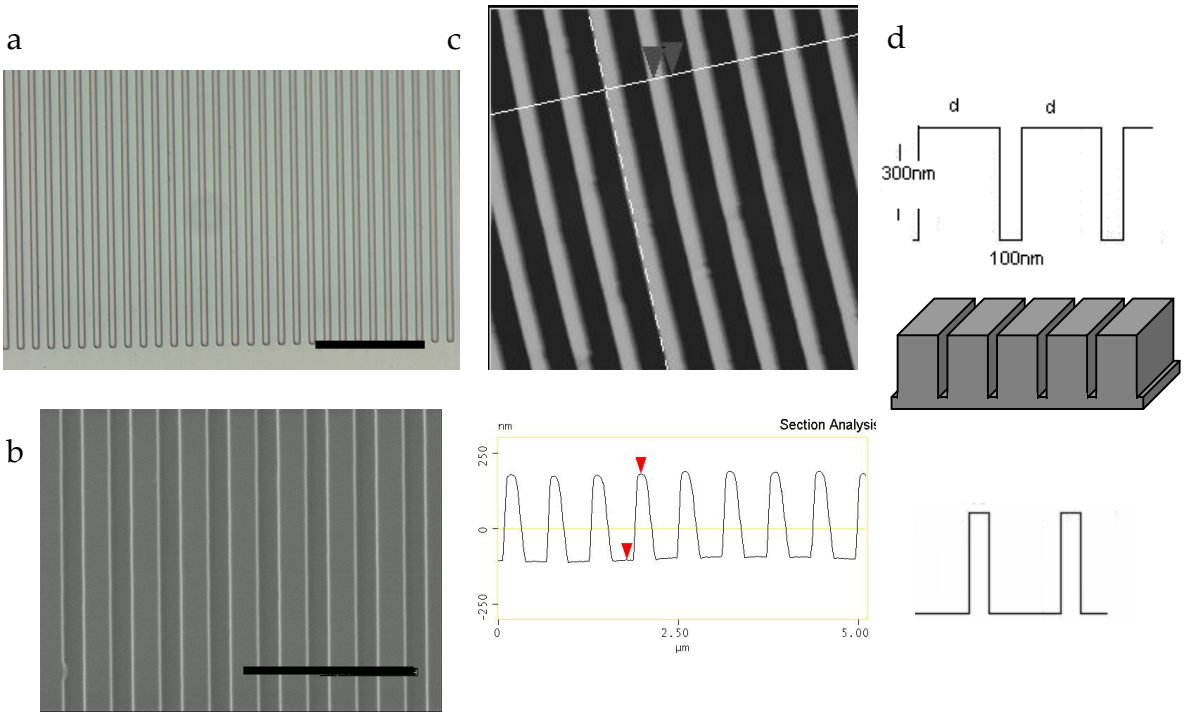

Figure 4. a) Optical micrograph (scale bar represents 100 µm) and b) Scanning electron micrograph (scale bar represents 50 µm) of PFPE replicas of a micro-structured silicon master, prepared by UV-imprinting. c) Atomic force micrograph (5 x 5 µm^2) of a PFPE replica using a silicon master with grooves of 100 nm in width and 300 nm in depth; spaced by d = 500 nm, as schematically depicted in d).

Positioning of gold nanoparticles on the pre-patterned substrates

The micro- and nanostructured substrates are used as a template to position gold nanoparticles from a block copolymer micelle solution. It is known from literature and also from experience in our own group that liquids do not wet a topographically structured surface in a homogeneous manner but rather accumulate preferentially in grooves and channels, according to so-called capillary filling. We have taken advantage of this physical phenomenon to position gold particles specifically in the grooves of the imprinted substrates. Figure 5 depicts the (preliminary) results for PFPE micro-structured substrates.

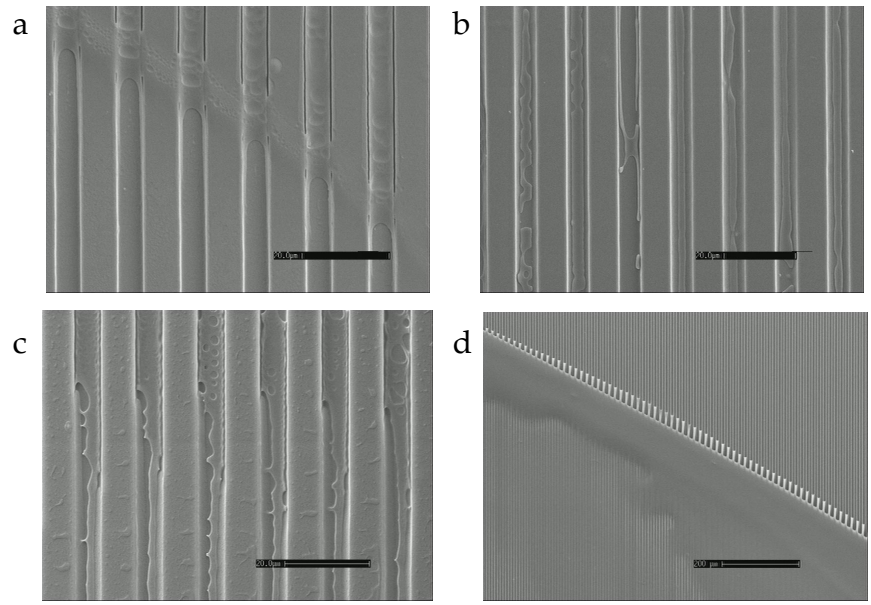

Figure 5. Micrometer-sized patterned PFPE substrates decorated with block copolymer micelles from toluene solution prepared by a) and b) drop-casting and draining excess solution, c) dip-coating and d) spin-coating.

The filling of the grooves by block copolymer micelle solutions was tested on micro-structured PFPE substrates (as shown in Figure 3). The solution was transferred to the substrate in 4 different ways (Figure 6), i.e. i) drop-casting and draining excess liquid, ii) dipping the substrate manually; rather fast, iii) dip-coating the substrate automatically at a constant and controlled rate (of 10 mm/min), iv) spin-coating the solution (at 4500 rpm). From the images it is evident, that capillary filling takes place in all cases. Notably the comb-like appearance of the edge of the droplet in Figure 6d clearly demonstrates this effect. Obviously, however, the process is not optimized and many parameters need to be investigated (e.g. concentration, solvent, surface treatment, procedure of wetting, etc.) in order to obtain more control and a higher fidelity. Nevertheless, the preliminary results are promising and suggest that the followed strategy to position gold particles on pre-patterned surfaces is feasible.