

Bifunctional, Chemically Patterned Flat Stamps for Microcontact Printing of Polar Inks

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Different methods to create chemically patterned, flat PDMS stamps with two different chemical functionalities were compared. The best method for making such stamps, functionalized with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTs) and 3-(aminopropyl)triethoxysilane (APTS), appeared to be full functionalization of a freshly oxidized flat PDMS stamp with either adsorbate, followed by renewed oxidation through a mask and attachment of the other adsorbate. These stamps were used to transfer polar inks (a thioether-functionalized dendrimer and a fluorescent dye) by microcontact printing. The PFDTs monolayer was used as a barrier against ink transfer, while the APTS SAM areas functioned as an ink reservoir for polar inks. The printing results confirmed the excellent transfer of hydrophilic inks with these stamps to gold and glass substrates, even from aqueous solutions. Attachment of a fluorescent dye on the amino-functionalized regions shows the possibility of the further modification of the chemically patterned stamps for tailoring of the stamps' properties.

Introduction

In recent years, soft lithography has become a widespread technique to chemically pattern various substrates.¹ As such, microcontact printing (μ CP)^{2,3} has triggered enormous interest because of its processing advantages in comparison to conventional lithographic techniques. In a typical μ CP approach, an elastomeric stamp with a relief structure is brought into intimate contact with a substrate to transfer ink molecules from the stamp to the substrate. In the contact areas, the ink forms a self-assembled monolayer (SAM), which can then be used, for instance, as a resist against etching. The lateral dimensions of the SAMs formed depend on the dimensions of the relief features on the stamp. It is possible to form relief features with lateral dimensions as small as 50 nm, but the replication of such structures by μ CP remains a challenge.^{4–10} The main limiting factors of downsizing the printed patterns are (i) the low mechanical stability of the elastomeric stamp, which is prone to collapse and deformation,^{4,11,12} and (ii) the absorption of ink in the stamp, promoting ink diffusion and overload of the surface.^{13–16} Several solutions

have been proposed to overcome these problems, such as developing new stamp materials^{17–20} and composite stamps^{11,21,22} to avoid stamp collapse during printing, inking with ink pads,²³ and utilizing heavyweight inks or catalytic microcontact printing to overcome ink diffusion.^{8,24,25}

Currently, the most common stamp material for μ CP is poly-(dimethylsiloxane) (PDMS). PDMS is a very soft, chemically cross-linked rubber that easily establishes conformal contact with a substrate and exhibits excellent printing characteristics with apolar inks, such as alkanethiols. However, the elastomeric character of PDMS is also the origin of some of the most serious technical problems. Deformation of the soft polymer stamps due to nonuniform pressures applied during printing, such as pairing, buckling, or roof collapse of structures, renders them unsuitable for high-resolution μ CP.

In principle, a flat stamp can solve many or all stamp stability issues. Delamarche et al.²⁶ have shown that flat PDMS stamps can be patterned by a combination of surface oxidation in an oxygen plasma using a mask and subsequent stabilization of the

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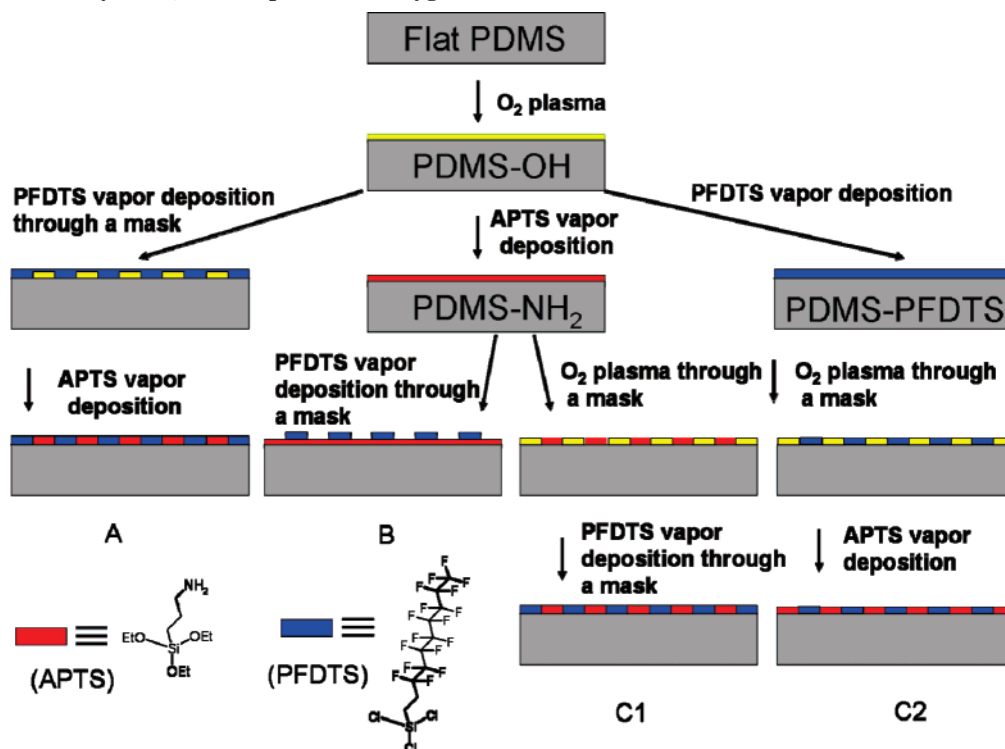
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Scheme 1. Fabrication Strategies of Bifunctional Flat PDMS Stamps: Deposition through a Shadow Mask (A), Grafting on an APTS Monolayer (B), Two Exposures to Oxygen Plasma with APTS First (C1) and with PFDTs First (C2)



