Microfluidic etching driven by capillary forces for rapid prototyping of gold structures

R. W. Stark, M. Sakai Stalder, A. Stemmer
Nanotechnology Group, Swiss Federal institute of Technology Zurich, ETH Center CLA, CH-8092 Zurich, Switzerland
stark@nano.mavt.ethz.ch

Keywords: microfluidic etching, rapid prototyping, soft lithography

Abstract

Soft lithographic methods based on poly(dimethylsiloxane) (PDMS) for pattern transfer are established alternatives to conventional lithographic methods. For applications in the biological sciences functionalized and structured noble metal surfaces are required. In order to allow for rapid prototyping of such gold structures a method is needed that does not change the surface chemistry. This can be achieved by a microfluidic system on a gold substrate that is filled with an etchant. From theoretical considerations simple thumb rules for the geometric and chemical design of such a microfluidic system were established. For experimental testing a microfluidic system was realized by contacting a structured PDMS stamp with a substrate consisting of a 50-nm-thick gold layer on a glass object slide. The etchant was applied to the entrance of the capillary and the acid was drawn into the fluidic system by capillary forces. Taking advantage of a PDMS stamp structured wetting and non-wetting regions no additional self-assembled monolayer was needed for masking.

1. Introduction

Soft lithographic methods for pattern transfer based on polymeric stamps fabricated with the elastomer poly(dimethylsiloxane) (PDMS) are established alternatives to conventional lithographic methods [1]. Most prominent techniques are micro contact printing [2,3] and micro moulding in capillaries [4-6]. In a similar approach PDMS stamps are used to create microfluidic networks by bringing the stamp in contact with a surface [7-10] or by creating 3-dimensional structures [11,12]. Using a 2-dimensional system, transport of a liquid over a distance of several millimeters from the original delivery point to the desired location was possible [7]. Patterned deposition of proteins in microfluidic networks was demonstrated successfully [13,14]. The confinement of the liquid in microfluidic devices can be enhanced by structuring the surface with wetting and non-wetting regions [15,13]. Moreover, the material PDMS has proven its stability against etchant in the fabrication of microstructures [16].

For applications in the biological sciences functionalized and structured noble metal surfaces are required. For rapid prototyping of such gold structures a method is desirable that does not completely change the surface chemistry as it is the case in conventional soft lithography, where the gold surface is masked by a covalently bound self-assembled monolayer of alkane thiols. As an alternative to lift-off techniques [17], a direct approach to etch gold structures by taking advantage of a microfluidic system and thus generating the structure directly with the PDMS stamp is investigated. In the following the strategy for microfluidic etching with open capillaries is discussed.
2. Design strategy for the microfluidic system

In order to achieve uniform etching it is most important to distribute the etchant efficiently in the micro-capillary system. The time needed to fill the capillary system should be smaller than the typical time-scale for the etching process. Figure 1 (a) shows the geometry of an open capillary with width \( w \) and height \( h \) that is filled with a volume \( V \) of etchant to the depth \( x \). The liquid is wetting the capillary surface \( A \). Three surfaces \( S \) of the capillary consist of PDMS with a solid – liquid interfacial free energy \( \gamma_{SL} \) and a solid – vapour interfacial free energy \( \gamma_{SV} \). The fourth surface \( S' \) is the gold on glass substrate with \( \gamma_{S'L} \) and \( \gamma_{S'V} \). The viscosity of the liquid is \( \eta \), and the liquid – vapour interfacial free energy is \( \gamma_{LV} \).

Under the assumption that the liquid drop at the entrance is large as compared to the dimensions of the capillary \( r >> w, h \) the rate of liquid flow in an open capillary system is given by [4,8]

\[
\frac{dx}{dt} = \frac{V/A}{4\eta x} \left[ \frac{2h+w}{2(h+w)} (\gamma_{SV} - \gamma_{SL}) + \frac{w}{2(h+w)} (\gamma_{SV} - \gamma_{SL}) \right] \\
= \frac{1}{8\eta x} \left( \frac{hw}{h+w} \right)^2 \left[ \frac{2(\gamma_{SV} - \gamma_{SL})}{w} + \frac{\gamma_{SV} - \gamma_{SL}}{h} + \frac{\gamma_{SV} - \gamma_{SL}}{h} \right] \approx \frac{\gamma_{LV}}{8\eta x} \left( \frac{hw}{h+w} \right)^2 \left[ \frac{2\cos \theta}{w} + \frac{\cos \theta + \cos \theta'}{h} \right].
\]

