CATALYTIC PROBE LITHOGRAPHY: CATALYST-FUNCTIONALIZED SCANNING PROBES AS NANOPENS FOR NANOFABRICATION ON SELF-ASSEMBLED MONOLAYERS

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Nanometer control over the positioning and size of various surface-confined chemical functionalities would enable one to design sensing materials with large capacities and to detect single molecules. Top-down and bottom-up manufacturing approaches or combinations of those are the key technologies used to fabricate nanostructures. There are new nano- and microfabrication technologies, such as microcontact printing (μCP)[1] and dip-pen nanolithography (DPN),[2] both using self-assembly as the key feature to produce patterned surfaces. Self-organization *e.g.* of thiols or disulfides onto gold leads to the formation of self-assembled monolayers (SAMs), the fabrication and properties of which have been described extensively.[3]

μCP is a soft lithography technique, which uses a patterned elastomer, such as poly(dimethylsiloxane) (PDMS), as a stamp. SAMs are formed only in the contacted areas. The smallest reported feature produced by μCP is about 50 nm. Dip-pen nanolithography (DPN) is an addition lithography technique providing an elegant way to write chemical nanopatterns on various surfaces in specific areas. It uses a scanning probe coated with the desired material to be transferred to the substrate. By scanning the surface, the ink will be transported from the tip to the substrate through the presence of a water meniscus. The mechanism of ink transport in DPN is not fully understood, the amount of ink transferred is not controllable, and the ink diffusion determines the pattern sizes created depending on temperature, humidity, ink nature, and contact time. These disadvantages may be overcome when scanning probe lithography is performed without the use of an ink.

There are only a few papers that describe the use of a catalytically active atomic force microscopy (AFM) tip.[4] In an early first attempt Schultz *et al.* showed, that by using Pt-coated AFM tips, the terminal azide groups of a monolayer on glass could be locally reduced to amino groups.[4a] To our knowledge the use of a catalytically active AFM tip by adhesion of a catalyst for lithographic applications was never reported before.

Here we present the use of scanning catalytic probe lithography for nanofabrication of patterns on self-assembled monolayers (SAMs) of reactive adsorbates. The principles of catalytic probe lithography are shown in Figure 1. Catalytic writing was carried out by scanning over bis(ω-tert-butyldimethyl-siloxyundecyl)disulfide SAMs using 2-mercapto-5-benzimidazole sulfonic acid-functionalized gold-coated AFM tips. The acidic tips induced local hydrolysis of the silyl ether moieties in the contacted areas, and thus patterned surfaces were created. Diffusion effects arising from the use of an ink are excluded in these type of experiments, therefore structures with well-defined shapes and sizes were produced (Figure 2). The smallest lines drawn by this technique were about 25 nm wide corresponding to the actual contact area of the tip. Dendritic wedges with thiol functions insert into the catalytically written areas, thus enhancing the height contrast. The created patterns open possibilities to build 3D constructions.

References:

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Figures:

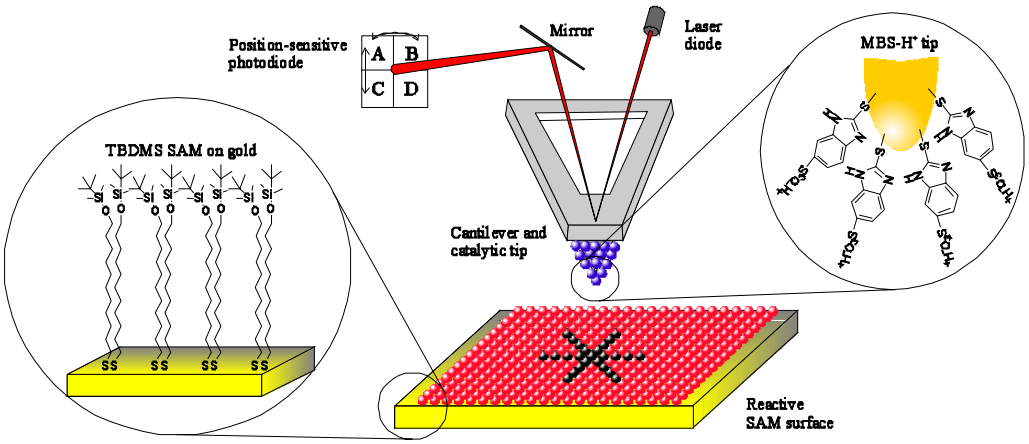

Figure 1. Schematic illustration of scanning catalytic probe lithography performed on a TBDMS SAM on gold using a gold-coated AFM tip covered with 2-mercapto-5-benzimidazole sulfonic acid (MBS-H^+)

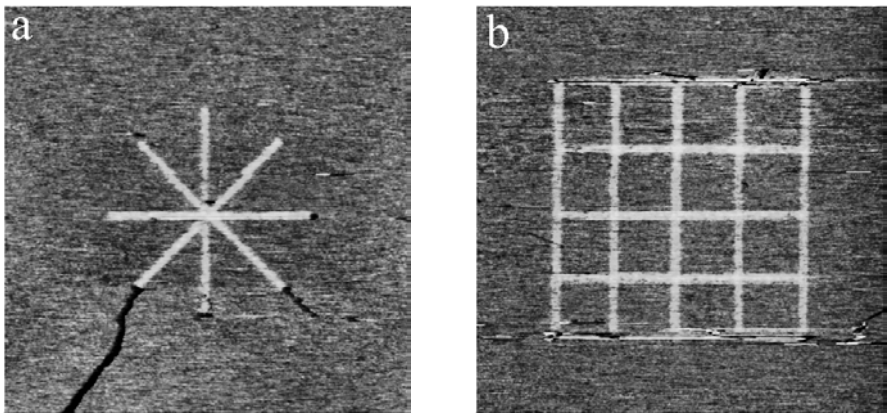

Figure 3. AFM friction images (z range 0.2 V) of nanostructures created on TBDMS SAMs by catalytic probe lithography (a: scan size 6 × 6 μm^2; b: 10 × 10 μm^2)