hydrophilized areas by reaction with a poly(ethylene oxide)-silane. These stamps have been used for the selective deposition and subsequent patterned transfer of proteins from the stamp surface. In our group, we have introduced the concept of flat, chemically patterned stamps for μ CP using regular thiol inks.²⁷ Stamp functionalization is achieved by local oxidation of a flat piece of PDMS through a mask, followed by adsorption of a fluorinated silane, 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTs). It was found that this silane forms densely packed SAMs on oxidized PDMS, which constitutes an effective barrier for ink transfer by μ CP. These flat PDMS stamps have been used to transfer patterns of alkanethiols to gold. A limitation of these fluorinated silane-modified stamps is that these stamps cannot be used to transfer hydrophilic inks, because polar inks do not wet the stamp surface.

Here we introduce bifunctional, chemically patterned flat stamps. Besides the fluorinated SAMs, (3-aminopropyl)triethoxysilane (APTS) was chosen to form the second SAM type on the remaining PDMS areas. It has short alkyl chains and shows high reactivity in silane chemistry, and the primary amino groups offer the possibility to interact with inks or of further modification to achieve different chemical functionalities on the stamp. APTS has, for example, been used for μ CP of DNA via electrostatic interactions.²⁸ The intermediate hydrophilicity of the APTS layer (typical advancing water contact angle $\theta_a = 75^\circ$) can be advantageous to adsorb polar and apolar inks alike. A bifunctional, flat stamp design is believed to eliminate diffusion (through the strong, specific interaction with the stamp) and overload (since only a monolayer is transferred), therefore leading to improved resolution of the printed patterns.

In this paper, we demonstrate the formation of the bifunctional, chemically patterned flat PDMS stamps. Three different methods

have been used to fabricate flat PDMS stamps functionalized with APTS and PFDTs. XPS, water contact angle and AFM measurements have been used to identify the two chemical patterns on the PDMS surface. A fluorescent dye was attached to the amino-functionalized regions to investigate the possibilities of the further modification of such bifunctional stamps. These PDMS stamps were used to transfer polar inks to gold and glass substrates. The stability of the chemically patterned PDMS stamps was tested by printing with the same stamps after 1 month.

Results and Discussion

Stamp Fabrication and Surface Characterization. Three different methods have been used to make chemically patterned flat PDMS stamps functionalized with two absorbates (Scheme 1). Since most of the organic solvents swell PDMS, APTS and PFDTs were deposited on the stamp surface by vapor-phase deposition. X-ray photoelectron spectroscopy (XPS) and water contact angle (CA) measurements were used to monitor the chemical changes that occur at the stamp surface.

In the first method, PFDTs and APTS were deposited on the PDMS surface using a shadow mask (Scheme 1A). First, a piece of flat PDMS was treated with oxygen plasma. Subsequently, chemical patterns were generated by reaction of the activated PDMS with PFDTs from the vapor phase through a contact mask. In order to prevent the hydrophobic recovery²⁹ of the oxidized PDMS after the PFDTs deposition, the deposition time was minimized to 15 min and the annealing step was omitted. After removal of the mask, the stamp was immediately transferred into the vapor of APTS for 30 min. So the two different chemical functionalities were patterned on the flat PDMS surface according to the patterns of the contact mask.

