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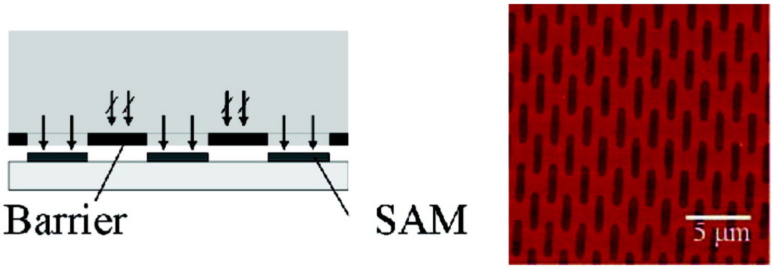

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Chemically Patterned Flat Stamps for Microcontact Printing

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Abstract: Locally oxidized patterns on flat poly(dimethylsiloxane) stamps for microcontact printing were used as a platform for the transfer of a hydrophilic fluorescent ink to a glass substrate. The contrast was found to be limited. These locally oxidized patterns were conversely used as barriers for the transfer of hydrophobic *n*-octadecanethiol. In this case a good contrast was obtained, but the pattern was found to be susceptible to defects (cracks) in the barrier layer. Local stamp surface oxidation and subsequent modification with 1H,1H,2H,2H-perfluorodecyltrichlorosilane, for use as a barrier in the transfer of *n*-octadecanethiol, 16-mercaptohexadecanoic acid, and octanethiol, resulted in remarkably good contrast and stable patterns. The improved ink transfer control is ascribed to the reduction of undesired surface spreading and a superior mechanical stability of the stamp pattern. This new approach substantially expands the applicability of microcontact printing and provides a tool for the faithful reproduction of even extremely low filling ratio patterns.

Introduction

Since the first reports on microcontact printing (μCP) in 1993, it has proven to be a very versatile technique for the parallel generation of patterns with (sub)micrometer-sized critical dimensions.[1] In conventional microcontact printing, a soft 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 most applications these ink molecules are chosen to form a patterned self-assembled monolayer (SAM) in the contact regions of the target surface. Because of the relief of the stamp, the contact areas are separated by void regions. Whereas the stamp material combines the functions of ink transport medium and ink reservoir, and provides mechanical stability to the whole, the voids should provide a barrier for ink transport to the noncontact areas (Figure 1a). The efficacy of this barrier, however, depends strongly on the ink that is being used.[2] A high surface- and/or gas-phase mobility of the ink molecules typically results in a spreading of the ink to the noncontact areas and/or the loss of contrast.

An important limiting factor for a variety of applications of μCP is the low mechanical stability of the employed stamp.[3,4] In particular, the printing of low filling ratio patterns and the use of high-aspect-ratio stamp features suffer from a poor reproduction of the original design. In the case of low filling ratio patterns and extended featureless areas the stamp roof is prone to collapse under the printing pressure. This instability results in undesired contact of the recesses of the stamp with the substrate surface and thus in undesired ink transfer. The buckling of the protruding high-aspect-ratio features further limits the quality of the printing results.

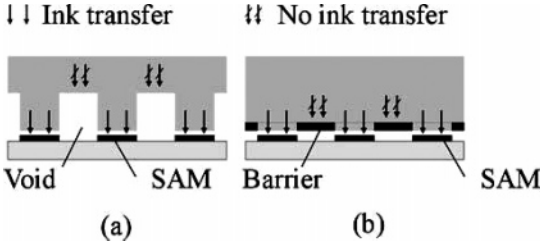

Figure 1. Schematic representation of ink transfer in μCP upon contact of a stamp with a relief structure (a) and of a flat stamp, which employs a thin-layer barrier integrated in the stamp surface (b).