Here, the relations \( \gamma_{SV} \approx \gamma_{LV} \cos \theta + \gamma_{SV} \) and \( \gamma_{SV} \approx \gamma_{LV} \cos \theta' + \gamma_{SV} \) between the interfacial free energies and the respective contact angles \( \theta \) and \( \theta' \) were used. The parameter \( h \) in Eq. (1) is usually fixed in typical rapid prototyping processes because the capillary height is given by the thickness of the photoresist. Thus, it is convenient to introduce the dimensionless rate of liquid flow \( \dot{\xi} \equiv \frac{x}{\gamma_{LV} h} \) and the capillary aspect ratio \( \alpha = w/h \) leading to

\[
\frac{d\xi}{dt} \approx \left( \frac{\alpha}{1 + \alpha} \right)^2 \left[ (2\alpha^{-1} + 1) \cos \theta + \cos \theta' \right].
\]

Figure 1 (b) illustrates the dependence of the normalized rate of capillary flow on the geometric dimensions as well as on the contact angle between PDMS and the etchant under the assumption of a perfectly hydrophilic substrate \( \theta' = 0 \). It is evident, that narrow capillary structures are filled at smaller rates because the contribution of the wetting substrate surface is reduced as compared to wide structures.

At \( \theta = 60^\circ \), which is a typical contact angle for water on plasma-treated PDMS, the normalized rate of liquid flow is \( \dot{\xi}_c = 1.5 \) for an infinitely wide structure. Already at \( \alpha = 1.38 \) the flow rate drops to \( \dot{\xi}_c \). Thus, in the design of the microcapillary system a minimum aspect ratio parameter \( \alpha \) has to be ensured in order to avoid large differences in the flow velocity to achieve a homogenous distribution of the etchant.

The conformal contact between the gold substrate and the PDMS can be disturbed by the surface roughness which gives rise to unwanted leakage capillaries perpendicular to the microcapillary. The rate of liquid flow in these leakage capillaries \( \dot{y}_{\text{leak}} \) is given by Eq. 1.
where now $h$ is the height of the leakage capillary and $w$ the respective width. Thus, from Fig. 1 (b) it is clear that two important parameters define the quality of the sealing between the capillaries: (i) The contact angle $\theta$ between the etchant and the PDMS should be as large as possible to reduce the leakage flow rate $\dot{V}_{\text{leak}}$, and (ii) the contact between the gold and the PDMS structure has to be as tight as possible because the leakage flow rate $\dot{V}_{\text{leak}}$ linearly scales with the height capillary of the leakage capillary.

For a capillary with square cross section ($h = w$) Eq. (1) simplifies to

$$\frac{dx}{dt} \approx \frac{h\gamma_{LV}}{32\eta_x}[3\cos \theta + \cos \theta'].$$  

With $\theta' = 0$ the flow rate $\dot{x}$ vanishes for $\theta = 109.5^\circ$. This means for example, that native PDMS capillaries will show poor performance in the transport of water because the contact angle between water and native PDMS is $\theta = 105^\circ$.

The maximum size of the structure can be estimated from the time needed to fill the longest capillary of the system. This time should be shorter as the timescale for the etching process. Integration of Eq. (3) yields the time needed to fill a capillary with length $l$:

$$t = \frac{16\eta^2}{h\gamma_{LV} \left(3\cos \theta + \cos \theta'\right)}.$$  

For example water ($\eta = 1.0 \times 10^{-3}$ Ns/m², $\gamma_{LV} = 72.8 \times 10^{-2}$ N/m) fills a typical plasma treated PDMS capillary on a glass substrate ($\theta = 60^\circ$, $\theta' = 0^\circ$, $h = 5 \mu m$) of $l = 1$ cm within $t = 4.4$ s.

Figure 1 (a): Scheme of a partially filled PDMS capillary on a gold on glass substrate with a liquid droplet at the entrance. The capillary is open at both ends. (b) 3-Dimensional representation of the normalized rate of capillary flow as a function of the geometric capillary aspect ratio $w/h$ and the contact angle $\theta$ of the etchant on the PDMS ($\theta' = 0$).
From these considerations it is clear that there are several parameters that can be manipulated in order to achieve enhanced capillary flow. Most important for the design are the capillary aspect ratio $\alpha$ and the contact angle $\theta$ between PDMS and etchant. This leads to the following rules for the design:

(i) The extension of the structure is limited to

$$l_{\text{max}} \leq \left[ \frac{h\gamma_{LV} (3\cos\theta + \cos\theta') t_{\text{etch}}}{16\eta} \right]^{1/2},$$

where $t_{\text{etch}}$ is the time scale of the etching process.

(ii) The minimum aspect ratio $\alpha_{\text{min}}$ should be selected to ensure that capillary flow rate $\tilde{\xi}(\alpha_{\text{min}})$ is of the same order of magnitude as the maximum flow rate $\tilde{\xi}_{\text{c}}$.

(iii) The capillary system must be chemically structured with wetting channels and non-wetting sealings in order to avoid unwanted etching.