In order to facilitate the characterization by contact angle and XPS, a model stamp was prepared according to Scheme 1A, by

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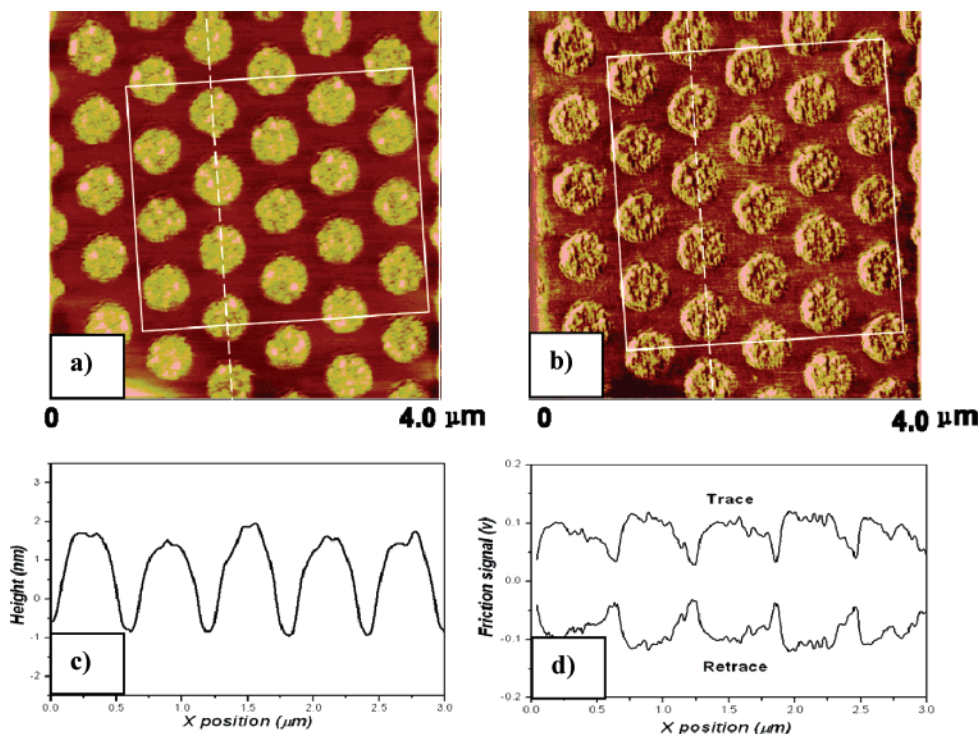


Figure 1. Contact mode AFM height (a) and friction (b) images, and the corresponding height profile (c) and friction loop (d) obtained at an applied normal load of 15 nN of the bifunctional flat PDMS stamp. The stamp was made by two exposures to oxygen plasma in which PFDTs was deposited first (see Scheme 1C2).

covering half of a flat piece of PDMS by a piece of Si wafer as the contact mask, thus generating macroscale pattern areas. For comparison, full layers of PFDTs and APTS were deposited on different PDMS slabs. CA measurements were performed to determine the hydrophilicity of the stamp surface. Results are summarized in Table 1.

The full PFDTs layer on PDMS had a typical advancing contact angle (θ_a) value of 120° . In contrast, the CA value of the PFDTs layer on the model stamp made by method A was lower ($\theta_a = 110^\circ$). XPS also showed that the fluorine content of the PFDTs layer on the patterned stamp was lower than on the full substrate, and some APTS was deposited within the PFDTs layer, as shown by the nitrogen content in the PDFTS layer. These results indicate that the PFDTs did not form a densely packed layer without annealing and thus resulted in the deposition of APTS everywhere on the stamp surface.

The second method (Scheme 1B) employs the possibilities to attach silanes onto an amino-coated surface. Amino groups of APTS SAMs on silicon react readily with chlorodimethylsilane from the vapor phase.³⁰ Probably the surface-bound amine has a low steric hindrance during this S_N2 reaction. Here we target the grafting of PFDTs onto a full APTS SAM through a shadow mask. First, a full layer of APTS was deposited on the oxidized flat PDMS surface by vapor-phase deposition. Then the chemical patterns were generated by exposure to PFDTs vapor for 20 min through a contact mask. The stamp was annealed at 60°C for 3 h to complete the coupling reaction.

XPS and CA measurements of the macropatterned model stamp made by this grafting method are summarized in Table 1. Both CA values and XPS data compare well with the full layers of APTS and PFDTs on flat PDMS. However, when using AFM to inspect the SAMs on the stamp surface, the patterns were not well defined (see Supporting Information). This is attributed to a rather poor quality of the full APTS SAM. This was confirmed

by the large hysteresis between the advancing and receding water contact angles ($\approx 40^\circ$) of this SAM. Apparently, this also leads to a poor-quality PFDTs SAM on top of the APTS SAM. Different attempts were made to improve the quality of the fluorinated layer, for example, by increase of the annealing time of the bottom APTS layer and extension of the PFDTs grafting reaction time. However, the quality of the patterns did not improve much, according to AFM.