Both the mechanical and the transport issues have been addressed in the literature, and solutions have been proposed that apply to a range of specific problems. Approaches to improve the mechanical stability of the stamp include the development of new stamp materials[5−7a] and composite stamps,[3,7b,c] establishing control over the applied pressure,[8,9] establishing

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rules for stamp design[4b,10] and “exotic” printing schemes such as positive μCP[11] and edge transfer lithography (ETL).[12] Approaches to gaining more control over the ink transfer process mainly focus on establishing rules for ink selection[2] and reducing the ink content of the printing medium (i.e., the stamp surface).[13,14]

The mechanical issues are a direct consequence of the inclusion of voids as the transport barriers. These voids, on the other hand, constitute poor transport barriers for certain inks such as those with a low molecular weight. A new transport barrier concept is therefore desired both to improve the mechanical stability of the stamp and to extend the range of applicable inks. Delamarche et al.[15] 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 hydrophilized areas by reaction with poly(ethylene oxide) silanes. These stamps have been used for the selective deposition and subsequent patterned transfer of proteins from the stamp surface, thus *without* the use of void barriers. Here we discuss how a flat piece of poly(dimethylsiloxane) (PDMS) can be chemically modified locally to create a stamp with a stable chemical pattern that still allows the transfer of ink molecules from the PDMS bulk reservoir (Figure 1b). The fabrication of such stamps comprises only two steps. In the first step, the PDMS surface is locally activated by oxidation through a contact mask, which consists of an impermeable material bearing openings in the shape of the desired pattern. In the second step, the activated areas are modified by reaction with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTS). The hydrophobic surface layer of exposed perfluoroalkyl groups reduces the interfacial energy, which stabilizes the pattern and provides a barrier for ink transfer. It is shown that these patterns can be used to transfer a diverse range of inks.

Experimental Section

Materials and Methods. The stamp material, Sylgard-184 poly(dimethylsiloxane) (PDMS), was obtained from Dow Corning. It was mixed in a 1:10 curing agent/prepolymer ratio and cured overnight at 60 °C. After curing, patterns were generated by exposure of the PDMS flat surface to a Tepla 300E microwave oxygen plasma (300 W, 0.25 mbar O$_2$) for 30 s, through a contact mask. Microsieves, which consist of a supported metal membrane permeated with micrometer-, or submicrometer-sized pores, were used as the masks. Different types of microsieves were purchased from Aquamarijn Micro Filtration B.V., The Netherlands (www.microfiltration.nl). 1H,1H,2H,2H−Perfluorodecyltrichlorosilane (PFDTS, purity 97%), as purchased from ABCR GmbH, was deposited for 30 min from its vapor phase onto locally oxidized PDMS. The stamp was thereafter cured in an oven for 3 h at 60 °C. PFDTS-modified stamps were used over the course of 6 months with identical results. 16-Mercaptohexadecanoic acid (MHDA, 90% purity), octadecanethiol (ODT, 98% purity) and octanethiol (OT, 98.5% purity) were purchased from Sigma-Aldrich, tetramethylrhodamine-5-(and-6)-isothiocyanate (TRITC) was obtained from Molecular Probes, Inc. All materials were used as received. Ink solutions were prepared by dissolution of MHDA, ODT, or OT in ethanol, and of TRITC in ultrapure water (resistivity > 18.2 M$\Omega\cdot$cm). Solutions with concentrations of 10 mM MHDA, 2 mM and 10 mM ODT, 1 mM OT, and 0.1 mM TRITC were used. Gold was deposited onto silicon for use as the substrate for the thiol inks (20 nm of sputtered gold on a 5-nm adhesion layer of sputtered titanium, on top of $\sim$250-nm thermal siliconoxide). Prior to use the substrates were rinsed with, successively, ultrapure water, ethanol, and heptane. Ethanol and heptane (both p.a. grade) were purchased from Merck. The gold substrates were exposed to a Tepla 300E microwave argon plasma (300 W, 0.25 mbar Ar) for 5 min immediately prior to use. TRITC was printed on glass which 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 applying a droplet of the appropriate thiol solution for 30 s, or by submersion in the TRITC solution for 15 min. Prior to printing they were rinsed briefly with neat ethanol or ultrapure water, respectively, and dried in a stream of nitrogen. Gold substrates were contacted with the thiol-inked stamps for times varying from 15 to 195 s and were subsequently etched prior to characterization. The glass substrates were contacted with the TRITC-inked stamps for approximately 2 min. A standard thiosulfate-based etch bath, to which octanol was added to decrease the sensitivity for pinholes, was used.[16,17]

Characterization. Optical and atomic force microscopy (AFM) images were taken of etched patterns. For AFM characterization, a Veeco “MultiMode Scanning Probe Microscope” was used in conjunction with a “Nanoscope IIIa” controller. The AFM was operated in contact mode (cm-AFM). Fluorescence was detected using a Zeiss LSM 510 confocal scanning microscope at an excitation wavelength of 543 nm.