3. Experimental

3.1 Materials and Methods

**Stamp fabrication:** A silicon structure or a structured photoresist served as a master for the production of the stamp (Fig. 2 a). The PDMS (Sylgard 184, Dow Corning) prepolymer components were mixed following the instructions by the manufacturer. After moderately evacuating the liquid PDMS to remove air bubbles it was poured onto the master (Fig. 2 b) and cured at 50°C for about 24 h to allow for cross linking. To make the material hydrophilic, the PDMS stamp was exposed to oxygen plasma for about 1 min (Fig. 2 c). After contacting the plasma treated stamp with a piece of native PDMS to stimulate hydrophobic recovery of the surface (Fig. 2 d) the stamp was ready to use. A simple model for the effect of plasma treatment and the hydrophobicity recovery is displayed in Fig. 3 (For details c.f. [18,19]).

**Substrate:** After deposition of a 1-nm-thick chromium layer a 50-nm-thick gold layer was evaporated onto a cleaned glass slide.

**Etching:** The microfluidic system was established by contacting a structured PDMS stamp with the gold-coated glass substrate (Fig 2 e). The quality of the contact between the gold surface and the PDMS stamp was estimated visually: The force onto the stamp was increased carefully until the total internal reflection due to the remaining air gap at the interface between the PDMS and the gold surface vanished. Then, the etchant (aqua regia) was delivered to the entrance of the capillary and the acid was drawn into the fluidic system by capillary forces. After several seconds of etching, the PDMS stamp and the glass substrate were separated under deionised water to immediately stop the etching process. The gold structure (Fig. 2 f) was then carefully rinsed with deionised water and blown dry with compressed air.
**Contact angle measurements:** The contact angle was determined by the sessile drop method (NRL Contact Angle Goniometer Model 100-00, Ramé-Hart, Inc., Mountain Lakes NJ, USA).

---

**Figure 2:** Fabrication process of gold structures by microfluidic etching. (a) A structured surface serves as a master for a PDMS stamp (b). (c) The stamp is made hydrophillic by O₂ plasma treatment. (d) To generate a hydrophobic sealing the stamp is brought into contact with an untreated PDMS surface. (e) A droplet of etchant is placed at the entrance of the fluidic system. (f) After removing the PDMS stamp a gold structure remains where the stamp contacted the surface.

---

**Figure 3.** Creation of a hydrophillic channel with hydrophobic sealing. (a) The native PDMS surface is treated with a O₂-plasma (b) leading to a hydrophillic surface with exposed OH-groups. (c) Hydrophobic recovery of the sealings is induced by mechanical contact with a native PDMS surface, which leads to (d) a rearrangement of the polymer. (e) As result hydrophillic channels with a hydrophobic sealing are obtained.
3.2. Experimental Results and Discussion

In order to determine the effect of the duration of plasma treatment contact angle measurements were carried out on treated PDMS surfaces (Fig. 4 (a)). Already a 1-minute exposition to the oxygen plasma was sufficient to reduce the contact angle between the PDMS surface and a water droplet to a value below 60°. For longer plasma treatment times there is a strong variation in the contact angle. It is evident that a defined contact angle of about 50° can easily be achieved by oxygen plasma treatment, whereas a further reduction of the contact angle is difficult to control.

As a first proof of concept a linear microcapillary structure was composed \( (h = 0.8 \mu m, w \approx 100 \mu m, \text{i.e. } \alpha \approx 125) \) and a 1-\( \mu l \)-droplet of etchant (aqua regia) was deposited at the entrance of the capillaries. After 4.5 minutes the PDMS structure was removed and the substrate was cleaned with pure water and blown dry with compressed air. The resulting gold structures were investigated by transmission light microscopy (Fig. 4 (b)). The dark linear structures in the image represent the remaining gold on the glass substrate (bright). This clearly demonstrates that the concept of hydrophilic channels in combination with a hydrophobic sealing allows one to protect the gold outside the channels from the aggressive etchant on the micrometer scale.

![Figure 4 (a): Contact angle of the PDMS surface after air-plasma treatment. (b) Light microscopic image (transmission) of gold contacts produced by microfluidic etching.](image.png)

4. Conclusions

A straight-forward approach to create gold structures with the aid of a microfluidic system has been investigated. Taking advantage of a hydrophilic/hydrophobic structured PDMS stamp, no additional self-assembled monolayer protecting the surface is needed for masking. Employing a stamp with hydrophilic capillaries and a hydrophobic sealing, gold structures on glass could be obtained. Simple rules limiting the design of the structure were developed from theoretic considerations. However, these limitations arise from the fact that the etching agent is only passively drawn into the system by capillary forces. With the help of active devices like micropumps the performance of the system can be enhanced. Promising fields of application for rapid prototyping of gold structures by microfluidic etching are the development of biosensors based on immobilized thiolated molecules and prototyping of electrode structures for dielectrophoresis.
Acknowledgements

We thank Dr. M. Müller (ETH, Zürich) for his support with the evaporation system, Prof. Nicolas Spencer (ETH Zürich) for his help with the contact angle measurements and G. Schitter (ETH Zürich) for fruitful discussions.

References