As outlined in Scheme 1C, chemically patterned PDMS stamps can also be fabricated via full SAM formation and oxidation through a mask to simultaneously remove the first SAM locally and reactivate the PDMS, followed by attachment of the second silane. Thus, the amino silane can be attached first, followed by the fluorinated silane (Scheme 1C1), or in reverse order (Scheme 1C2). It has been reported that prolonged exposure to oxygen plasma can lead to physical damage of the PDMS surface, producing “cracks” or other microstructures.³¹ To our knowledge, no studies have been reported so far on using oxygen plasma twice on PDMS. Thus, the conditions for the second plasma-etching were optimized to ensure complete removal of the first silane monolayer while a smooth PDMS surface was maintained (see Supporting Information). The best conditions were found with an oxygen plasma (10 W, 10 mTorr of O_2) treatment for 20 s.

XPS and CA measurements of the macropatterned model stamps made via method C are summarized in Table 1. Both CA values and XPS results show a clear difference between the APTS- and PFDTs-functionalized regions on the model stamp. The data also compare well with the full layers of APTS and PFDTs on flat PDMS.

Figure 1 shows the AFM height and friction images obtained for a chemically functionalized, submicron-patterned stamp made by using oxygen plasma twice and deposition of PFDTs first (Scheme 1C2), using the mask with 350 nm holes. In this case,

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Table 1. XPS and Water Contact Angle Data of Flat PDMS Stamp Surfaces on Full Layers of APTS and PFDTS and on Macropatterned Model Stamps Using the Different Methods Shown in Scheme 1

samples	XPS atomic concentration (%)			θ_a/θ_r (deg)	
	N1s	F1s	Cl2p		
APTS (full)	5.49	0.11	1.76	75/37	
PFDTS (full)	0.00	22.51	0.00	120/105	
A	APTS	4.95	0.21	1.73	80/45
	PFDTS	1.94	8.56	0.36	110/75
B	APTS	5.48	1.28	1.55	80/41
	PFDTS	4.05	24.26	3.69	120/85
C1	APTS	6.12	0.89	1.28	75/40
	PFDTS	0.02	21.89	0.13	118/100
C2	APTS	5.18	0.99	1.88	80/42
	PFDTS	0.10	19.38	0.02	119/102

APTS is expected inside the dot patterns and PFDTS at the surroundings. The height image (Figure 1a) clearly shows well-defined 350 nm dots patterns. A cross-sectional profile (Figure 1c) shows that the dot patterns are 2 nm high. Since the height difference between a PFDTS and an APTS monolayer is less than 1 nm, the height difference is attributed to the second oxygen plasma treatment. However, such a small height is not expected to influence the contact printing properties. The bright areas in the friction image (Figure 1b) correspond to regions of high friction or strong interaction between the AFM tip and the functional groups on the surface. Combined with the friction loop (Figure 1d), this shows that these regions of high friction correspond to the APTS-functionalized areas. Low-friction regions were at the surroundings, where PFDTS is immobilized. This is in agreement with previous studies, which showed that Si_3N_4 AFM tips have higher frictional forces at surfaces with higher surface energy, here the amino-terminated areas.³² Moreover, the friction patterns are clearly well defined.

In summary, the modification via exposure to oxygen plasma two times is the most efficient method to fabricate bifunctional flat PDMS stamps, and these stamps were therefore used in the remainder of this study. Their stability was shown to be excellent, as printing was reproducible after storing the stamps for 1 month (see below).

In order to support the formation of amino groups on the stamp surface, these bifunctional stamps were reacted with the fluorescent compound 5-(and-6)-carboxytetramethylrhodamine succinimidyl ester [5(6)-TAMRA-SE], of which the succinimidyl ester group reacts readily with amino groups. The attachment of TAMRA was achieved by contact printing using an oxidized flat PDMS stamp, inked with TAMRA-SE, on bifunctional micron-patterned PDMS stamps made by methods C1 and C2 (Scheme 1). To the best of our knowledge, this is the first example where reactive μCP^{33-39} is used to functionalize another PDMS surface.