Software for Analysis Images were analyzed using “ImageJ”, a public domain image processing program by the U.S. National Institutes of Health (NIH),[18] and Nanotec’s “WSxM” a freeware data acquisition and processing program for scanning probe microscopy (SPM).[19]

Results and Discussion

Transfer of Polar Ink from Hydrophilic Patches. Currently, PDMS is the most frequently used stamp material for μCP. A wide body of literature is testament to its excellent ink transfer properties in conjunction with apolar inks, such as alkanethiols. Due to its hydrophobicity, however, it is deemed incompatible with more polar inks. A common strategy to bypass this problem is to oxidize the PDMS surface, rendering it hydrophilic.[20−22] This suggests that a flat piece of PDMS, when locally oxidized to create a surface oxide pattern, may be suitable for a controlled transfer of hydrophilic inks from the surface oxide pattern to the substrate.[15] In this case the non-oxidized parts of the stamp would constitute the transport barriers. To test this hypothesis, the hydrophilic and fluorescent tetramethylrhodamine-5-(and-6)-isothiocyanate (TRITC) was used as an easily traceable ink. A pattern of hydrophilic dots measuring approximately 500 nm in diameter and arranged in mutually perpendicular bundles of

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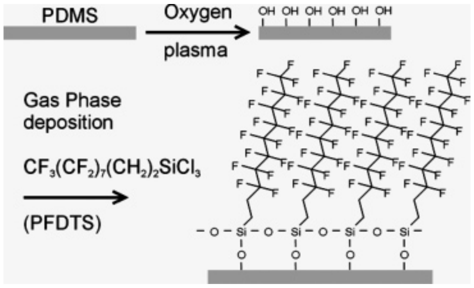

Figure 2. Schematic description of chemical barrier formation. PDMS is locally activated by oxidation. Oxidized PDMS itself is active in either expediting or blocking ink transfer (dependent on the choice of ink). A more stable and versatile, optional modification is the subsequent covalent attachment of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTS).

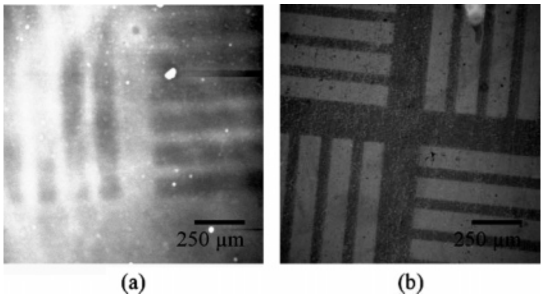

Figure 3. Fluorescence micrographs of a flat piece of PDMS, patterned with oxidized patches arranged in stripes and inked with the hydrophilic, fluorescent ink TRITC (a) and the ink pattern as transferred from this stamp to a glass substrate (b). Images a and b show different areas of the pattern. Although the ink was predominantly transferred from the hydrophilic patches, a background is clearly visible, originating from the nonmodified areas. Within the stripes itself, due to lack of contrast, the pattern is no longer discernible.

parallel ribbons, was created on a flat piece of PDMS by local oxidation through a contact mask (Figures 2 and 3). Inspection of the inked stamp using fluorescence microscopy revealed a pattern, which appeared blurred and showed lower fluorescence intensity in the oxidized areas than in the nonoxidized areas (Figure 3a). The pattern that was transferred using this stamp to a glass substrate showed an inverse intensity profile. This pattern also had a sharper appearance (Figure 3b). The pattern as shown in Figure 3b indicates a preferred transfer of TRITC molecules from the oxidized areas, presumably due to a higher surface concentration on the stamp in these areas. This concentration was apparently high enough to induce self-quenching, which can explain the inverted fluorescence pattern of the inked stamp prior to printing.[23] There was, however, also TRITC present on the nonmodified stamp areas, which caused the less quenched fluorescence in the nonoxidized areas. The lateral density differences (possibly owing to multilayer presence) on the stamp surface account for the blurred, blotchy appearance. The resulting lack of contrast causes the original pattern within the ribbons (the dot array) to be indiscernible even in the transferred pattern, in which the ink concentration at any location is lower than on the stamp.

