4.1 Alkanthiol Printing

Microcontact Printing of Alkanethiols on Gold

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: IBM Research Laboratory
Address: CH-8803 Rueschlikon / Switzerland
Web-Address: http://www.zurich.ibm.com/
Process: microcontact lithography
Responsible: Heiko Wolf
E-mail:

Process description: Microcontact printing (μCP, mCP) of alkanethiols on gold
Purpose: A process is described for transferring a pattern from a silicon master via an elastomeric stamp onto a solid substrate.
Major advantages: In comparison to standard photolithography, microcontact printing is a low-cost, large-area, high-resolution patterning process.

References:

[1] Libioulle, L.; Bietsch, A.; Schmid, H.; Michel, B.; Delamarche, E. *Langmuir* **1999**, *15*, 300-304.
[2] Larsen, N. B.; Biebuyck, H.; Delamarche, E.; Michel, B. *Journal of the American Chemical Society* **1997**, *119*, 3017-3026.
[3] Geissler, M.; Wolf, H.; Stutz, R.; Delamarche, E.; Grummt, U.-W.; Michel, B.; Bietsch, A. *Langmuir* **2003**, *19*, 6301-6311.

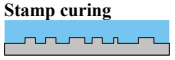
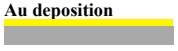
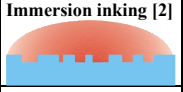
Contact address:

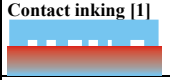
IBM Research Laboratory
Saeumerstrasse 4
CH-8803 Rueschlikon / Switzerland
http://www.zurich.ibm.com/

LoP2007_mCP001_microcontact printing alkalethiols. PDF

Alkanethiol 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 separation 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	*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 stamp off master. Rinse stamp three times with EtOH and dry under a flow of N_2 for 30 s.	
2	**Ink [1]**		
2.1	**Alkanethiols as ink**	Chose an alkanethiol, e.g. dodecanethiol (DDT), hexadecanethiol (HDT) octadecanethiol (ODT) or eicosanethiol (ECT)	*higher molecular weight thiols decrease ink diffusion, but increase disorder of monolayer and tend to crystallize at the stamp surface*
2.2	**Purification (optional)**	Purify by chromatography using silica gel (20:1 hexane-ethyl acetate on Silica Gel 60, ~200 g per 0.5 mL of thiols), and degas by successive freeze-pump-thaw cycles at a pressure of <100 mTorr for 24 h.	*purification removes low-molecular-weight thiols*
2.3	**Ink solution**	Prepare diluted thiol solution in ethanol, e.g. 0.1 mM	*changing the concentration allows to control the amount of ink transferred to the stamp*
2.4	**Storage**	Store purified ink solution at 4 °C in the dark for up to one week.	
3	**Substrate [1]**		
3.1	**Surface preparation**	Evaporate ~1 nm Ti onto a Si/SiO_2 wafer, e.g. with an e-beam evaporator at ~$2x10^{-7}$ Torr and a rate of ~0.5 nm s^{-1}.	
3.2	**Au deposition** 	Immediately following, evaporate 15 nm gold (same evaporation parameters)	
4	**Inking**		
4a	**Immersion inking [2]** 	Inking by placing a drop of ink solution onto the stamp.	*only the average amount of ink transferred can be controlled.*
4a.1	**Inking**	Place two drops (~0.2 mL) of the freshly prepared (<1 h) ink solution on top of the stamp. After 30 s remove liquid quickly (<0.5 s)	*make sure there's enough liquid to cover the surface.*

		under a stream of N_2.	
4a.2	**Drying**	Continue the flow of N_2 for 30 s after evident disappearance of the bulk drop to evaporate residual EtOH, use within 15 s.	
4b	**Contact inking [1]** 	Inking with an ink pad selectively directs the ink where it is needed.	*quality of monolayer is less dependent on pattern geometry, diffusion is minimized.*
4b.1	**Ink pad fabrication**	Prepare small blocks (~2 cm^2 and 4mm thick) of cured PDMS as ink pads.	
4b.2	**Impregnation**	Immerse the ink pad in the thiol-solution for at least 12 h.	
4b.3	**Drying and storage**	Withdraw from the solution, dry in a stream of N_2 for 10 s and store in a small glass flask.	
4b.4	**Inking**	Place the patterned stamp on the ink pad without applying pressure for 40s.	*conformal contact allows transfer of thiols. Inking times control amount of thiols transferred.*
5	**Printing**		
5.1	**Making Contact** 	Place stamp onto gold substrate, monitor formation of conformal contact optically.	*conformal contact is made by the stamps own weight.*
5.2	**Detaching**	Remove the stamp after 10-20 s.	*the longer the printing time, the fewer the defects in the printed monolayer, but the higher the ink diffusion.*
6	**Etching [3]**		
6.1	**Preparation of etch bath**	Prepare a ferric nitrate etch bath (20 mM $Fe(NO_3)_3 \cdot 9H_2O$ and 30 mM thiourea in DI water, adjusted to pH 2.0 using HCL)	*the concentration of the ferric and thiourea in solution determine the etch rate*
6.2	**Etching** 	The bath should be operated at 23-25 ºC with moderate stirring and has an etch rate of ~ 10 nm min^{-1}.	*the granularity of the gold substrate limits the edge resolution to the size of the gold grains (15-30 nm).*

4.2 Protein Patterning

Fabrication of high resolution protein patterns

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: IBM Research Laboratory
Address: CH-8803 Rueschlikon / Switzerland
Web-Address: http://www.zurich.ibm.com/
Process: microcontact lithography
Responsible: Heiko Wolf
E-mail:

Process description: Subtractive Printing of High Resolution Protein Nanopatterns
Purpose: The Ink-Subtract-Print strategy is described in which an inked elastomer is patterned by subtracting proteins from the surface using a nanotemplate followed by printing from the elastomer to a final substrate.
Major advantages: This technique is designed to produce high resolution patterns of single or multiple proteins with intrinsic alignment. Other advantages include: easy to use, high throughput pattern production, large area patterns, and no stamp collapse.

General:

References:

[1] S. R. Coyer, A. J. García, E. Delamarche, *Angew. Chem. Int. Ed.* **2007**, *46*, 6837-6840 .
[2] J. L. Tan, J. Tien, C. S. Chen, *Langmuir* **2002**, *18*, 519-523.
[3] A. Bernard *et al.*, *Langmuir* **1998**, *14*, 2225-2229.

Contact information:

IBM Research Laboratory
Saeumerstrasse 4
CH-8803 Rueschlikon / Switzerland
http://www.zurich.ibm.com/

LoP2007_mCP002_Protein Patterning. PDF