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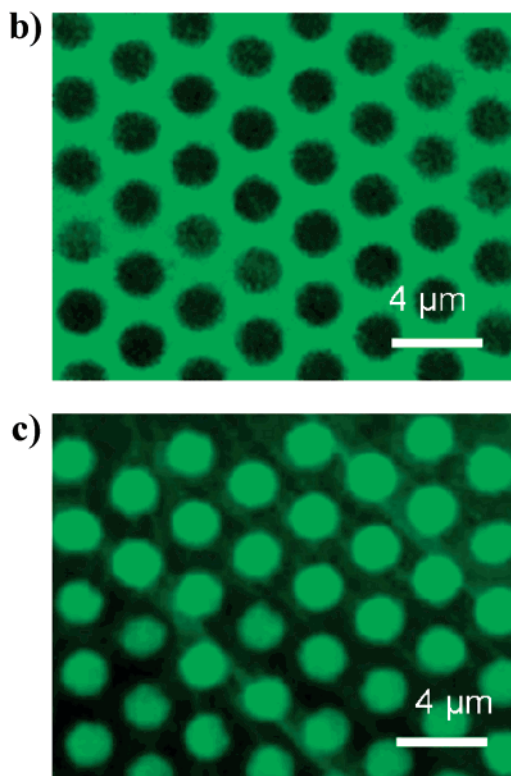
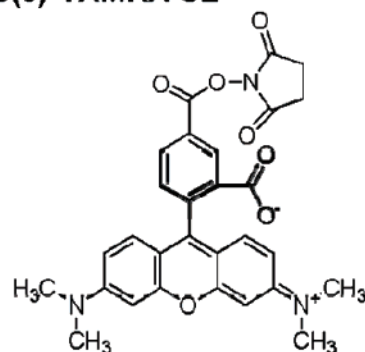
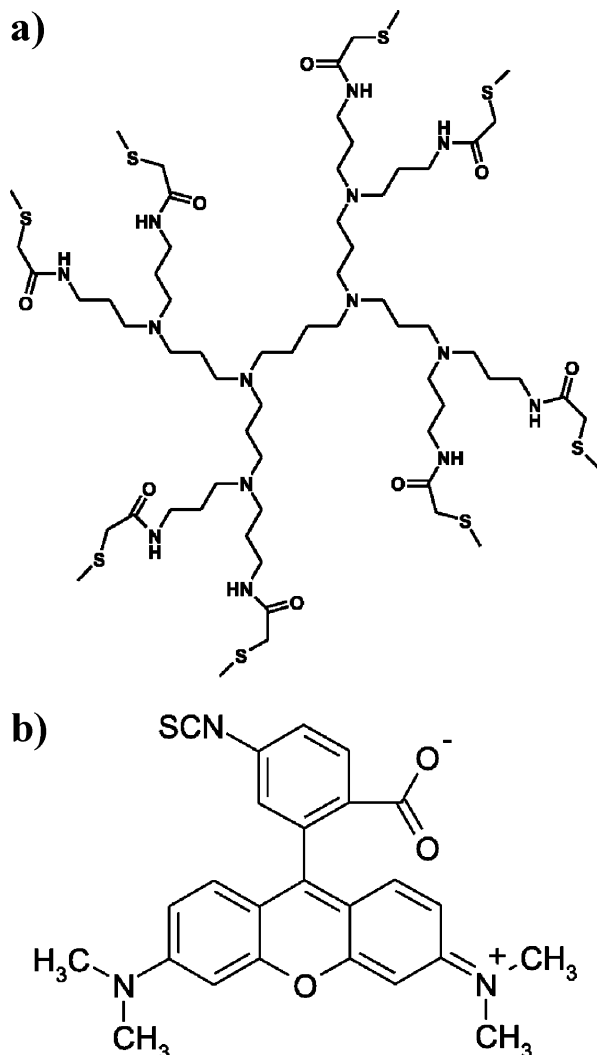


Figure 2. Chemical structure of the fluorophore TAMRA-SE (a). Fluorescence microscopy images of the TAMRA patterns on the bifunctional flat PDMS stamps that are fabricated via two exposures to oxygen plasma with method C1 (b) and method C2 (b) (Scheme 1).

Figure 2 shows the fluorescence microscopy images of the PDMS stamps after attachment of TAMRA and excessive rinsing and sonication. All patterns were made using a shadow mask with holes of a diameter of $2\ \mu\text{m}$. It is evident from the fluorescence images that the $2\ \mu\text{m}$ features of the shadow mask are reproduced well on the PDMS substrate into amino and subsequently fluorescent patterns. The resulting fluorescent TAMRA remained present on the bifunctional PDMS stamps, in spite of extensive rinsing and sonication; thus, any type of adsorption other than covalent immobilization through amide formation is unlikely. This is also indicated by the fact that TAMRA is absent in the fluorinated areas.

The successful patterning of fluorescent molecules on a PDMS surface confirms the formation of the two chemically distinct patterns on the PDMS stamp via exposure to oxygen plasma two times and it also shows the possibility of further modification of the amino groups on the PDMS surface to tailor the chemical design of the stamp surface.