Clearly, nonmodified PDMS is still capable of transferring some quantity of TRITC, and this is likely to hold true for other polar inks as well. When using oxidized PDMS as the ink transfer medium for polar inks, the spatial selectivity will therefore be limited. Another inherent disadvantage of using the oxidized PDMS as transfer medium is that, although the surface becomes compatible with polar inks, it is highly unlikely that these inks will be able to penetrate the bulk of the stamp, and therefore, the amount of available ink in this reservoir will conceivably be rather small. Since the surface of the stamp can have such a large impact on the ink transport behavior, however, it can be reasoned conversely that oxidized PDMS (whereas it *allows* transfer of *polar inks*) can constitute a *barrier* for the transfer of *apolar inks*.

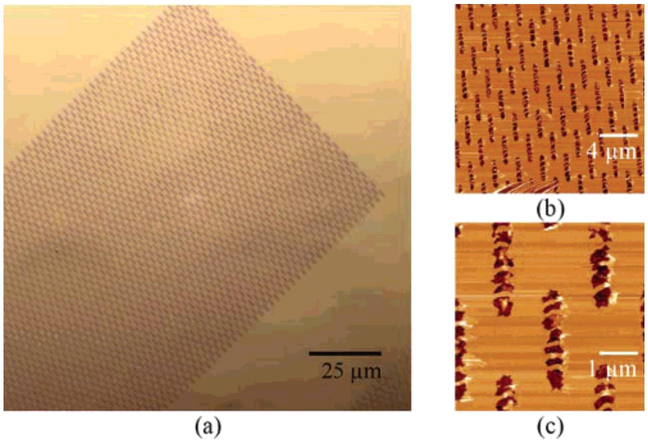

Figure 4. Optical micrograph of gold samples after printing of ODT with a locally oxidized flat PDMS stamp and subsequent wet etching (a). Individual holes within a ribbon are clearly distinguishable. Contact mode AFM micrographs of the same sample (b and c). Fine horizontal gold lines appear as light stripes crossing the ellipsoidal dark (etched) areas, about 3 × 0.6 μm^2.

Blocking of Apolar Ink Transport by Hydrophilic Patches. On a flat piece of PDMS, a hydrophilic pattern of oxidized areas was created by its exposure, through a contact mask, to an oxygen plasma. The mask consisted of narrow slits, measuring approximately 3 μm in length and 600 nm across. Apolar *n*-octadecanethiol (ODT) was used to ink the stamp, since the hydrophobic thiol was expected to be incompatible with the hydrophilic oxide barrier. The selectivity of the ink transfer with this stamp can be deduced from the patterns observed on printed and subsequently etched gold samples (Figure 4). The individual holes within the ribbons are clearly distinguishable using optical microscopy, and the contrast appears to be good. Upon closer inspection using AFM, however, the individual holes were found to be interspersed with almost parallel lines of intact gold (Figure 4b and c). The morphology of these lines (regarding regularity and anisotropy) indicates that they are a result of ink transport at the location of stress-induced cracks in the brittle, silica-like, oxidized PDMS layer. Stress may result from mechanical deformation (externally applied stress) or from compression of the surface upon oxidation.

The orientation of the lines is nearly in registry across the different holes. Hillborg et al. showed that PDMS remains smooth and crack-free over large areas upon oxidation in microwave plasma, in the absence of mechanical handling.[24] It can therefore be assumed that the cracks are caused by the mechanical handling of the stamps.

PFDTS as Ink Transfer Barrier. Oxidized PDMS has been shown to constitute a good barrier to ink transport; however, some problems are to be expected when using oxidized PDMS

