

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

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Process: microcontact lithography
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Process description: Microcontact printing (μ CP, 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.
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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	<i>ideal with smooth bottom surfaces and smooth vertical sidewalls</i>
1.2	Master preparation	Coat master with fluorinated separation layer	<i>hydro-phobic surface treatment to facilitate stamp separation</i>
1.3	Mixing of PDMS	Mix precursor SYLGARD 184 elastomer base with curing agent 10:1	<i>good mixing required for catalytic reaction,</i>
1.4	Degasing	Degas mixture to avoid air bubbles in stamp	<i>premixed aliquots can be stored at -20 °C for 1-3 months</i>
1.5	Stamp curing	Pour liquid prepolymer onto master inside of petri dish and cure at 60 °C 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)	<i>higher molecular weight thiols decrease ink diffusion, but increase disorder of monolayer and tend to crystallize at the stamp surface</i>
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.	<i>purification removes low-molecular-weight thiols</i>
2.3	Ink solution	Prepare diluted thiol solution in ethanol, e.g. 0.1 mM	<i>changing the concentration allows to control the amount of ink transferred to the stamp</i>
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.	<i>only the average amount of ink transferred can be controlled.</i>
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)	<i>make sure there's enough liquid to cover the surface.</i>

4a.2	Drying	under a stream of N ₂ . 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.	<i>quality of monolayer is less dependent on pattern geometry, diffusion is minimized.</i>
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.	<i>conformal contact allows transfer of thiols. Inking times control amount of thiols transferred.</i>
5	Printing		
5.1	Making Contact	Place stamp onto gold substrate, monitor formation of conformal contact optically.	<i>conformal contact is made by the stamps own weight.</i>
5.2	Detaching	Remove the stamp after 10-20 s.	<i>the longer the printing time, the fewer the defects in the printed monolayer, but the higher the ink diffusion.</i>
6	Etching [3]		
6.1	Preparation of etch bath	Prepare a ferric nitrate etch bath (20 mM Fe(NO ₃) ₃ •9H ₂ O and 30 mM thiourea in DI water, adjusted to pH 2.0 using HCL)	<i>the concentration of the ferric and thiourea in solution determine the etch rate</i>
6.2	Etching	The bath should be operated at 23-25 °C with moderate stirring and has an etch rate of ~ 10 nm min ⁻¹ .	<i>the granularity of the gold substrate limits the edge resolution to the size of the gold grains (15-30 nm).</i>

4.2 Protein Patterning

Fabrication of high resolution protein patterns

Process: microcontact printing lithography



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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. Garcia, 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.

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