Chart 1. Chemical Structures of Polar Inks: (a) A Second-Generation Poly(propylene imine) Dendrimer with Dialkyl Sulfide End Groups (G2-S), and (b) the Fluorophore Tetramethylrhodamine 5-(and-6)-isothiocyanate (TRITC)



Microcontact Printing using Bifunctional Flat PDMS Stamps. In order to test the stamps in μ CP, hydrophilic inks were transferred to gold substrates. A second-generation PPI dendrimer (G2-S, Chart 1) with eight short dialkyl sulfide ($\text{CH}_3\text{-SCH}_2\text{-}$) end groups was used as an ink for positive microcontact printing [(+) μ CP].⁴⁰ In this technique, the pattern is transferred by printing a poorly etch resistant ink, followed by immersion of the sample in a solution of a second, etch-resistant adsorbate, which fills the noncontacted areas and acts as a resist in the subsequent etching step.

In our group, a series of poly(propylene imine) dendrimers with dialkyl sulfide end groups was prepared and used as inks for (+) μ CP on gold.²⁵ The multivalent sulfide attachment and the relatively high molecular mass of these dendrimers ensured minimal lateral ink spreading and thus optimal feature reproducibility. Among these dendrimeric inks, the second-generation dendrimer with short dialkyl sulfide end groups (G2-S) was too polar to be printed by conventional PDMS stamps, and also with oxidized stamps the resolution was poor.

This polar dendritic ink (G2-S, $c \approx 2 \times 10^{-5}$ M in ethanol) was printed on a gold surface for 1 min using a bifunctional flat

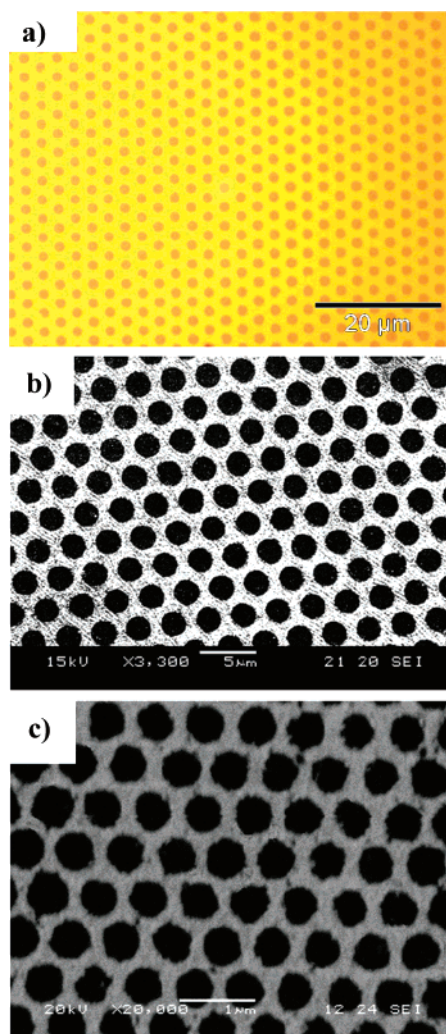


Figure 3. Optical (a) and scanning electron microscopy (SEM) (b) images of $2 \mu\text{m}$ hole patterns and a SEM image (c) of 350 nm hole patterns of gold by (+) μ CP of G2-S using bifunctional flat PDMS stamps and wet etching. Stamps were fabricated according to Scheme 1C2.

PDMS stamp, prepared according to Scheme 1C2. Thereafter, the samples were immersed in an octadecanethiol (ODT) solution ($c = 10^{-4}$ M in ethanol) for 10 s for back-filling. ODT forms an etch-protective SAM on the rest of the surface. After printing and back-filling, the gold substrates were etched in an acidic solution of 10 mM $\text{Fe}(\text{NO}_3)_3$, 15 mM thiourea, and 1.2% HCl at 45°C for 2.2 min.²⁵ The dendrimer SAM was not etch-resistant and the gold underneath the dendrimer was etched away to give the positive pattern of the original shadow mask that was used in the stamp fabrication. Optical microscopy and scanning electron microscopy (SEM) images of etched gold features on a silicon wafer are shown in Figure 3.

In Figure 3, the dark areas in the images correspond to the printed parts of G2-S, and the bright areas to the back-filled, etch-resistant ODT SAM areas. Figure 3a,b shows the $2 \mu\text{m}$ good-quality gold patterns over a large area without defects. Using stamps made by a shadow mask with a hole diameter of 350 nm , replication was also achieved (Figure 3c), now leading to features of about 450 nm . The size enlargement is attributed in part to the steps involving the mask in the stamp fabrication process and in part to the wet etching of the final structure after the contact printing process.