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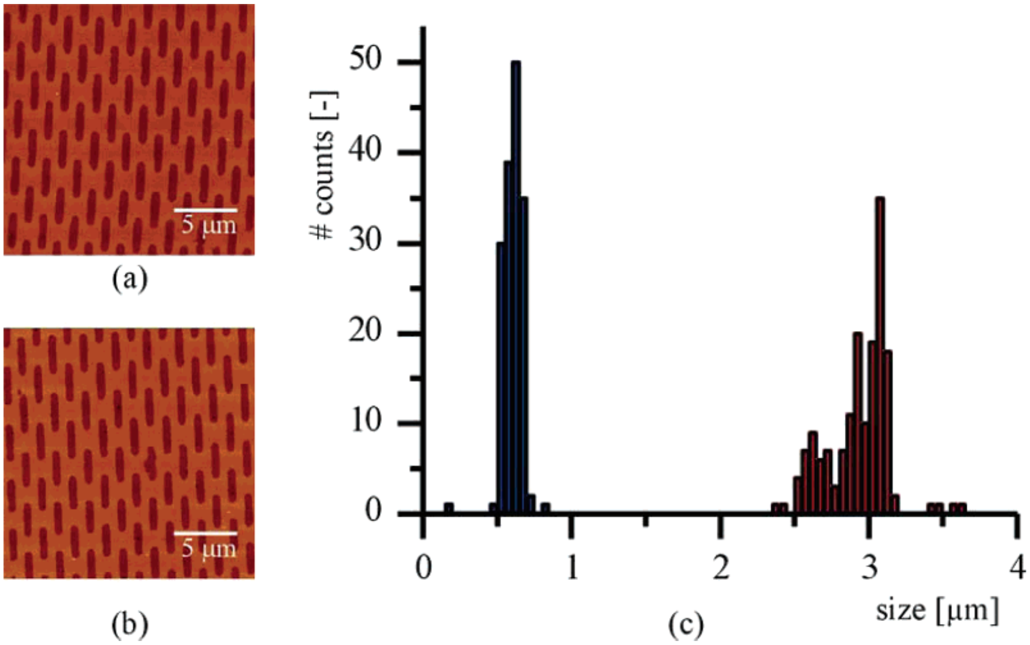

Figure 5. cm-AFM images of etched gold, which were patterned using ODT (a) or MHDA (b) transferred from PFDTS-modified, patterned flat stamps. Panel (c) shows the distribution of the widths and lengths of the holes measured over several samples and using both inks. The contact time was 1 min.

as a template for patterning. Polymer chains at the PDMS surface are reported to have a high mobility.[25] To minimize the surface free energy, sidegroups can be reoriented toward or away from the surface, depending on the external medium. Furthermore, PDMS is suspected to contain mobile, low-molecular weight and noncross-linked PDMS fragments that are able to permeate to the surface.[26,27] Both mechanisms are held responsible for a phenomenon known as hydrophobic recovery,[27] which describes the observation that an oxidized PDMS surface is unstable in ambient air and becomes increasingly apolar over time. The interfacial free energy is a strong driving force for this process, as can be inferred from the fact that oxidized PDMS is stable during storage in water.[27b]

To prevent loss of contrast due to hydrophobic recovery, the oxidized areas were modified by exposure to 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTS). PFDTS, when attached to oxidized PDMS, is reported to have a surface free energy as low as 12.7×10^{-3} J/m^2, as determined from contact angle measurements using hexadecane.[28] In the same study it was found that a methyl-terminated monolayer (undecyltrichlorosilane) on oxidized PDMS has a surface free energy of 22.0×10^{-3} J/m^2. This indicates that adsorption of aliphatic molecules (such as alkanethiols) is likely to increase the surface free energy of a PFDTS surface. Since that would be thermodynamically unfavorable, PFDTS, although hydrophobic, may be expected to repel apolar as well as polar alkanethiols and thus to constitute a versatile barrier layer. A schematic of the PFDTS attachment to PDMS is shown in Figure 2.

PFDTS-modified flat PDMS stamps were used to transfer patterns of ODT, MHDA, and OT to gold substrates. Ink was applied freshly on stamps which had been prepared up to 6 months earlier. The quality of etched substrates was identical for the ODT and MHDA patterns (Figure 5) and was found to be independent of the age of the stamp. The same stamp was used up to 10 times without impairing the results. The distribution of the dimensional sizes (length and width) of the holes closely matched the manufacturer's specifications of the mask that was used for selective oxidation, having an average width of 600 nm and a standard deviation of <100 nm. The frequency count presented in Figure 5c shows a broad peak for the hole length, with a tail toward smaller sizes, which is likely to be a result of the mask fabrication. Even with a contact time as long as one minute virtually no increase of the pattern size was observed when using either MHDA or ODT. In both cases a high etch contrast was retained. This result is specifically remarkable for MHDA. The used high ink concentration (10 mM) is known to be a prerequisite for proper packing and etch resistance.[29] It is, however, also known to result in significant spreading during contact using relief stamps. It can be estimated that 1 min of contact with a relief stamp, inked with 10 mM MHDA, results in approximately 2 μm lateral growth of the SAM pattern, which would have resulted in the disappearance of 600-nm wide holes. This indicates that the PFDTS barrier layer prevents spreading of the MHDA ink on the substrate suface more effectively than a standard ambient air (void) barrier.

