Large area \( \mu \text{m} \) and sub-\( \mu \text{m} \) structuring of gold layers with microcontact printing using 4" and 1" PDMS stamps

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Abstract. Microcontact printing (\( \mu \text{CP} \)) using PDMS stamps and alkanethiol chemistry is a straightforward method for the structuring of gold layers. We fabricated PDMS stamps from 4" Si wafers structured by photolithography, as well as from 1" masters produced with UV-nanoimprint lithography (UV-NIL) directly on a rigid glass back-plate. Large area \( \mu \text{m} \) and sub-\( \mu \text{m} \) structuring of gold layers was demonstrated using these PDMS stamps. The masters, the stamps and the resulting gold structures were analyzed using scanning electron microscopy (SEM), atomic force microscopy (AFM) and optical microscopy.

1. Introduction

Microcontact printing (\( \mu \text{CP} \)) is a simple yet excellent method to functionalize surfaces by using a structured elastomeric stamp to transfer patterns of the desired substances directly onto the substrate surface. \( \mu \text{CP} \) of alkanethiols on gold was the first representative of soft-lithography processes [1]. The principle of \( \mu \text{CP} \) is schematically shown in figure 1.

One of the key elements of \( \mu \text{CP} \) is the stamp made of poly(dimethylsiloxane) (PDMS) which is the negative copy of a master. In this work the stamp was used for printing alkanethiols onto a gold surface which form a self-assembled monolayer (SAM) on gold. The structured SAM acts as an etch mask during wet chemical etching and the pattern is transfer into the gold layer.

We fabricated PDMS stamps directly on a rigid glass back-plate. As masters we used 4" Si wafers structured by photolithography and 1" masters structured by UV-nanoimprint lithography (UV-NIL). Large area \( \mu \text{m} \) and sub-\( \mu \text{m} \) structuring of gold layers was demonstrated using these 4" and 1" PDMS stamps.

2. Experimental procedure

Often PDMS stamps for \( \mu \text{CP} \) are fabricated by simply pouring the liquid prepolymer over a structured master. This normally results in a considerable lateral thickness variation of the stamps being unfavorable for the printing quality since it induces a variation of the printing pressure. Spin-casting can reduce the thickness variation problem but suffers from edge bead and thin stamps difficult to handle.
We produced PDMS stamps directly on a rigid glass back-plate using a PDMS stamp fabrication tool (figure 2 left). The well-defined geometry of the tool allows a fast and reproducible fabrication of PDMS stamps. The rigid glass back-plate supports the 960 µm thick PDMS layer (figure 2 right) ensuring safe handling and compatibility to the printing device.

To prolong the durability of the masters and to ensure a complete separation of the master and the hardened PDMS stamp an anti-sticking layer was spin-coated onto the masters prior to stamp fabrication. Both masters and stamps were analyzed using SEM, AFM and optical microscopy.

For the printing process the stamps were inked by immersion inking with a solution of octadecanethiols (ODTs) [CH$_3$(CH$_2$)$_{17}$SH] dissolved in ethanol, dried with N$_2$ and brought into contact with the gold substrate (figure 1). The printing process itself was performed with an EVG® 620 mask aligner under clean room conditions to guarantee best possible control over important process parameters such as contact pressure, contact time and uniformity of pressure. In the area of contact between stamp and substrate, ODTs form a SAM on the gold surface by chemisorption due to the linking of the molecule to the gold surface by the sulfur group [2]. During etching with a solution of thiourea and ferric nitrate, ODTs act as etch mask for the underlying gold layer (figure 1) [2], [3]. The resulting gold structures were analyzed using AFM and optical microscopy.
3. Results and Discussion

3.1. μm structuring of gold layers with 4" PDMS stamps

The 4" PDMS stamp fabrication could be done routinely and the entire area of a 4" Si master could be accurately replicated. Due to the usage of an anti-sticking layer the masters could be used so far without recognizing any change in the quality of the stamps and the gold structures.

The AFM images in figure 1 show structures with a period of 6 μm. Due to the finite size of the tip the structures in the AFM image of the Si master (figure 1 right, top) are scaled down whereas the structures in the AFM image of the PDMS stamp (figure 1 right, middle) are broadened. Nevertheless, the determination of a period of 6 μm verifies an accurate molding of the master and pattern transfer into the gold layer (figure 1 right, bottom).

The entire gold layer on a 4" Si wafer was structured homogeneously with a single contact step and subsequent etching (figure 3).

![Figure 3. Photograph of a structured gold layer on a 4" Si wafer surrounded by the corresponding optical bright-field micrographs of the gold structures](image)

3.2. sub-μm structuring of gold layers with 1" PDMS stamps

To overcome the resolution limitations of photolithography we additionally used masters structured by UV-nanoimprint lithography (UV-NIL). The principle of UV-NIL is the imprinting of a rigid quartz stamp into a UV-curable polymer spin-coated on a Si wafer as a substrate. For details see for example references [4] and [5]. The structured and cured polymer (figure 4 left) was used as master for the stamp fabrication in the same way as described above.

![Figure 4. left: Photograph of a 1" UV-NIL imprint used as master for PDMS stamp fabrication; right: 1" PDMS stamp on a rigid glass back-plate (not visible) molded from a UV-NIL imprint](image)

The 1" PDMS stamp fabrication from imprints could be done routinely and the entire 1" area could be accurately replicated (figure 4 right). One essential step is once again the spin-coating of an anti-
sticking layer onto the imprint prior to stamp fabrication. Otherwise the imprinted polymer sticks to
the hardened PDMS and is torn off the substrate during the separation.

The smallest structures in gold fabricated with PDMS stamps molded from UV-NIL imprints are
down to 700 nm in size (figure 5 right and figure 6).

Figure 5. left: SEM image of a UV-NIL imprint used as master for PDMS stamp fabrication; right: AFM image of 26 nm deep structures in gold and corresponding line scan

Figure 6. left: AFM image of structured gold layer; right: corresponding line scan

4. Outlook and Acknowledgement

Based on this work the resolution of the process will be pushed down into the nanocontact printing
(nCP) regime to create gold structures for single molecule detection by using a novel stamp design.

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