4.3 Polar Ink Printing

Surface Modification of PDMS Stamps for Microcontact Printing of Polar Inks

Process: microcontact printing lithography

Figure:
Casting PDMS (silicone) precursor onto a structured template in a Petri dish.

Process:
Casting PDMS (silicone) precursor (elastomer base and curing agent) onto a structured template in a Petri dish. Curing (hardening) by heat (60°C, 12-24 h).

Application:
Microfluidic devices
Photonic crystals

Keywords: microcontact lithography, soft lithography, protein patterning, PDMS

Project leader: MESA+ University of Twente
Address: 7500 AE Enschede / The Netherlands
Web-Address: http:// http://mnf.tnw.utwente.nl/ l/
Process: microcontact lithography
Responsible: Jurriaan Husken
E-mail:

Process description: Plasma polymerization of allylamine; a process for surface modification.

Purpose: A process is described for surface modification of polydimethylsiloxane (PDMS) stamps and transferring a hydrophilic ink pattern from the modified stamp to various substrates with different chemistry of inks and substrates.

Major Advantages: In comparison to general oxygen plasma method to treat the stamp surface, plasma polymerization process is efficient, stable and substrate independent, high density of functional groups on the surface, versatile chemical structures, and suitable for further surface modification based on reactive amine groups.

References:

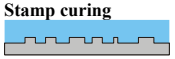
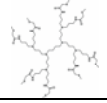
[1] Sadhu, V. B.; Perl, A.; Péter, M.; Rozkiewicz, D. I.; Engbers, G.; Ravoo, B. J.; Reinhoudt, D. N.; Huskens, J. *Langmuir* **2007**, *23*, 6850-6855.
[2] Perl, A.; Péter, M.; Ravoo, B. J.; Reinhoudt, D. N. ; Huskens, J. *Langmuir* **2006**, *22*, 7568-7573.
[3] Mulder, A.; Auletta, T.; Sartori, A.; Del Ciotto, S.; Casnati, A.; Ungano, R.; Huskens, J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2004**, *126*, 6627-6636.
[4] Onclin, S.; Mulder, A.; Huskens, J.; Ravoo. B. J.; Reinhoudt, D. N. *Langmuir* **2004**, 20, 5460-5466.
[5] Maury, P.; Onclin Péter, M.; Crespo-Biel, O.; Ling, X. Y.; Reinhoudt, D. N. ; Huskens, J. *Nanotechnology* **2007**, *18*, 1-9.

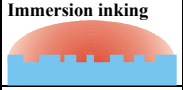
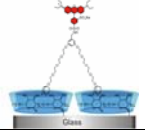
Contact information:
MESA+
University of Twente
P.O. Box 217
7500 AE Enschede
The Netherlands

LoP2007_mCP003_polar ink printing. PDF

Polar Ink Printing

Process: microcontact printing lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.	**Stamp**		
1.1	**Master fabrication** 	Fabricate patterned silicon master by photo- or E-beam lithography.	*Ideal with smooth bottom surfaces and smooth vertical sidewalls.*
1.2	**Master preparation**	Coat master with fluorinated anti-sticking layer.	*Hydro-phobic surface treatment to facilitate stamp separation.*
1.3	**Mixing of PDMS**	Mix precursor SYLGARD 184 elastomer base with curing agent 10:1 by volume.	*Good mixing required for catalytic reaction.*
1.4	**Degasing**	Degas mixture to avoid air bubbles in stamp	*Premixed aliquots can be stored at -20 ºC for 1-3 months.*
1.5	**Stamp curing** 	Pour liquid prepolymer onto master inside of petri dish and cure at 60 ºC for 12-24 hours.	
1.6	**Stamp work-up**	Cut and peel off the stamp from master. Rinse stamp three times with EtOH and dry under a flow of N_2 for 30 s.	
2	**Plasma Deposition of Allylamine [1]**		
2.1	**Chamber cleaning**	Plasma coating system (CCR, Rheinbreitbach, Germany). cleaning chamber with air plasma (30 min, 300 W). After plasma deposition chamber was brought to atmospheric pressure with argon.	*Cleaning removes all impurities in the chamber*
2.2	**Plasma deposition**	samples were positioned on the base plate at the same distance from the center of the reactor. Deposition of allylamine for 1 min at 300 W.	*Optimized conditions. No physical damage of the surface. Stable and high density of functional groups can be achieved.*
2.3	**Stamps storage**	Samples were transferred to storage container, sealed in an aluminum foil pouch under a nitrogen atmosphere at reduced (30 %) pressure and stored at -20 °C.	*This way modified surfaces are stable for longer periods (more than a year).*
3	**Inks [1]**		
3.1	**G2-S Dendritic ink [2]** 	A second generation of dendritic ink having 8 dialkyl sulfide end groups as positive ink on gold substrate yield positive gold patterns by positive microcontact printing (μCP).	*Low diffusion ink with polar end groups. This could be used to create positive patterns of Si master.*
3.2	**Ink solution**	Prepare diluted G2-S ethanol, e.g. $c = 2 \times 10^{-5}$ M.	*Optimized ink concentration.*
3.3	**ODT ink [2]**	Octadecanethiol ink in ethanol as backfilling ink for positive μCP. $c = 10^{-4}$ M	*Increasing the concentration causes to replace printed G2-S molecules and distorted patterns.*
3.4	**Divalent Guest ink [3]**	Divalent guest bearing two adamantyl units and labeled with	