In the AFM images, the stripes across the holes that marked cracks in the oxidized PDMS layer (Figure 4) were not observed, even though no special precautions were taken to avoid mechanical deformation. Because the handling of PFDTS-treated and untreated oxidized PDMS stamps was identical, it can be assumed that cracks are present in both types of stamps. The PFDTS modification, however, appears to inhibit ink penetration through those channels effectively. Possibly the cracks get sealed due to steric constraints imposed by the additional layer. More

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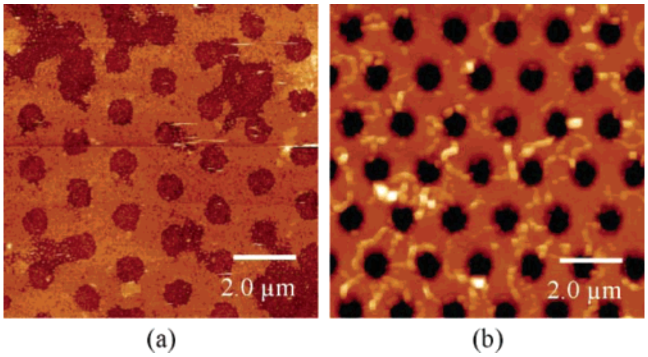

Figure 6. cm-AFM image of an etched gold substrate that was patterned with OT using a PFDTS-modified flat stamp (a), and a cm-AFM image of the microsieve that was used as oxidation mask for the stamp modification (b).

likely the PFDTS layer lowers the surface energy on the crack edges sufficiently to prevent preorganization of the ink on the surface of these edges, which is thought to be a prerequisite for ink transfer in ink/stamp systems with low mutual affinity.[29] Preferential preorganization on stamp edges and the necessity of surface ink presence has been previously discussed for low concentrations of MHDA in PDMS.[29]

The results for OT patterning with a PFDTS-modified flat stamp, at first glance, seem less impressive (Figure 6). The used stamp was oxidized locally using the same mask as used for the earlier TRITC experiments (an array of 500-nm dots). A significant number of defects in the printed and subsequently etched gold substrate and a poorer contrast are indicative of the expected low etch resistance of the very thin OT monolayer and the high mobility of the OT molecules. Comparison with the cm-AFM image of the mask, which was used for selective stamp oxidation, nevertheless reveals that the demarcation of the modified areas closely follows the dimensions of the pores in the mask. The occurrence of some large overetch defects, i.e., insufficiently protected gold areas (Figure 6a), suggests undesired fluorination of corresponding regions of the stamp surface. These areas were most probably activated during the plasma treatment step, which in turn indicates incomplete contact between mask and stamp. As expected a lower contrast was observed with OT than with ODT as the ink. OT bears only a short alkyl chain and the intermolecular van der Waals attraction is comparably small. For alkyl chains shorter than nine methylene groups this attraction is insufficient for achieving two-dimensional crystallization, which results in a poor etch resistance.[17,30−32] Due to their low molecular mass, short-chain alkanethiols also exhibit relatively large vapor pressures. Therefore, no direct contact between stamp and surface is necessary for thiol transfer. For example, Delamarche et al., showed that a contact time of 20 s with a dodecanethiol-inked stamp was sufficient to annihilate contrast in a relief stamped pattern with 600 nm wide holes, even though the used ink concentration was as low as 0.5 mM.[2] In the case of a flat stamp, gas-phase transport is impossible when the patterned stamp is in contact with the substrate. Only in the instances just before and after contact may some ink be transferred. It is, furthermore, feasible that, in contrast to ODT and MHDA, the smaller OT molecules are more likely to penetrate the PFDTS barrier layer, which during contact constitutes not a PFDTS/air interface anymore, but a PFDTS/gold interface with a different interfacial energy. Despite these shortcomings of the OT ink, the mere observation of a contrast in etched substrates is remarkable when considering that dodecanethiol, bearing an even longer alkyl chain, proved to be an unsuitable ink for use with a conventional relief stamp.[2]

Table 1. Overview of Various Traditional Printing Techniques and Their Soft-Lithographic Analogues[a]

printing	soft lithography
flexography (relief printing)	microcontact printing
intaglio printing	printing from microcontainers or microwells
screen printing	printing through openings in a membrane
electrophotography (Xerography)	charge patterning in thin organic films
(stone-) lithography	*chemically patterned stamps*

[a] Offset printing may be included by using a nonfunctional elastomeric flat stamp as an intermediate for pattern transfer with any of the listed analogues.