To show the chemical versatility of the APTS- and PFDTs-modified stamps using a different ink–substrate combination,

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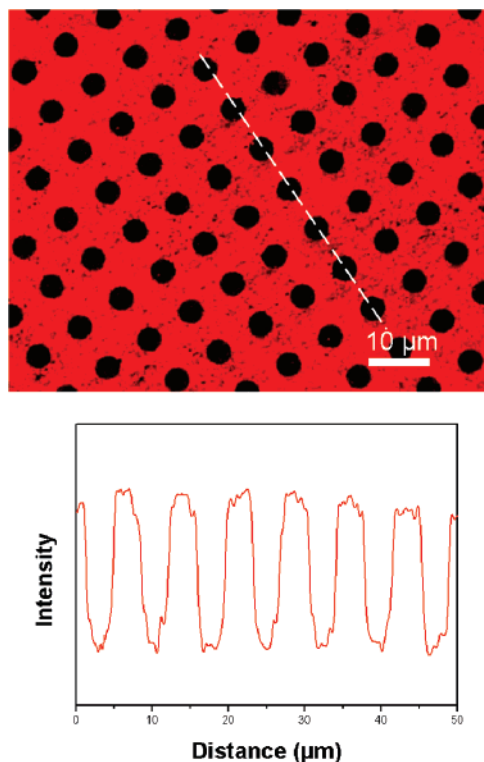


Figure 4. Fluorescence microscopy image after μ CP of TRITC on a glass substrate. The bifunctional flat PDMS stamp was inked from an aqueous solution (0.1 mM). Printing time was 2 min. Substrates were rinsed with water after printing. The patterned stamps were made from a shadow mask with 4 μ m holes.

the hydrophilic and fluorescent tetramethylrhodamine 5-(and-6)-isothiocyanate (TRITC) was chosen as an easily traceable ink. A patterned bifunctional stamp with 4 μ m dots was made according to Scheme 1C1. The stamp was inked with an aqueous TRITC solution (0.1 mM). Because of its hydrophilicity, TRITC is expected to reside at the amino-functionalized areas. Thereafter, it was transferred to a clean glass substrate. Figure 4 shows the resulting fluorescence patterns, giving direct evidence of transfer of the ink molecules from the stamp to the substrate. This indicates that aqueous ink solutions can also be used for μ CP with the bifunctional chemically patterned flat stamp.

In order to estimate the stability of the chemically functionalized PDMS stamps, μ CP of G2-S was repeated by reusing the same stamps (stored at -20 $^{\circ}$ C, under nitrogen), after 1 month. Ink and etching solutions were freshly prepared. After printing and etching, substrates were analyzed by SEM. The resulting gold patterns (see Supporting Information) were identical to the results of the experiments shown in Figure 3. This indicates a long-term stability of the PFDTS and APTS monolayers on the PDMS surface. This is in contrast to oxidized PDMS, for which hydrophobic recovery occurs after a few hours.

Conclusions

Three different methods have been used to fabricate APTS- and PFDTS-functionalized flat PDMS stamps. The method using oxygen plasma twice via full SAM formation and oxidation through a mask to simultaneously remove the first SAM locally and reactivate the PDMS, followed by attachment of the second silane, has been proved to be the most efficient method. XPS, water contact angle, and AFM measurements have confirmed the chemical patterns on the PDMS surface. Attachment of the TAMRA fluorescent dye to the amino-functionalized regions shows the possibility of further modification of the bifunctional

stamps to achieve different chemical functionalities on the stamp. This new stamp design showed a good performance in micro-contact printing of polar inks (G2-S dendrimer and TRITC dye) in both (+) μ CP and (-) μ CP. Printing results of the G2-S dendrimer using the same stamps after 1 month confirmed the long-term stability of the chemically functionalized PDMS stamps. Future developments will be in the chemical modification of the amine areas for creating specific ink recognition areas.

Experimental Section

Materials and Methods. PFDTS (purity 97%) was purchased from ABCR GmbH. APTS (purity 99%) and octadecanethiol (ODT, 98% purity) were purchased from Sigma-Aldrich. Fluorophores TAMRA-SE and TRITC were obtained from Molecular Probes, Inc. All materials were used as received without further purification. The second-generation dendrimer G2-S was synthesized according to a reported procedure.²⁵ Microsieves, which consist of a supported metal membrane permeated with micrometer or sub-micrometer-sized pores were used as the masks. Different types of microsieves were purchased from Aquamarijn Micro Filtration B.V., The Netherlands.

Preparation of Flat PDMS Stamps. The stamp material, Sylgard-184 PDMS, was obtained from Dow Corning. Flat PDMS stamps were prepared by mixing the curing agent and the prepolymer manually in 1:10 volume ratio and curing overnight at 60 $^{\circ}$ C against a polished Si wafer. After curing, the stamps were peeled off from the Si wafer.

Preparation of Oxidized PDMS Stamps. Oxidized flat PDMS stamps were prepared by exposure of flat PDMS stamps to a PlasmaTherm 790 reactive ion etching oxygen plasma (10 W, 10 mTorr O₂) for 10 s. Oxidized patterns were generated by exposure of the PDMS flat surface to the same oxygen plasma through a microsieve.