		lissamine rhodamine dye. Substrate: β-cyclodextrin terminated glass.	
3.5	**Ink solution**	Prepare diluted solution of divalent guest in water, e.g. 10 µM	*Low concentration is good enough to transfer monolayers from the stamp.*
4	**Substrates [1]**		
4.1	**Gold substrates** 	Evaporate ~2 nm Ti onto a Si/SiO_2 wafer. Immediately following, evaporate 20 nm gold.	*Used gold substrates are commercially available by Ssens B.V., Hengelo, Netherlands.*
4.2	**β-Cyclodextrin glass [4,5]** 	β-cyclodextrin terminated glass substrates are fabricated in 3 steps starting from amine terminated glass.	*Please see ref.* [4,5] *for fabrication of β-cyclodextrin terminated substrates.*
5	**Inking**		
5.1	**Immersion inking** 	Inking by placing a drop of ink solution onto the stamp.	
5.2	**Inking**	Place two drops (~0.2 mL) of the freshly prepared (<1 h) ink solution on top of the stamp. After 60 s remove liquid quickly (<0.5 s) under a stream of N_2.	*Make sure there's enough liquid to cover the surface.*
5.3	**Drying**	Continue the flow of N_2 for 30 s after evident disappearance of the bulk drop to evaporate residual EtOH or water, use within 15 s.	
6	**Printing**		
6.1	**Making Contact** 	Place stamp onto gold or glass substrate, monitor formation of conformal contact.	*Conformal contact is made by the stamps own weight. If needed apply slight pressure with tweezers.*
6.2	**Detaching**	Remove the stamp after 60 s.	*The longer the printing time, the fewer the defects in the printed monolayer.*
7	**Case Studies[a]**		
7a	**µCP of G2-S**	G2-S dendrimer is printed on a gold surface with modified PDMS stamp. After printing, non-printed areas is backfilled with ODT for 10 s. Then the gold is etched away in etching bath.	*ODT backfilling time is optimized. If backfilling time is increased printed G2-S replaces by ODT.*
7a.1	**Preparation of etch bath**	Prepare an acidic solution of 10 mM $Fe(NO_3)_3$, 15 mM thiourea and 1.2 % HCl. etch at 45 °C for 2.2 min.	*The concentration of the ferric and thiourea in solution determine the etch rate.*
7a.2	**Etching & SEM image** 	Use scanning electron microscopy (SEM) or optical microscopy to analyze gold patterns after gold etches.	*Positive gold patterns are clearly visible in the SEM image.* 
7b	**µCP of Divalent Guest**	Divalent guest labeled with lissamine rhodamine dye is printed on cyclodextrin terminated glass. Ink should bind on substrate via host-guest supramolecular interactions.	
7b.1	**Fluorescence Microscopy Analysis**	Use fluorescence microscopy to analyze fluorescent patterns which	*Fluorescent pattern clearly indicates supramolecular binding of ink.*

		obtains from binding guest molecules on glass via supramolecualr interactions during printing.