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.
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 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 suitable independent, high density of functional groups on the surface, versatile chemical structures, and suitable for further surface modification based on reactive amine groups.

Optimized conditions. No physical damage of the surface. Stable and high density of functional groups can be achieved.

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### 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-cyclocodextrin terminated glass substrates are fabricated in 3 steps starting from amine terminated glass. Please see ref. [4,5] for fabrication of β-cyclocodextrin 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

#### 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 cyclocodextrin 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 obtains from binding guest molecules on glass via supramolecular interactions during printing.

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**Notes:**
- Low concentration is good enough to transfer monolayers from the stamp.
- Used gold substrates are commercially available by Ssens B.V., Hengelo, Netherlands.
- Please see ref. [4,5] for fabrication of β-cyclocodextrin terminated substrates.
- Make sure there’s enough liquid to cover the surface.
- ODT backfilling time is optimized. If backfilling time is increased printed G2-S replaces by ODT.
- The concentration of the ferric and thiourea in solution determine the etch rate.
- Positive gold patterns are clearly visible in the SEM image.
- Fluorescent pattern clearly indicates supramolecular binding of ink.