SOFT AND PROBE LITHOGRAPHY WITHOUT INK TRANSFER

Jurriaan Huskens, Xuemei Li, Mária Péter, David N. Reinhoudt
Laboratory of Supramolecular Chemistry and Technology, MESA+ Institute for Nanotechnology, University of Twente, Enschede, PO Box 217, 7500 AE Enschede, The Netherlands; phone: +31-53-4892995; fax: +31-53-4894645; E-mail: j.huskens@utwente.nl

Microcontact printing[1] (μCP) is a versatile technique for the creation of patterned surfaces. It commonly employs the transfer of an ink (e.g. a thiol) onto a surface (e.g. a gold-coated substrate) thus forming a self-assembled monolayer (SAM). Patterns of different thiols can be crreated using self-assembly of a second thiol from solution, or the printed patterns can be used directly as etch resists allowing the structuring of the underlying substrate itself. This technique has been extended to probe lithography in the recently developed dip-pen nanolithography (DPN).[2]

Resolution of these techniques is typically around 200 nm, diffusion of the ink during the printing or writing stage being the main limiting factor.[3] Diffusion can be limited when heavy inks are used, such as high-molecular-weight thioethers[4] or proteins[5] or nanoparticles.[6] We have shown that nanoparticles can be coated with catalytically active acid groups to hydrolyze protecting silyl ether groups on a homogeneous SAM when transferred onto this SAM by μCP.[7] This has led to patterned SAMs with an edge resolution below 100 nm. Also, we have shown that oxidized PDMS stamps can catalytically cleave the same silyl ether groups of these SAMs in an ink-free μCP process.[8]

The present study will show examples of novel strategies for eliminating diffusion as an underlying principle of μCP and DPN. The preparation and use of catalytically active stamps will be shown with a catalyst attached directly to the stamp surface (Figure 1, left). With these stamps it is possible to form patterned SAMs without any transfer of ink (Figure 1, right). These stamps are more active than the earlier developed oxidized stamps and provide an ink-free μCP scheme allowing more versatile catalytic reactions. Furthermore, an extension to catalytic probe lithography will be given. Here we will show line patterns with sub-100 nm widths created by scanning a catalytically active tip functionalized with a catalyst across a reactive SAM substrate (Figure 2). Utilization of such μCP and DPN patterns in physical and chemical pattern enhancement and guided deposition will be shown as well.

References

1. Xia, Y. N.; Whitesides, G. M. *Angew. Chem. Int. Ed.* **1998**, *37*, 551-575; Michel, B.; Bernard, A.; Bietsch, A.; Delamarche, E.; Geissler, M.; Juncker, D.; Kind, H.; Renault, J.-P.; Rothuizen, H.; Schmid, H.; Schmidt-Winkel, P.; Stutz, R.; Wolf, H. *IBM J. Res. Dev.* **2001**, *45*, 697-719.
2. Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, *283*, 661-663; Mirkin, C. A.; Hong, S.; Demers, L. *ChemPhysChem* **2001**, *2*, 37-39.
3. Libioulle, L.; Bietsch, A.; Schmid, H.; Michel, B.; Delamarche, E. *Langmuir* **1999**, *15*, 300-304.
4. Liebau, M.; Huskens, J.; Reinhoudt, D. N. *Adv. Funct. Mater.* **2001**, *11*, 147-150.
5. Bernard, A.; Renault, J. P.; Michel, B.; Bosshard, H. R.; Delamarche, E. *Adv. Mater.* **2000**, *12*, 1067-1070.
6. Hidber, P. C.; Helbig, W.; Kim, E.; Whitesides, G. M. *Langmuir* **1996**, *12*, 1375-1380; Hidber, P. C.; Nealey, P. F.; Helbig, W.; Whitesides, G. M. *Langmuir* **1996**, *12*, 5209-5215.
7. Li, X.-M.; Paraschiv, V.; Huskens, J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2003**, *125*, 4279-4284.
8. Li, X.-M.; Péter, M.; Huskens, J.; Reinhoudt, D. N. *Nano Lett.* **2003**, *3*, 1449-1453.

Figures

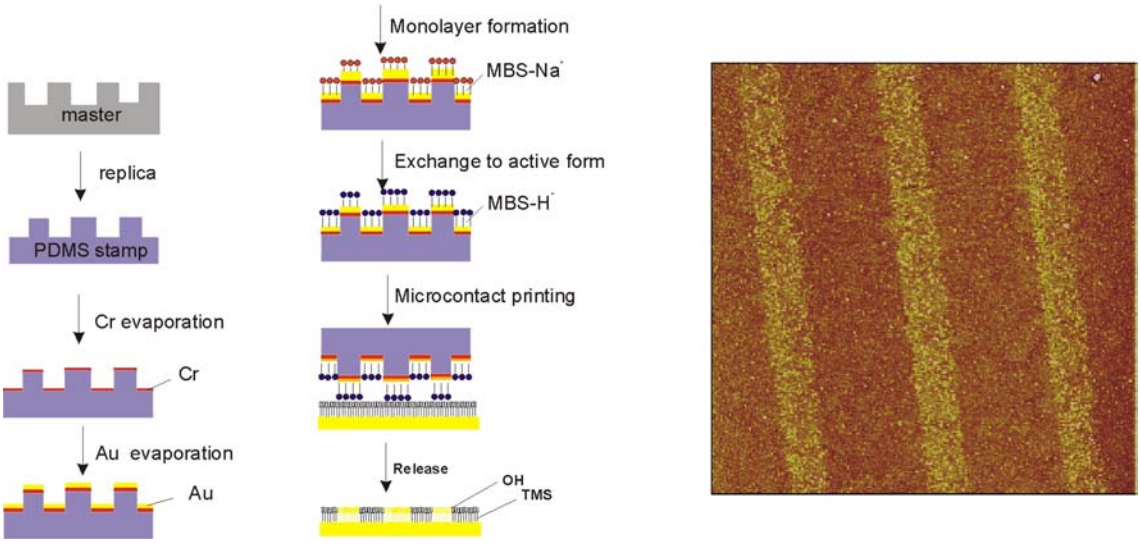

Figure 1. General μCP scheme for attaching a catalyst to a PDMS stamp and ink-free pattern generation on homogeneous reactive SAMs (left) and a friction AFM image (25×25 μm^2) of a silyl ether SAM patterned by an acid-catalyst-functionalized PDMS stamp (right).

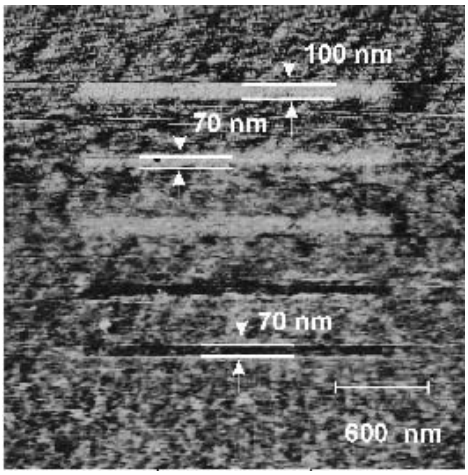

Figure 2. Line patterns with sub-100 nm widths created on silyl ether SAMs by catalytic probe lithography using an acid-functionalized AFM tip: bright lines: with an active tip, dark lines: with an inactive tip.