In Table 1, a short overview (adapted from B. Michel et al. *IBM J. Res. Dev.* **2001**, *45*, 697−719) is presented of known soft-lithography analogues to traditional printing techniques. Until now, an analogue for (stone-)lithography,[33] the namesake to all modern high-resolution printing, has not been reported. The here described PDMS modification is a veritable lithography analogue making use of hydrophilic/hydrophobic interactions to organize the ink within the contact plane. In keeping with traditional lithography, it allows the progressive addition of patterned structures on the same stamp by stepwise modification of pristine areas. Stretching the metaphor, this would enable complex patterning schemes involving even multiple inks (color printing analogue). In successive prints the presence of the pattern on the substrate that is transferred in a previous step is likely to block further transfer of ink in those regions. In such a color printing analogue (successive prints using different inks in each step), it is therefore feasible that the same stamp may be used onto which in situ additional pattern features are written, which would simplify alignment issues.

Since the concept of chemical patterning is independent of the here-proposed method, better results may be obtained when using more dedicated instruments. Stamps with a higher resolution may, for instance, be obtained by using a focused ion beam to create a surface pattern of activated stamp areas in a sequential writing process. This approach may prove valuable as the basis of a direct-write stamp production process, which would liberate soft lithography from the dependence on time-consuming and expensive master fabrication.[34,35] It is clear that chemical patterning of PDMS offers far more possibilities than can be discussed here.

Conclusions

The problem of mechanical instability and poor barrier properties of relief stamps for μCP was addressed by developing

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(30) Ulman, A. *Chem. Rev.* **1996,** *96*, 1533−1554.
(31) Larsen, N. B.; Biebuyck, H.; Delamarche, E.; Michel, B. *J. Am. Chem. Soc.* **1997**, *119*, 3017−3026.
(32) Schreiber, F. *Prog. Surf. Sci.* **2000**, *65*, 151−256.
(33) The process of printing from a plane surface (e.g., a smooth stone) on which the image to be printed is made ink-receptive, and the blank area, ink-repellent. (Stone-)lithography was invented in 1796 by German playwright Alois Senefelder.
(34) Grzybowski, B. A.; Haag, R.; Bowden, N.; Whitesides, G. M. *Anal. Chem.* **1998**, *70*, 4645−4652.
(35) Zilch, L. W. et al. *Rev. Sci. Instrum.* **2004,** *75*, 3065−3067.

new stamp designs. Local oxidation of flat PDMS stamps and their subsequent modification with perfluoroalkyl groups has been shown to be an effective route to solve these problems without compromising intrinsic advantages of the technique, which include ease of use and the potential for a high cost efficiency. The developed flat stamp design has the potential to even increase the flexibility of the patterning technique, since it allows the use of ink molecules that have so far been considered unsuitable because of their high surface-spreading tendencies.

Locally oxidized PDMS alone has been shown to differ too little from nonmodified PDMS to allow high-contrast transfer of a polar ink, such as TRITC. It has, however, been shown to be an excellent barrier to transfer of apolar alkanethiols such as ODT. The local modification of oxidized surface areas with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFDTS) extends the barrier functionality lifetime to more than 6 months, while blocking the transfer of alkanethiols with apolar (OT and ODT) as well as polar headgroups (MHDA).

In terms of ink-blocking properties, the example of octanethiol patterning shows that a high mobility of the ink (through air and/or through the PFDTS layer) may still pose a problem for some ink types in view of an observed loss of contrast. Moreover, considering the large number of ink types and their differing properties used in soft lithography, it appears unrealistic to wish for a single universal barrier layer. The concept of chemical modification, however, offers a flexible toolbox for the development of optimized barriers for individual inks and offers great potential for new stamp replication processes to make microcontact printing even simpler to use.

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Supporting Information Available: Complete refs 4a and 35. This material is available free of charge via the Internet at http://pubs.acs.org.

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