Preparation of Amino-Functionalized PDMS Stamps. APTS was deposited for 30 min from its vapor phase onto fully or locally oxidized PDMS stamps, under reduced pressure ($\approx 10^{-2}$ – 10^{-3} Torr). The adsorbed APTS was assumed to react with the silanol groups present on the oxidized PDMS to yield an amino-terminated stamp. The reaction was carried out in an oven at 90 $^{\circ}$ C for 30 min. Physisorbed APTS was removed by sonicating the stamp in ethanol for 3 min.

Preparation of Fluorinated PDMS Stamps. PFDTS was deposited for 30 min from its vapor phase onto fully or locally oxidized PDMS stamps. The stamps were thereafter cured in an oven for 3 h at 60 $^{\circ}$ C.

Attachment of TAMRA onto the Bifunctional Flat PDMS Stamp. The attachment of the fluorophore TAMRA to the bifunctional flat PDMS stamp was achieved by putting the bifunctional PDMS stamp in contact with another oxidized flat PDMS stamp that had been inked with 0.23 mM acetonitrile solution of TAMRA-SE for 2.5 min. After separation of the two PDMS slabs, the bifunctional flat PDMS stamp was rinsed with excess ethanol and dried in a nitrogen steam.

G2-S Printing. Gold substrates were obtained from Ssens BV (Hengelo, The Netherlands) as a layer of 20 nm gold on titanium (2 nm) on silicon. Before use, the substrates were treated with oxygen plasma, immersed in ethanol for 1 h, rinsed with water (Millipore) and ethanol, and dried with nitrogen.

The stamps were inked with a few drops of solution of the G2-S in ethanol (10^{-5} M) and dried in a steam of nitrogen. After drying the stamps with nitrogen the stamps were placed manually on the substrate to achieve the conformal contact between the stamp and the substrate. The stamps were pressed slightly against the gold or glass surface at the initial stage of the printing to induce the formation of conformal contact.

An etching solution consisting of 10 mM Fe(NO₃)₃, 15 mM thiourea, and 1.2% HCl was used to etch the dendrimer-printed area on gold in (+) μ CP. For every experiment the freshly prepared etching solution was kept at 45 $^{\circ}$ C in a warm bath for 10 min before the samples were etched. The etching time was 2.2 min.

TRITC Printing. TRITC was printed on glass that was cleaned and activated by submersion in boiling piranha (2:1 mixture of sulfuric acid and hydrogen peroxide. **CAUTION! Piranha solutions should be handled with great care in open containers in a fume hood. Piranha is highly corrosive and toxic and potentially explosive.**) Stamps were inked by submersion in the solution of TRITC (0.1 mM) in ultrapure water (resistivity $> 18.2 \text{ M}\Omega\cdot\text{cm}$) for 15 min. Prior to printing, they were rinsed briefly with ultrapure water and dried in a stream of nitrogen. The glass substrates were contacted with the TRITC-inked stamps for approximately 2 min.

Measurements. Contact angles were measured on a Krüss G10 contact angle setup equipped with a CCD camera. Advancing and receding contact angles were determined automatically during growth and reduction of a clean water droplet by the droplet shape analysis routine.

XPS measurements were performed on a Quantera Scanning X-ray Multiprobe instrument from Physical Electronics, equipped with a monochromatic Al K α X-ray source producing approximately 25 W of X-ray power. XPS data were collected from a surface area of $1000 \text{ pm} \times 300 \text{ pm}$ with a pass energy of 224 eV and a step energy of 0.8 eV for survey scans and 0.25 eV for element scans with an equal number of sweep for all elements. Spectra were referenced to the main C 1s peak set at 284.0 eV.

AFM analyses were carried out with a NanoScope (Veeco/Digital Instruments, Santa Barbara, CA) Multimode Atomic Force Microscope equipped with a J-scanner, in contact mode by using Si $_3$ N $_4$

cantilevers (Nanoprobes, Veeco/Digital Instruments) with a nominal spring constant of about 0.32 Nm^{-1} . AFM imaging was performed at ambient conditions.

Fluorescence microscopy was performed using an Olympus inverted research microscope (IX71) equipped with a mercury burner (U-RFL-T) as light source and a digital camera (Olympus DP70, 12.5 million-pixel cooled digital color camera) for image acquisition. Red emission light ($\lambda > 590 \text{ nm}$) was filtered using a U-MWG Olympus filter cube.

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Supporting Information Available: Water contact angle results and AFM images of the PFDTS-modified PDMS surface after the second exposure to oxygen plasma, SEM image of the gold patterns printed by bifunctional flat PDMS stamps that has been kept for 1 month. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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