NANO LETTERS

2006
Vol. 6, No. 6
1235−1239

Edge Transfer Lithography Using Alkanethiol Inks

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Received April 6, 2006

ABSTRACT

Edge lithographic patterning techniques are based on the utilization of the edges of micrometer-sized template features for the reproduction of submicrometer structures. Edge transfer lithography (ETL) permits local surface modification in a single step by depositing self-assembled monolayers onto a metal substrate selectively along the feature edges of an elastomeric stamp. In this report two stamp designs are described that now allow for the use of alkanethiol inks in ETL and their use as etch resists to reproduce submicrometer structures in gold. Anisotropically modified stamps are shown to combine the potential for very high-resolution patterning with the versatility and simplicity of microcontact printing.

The demand for ever-increasing miniaturization critically depends on fabrication methods of ever-increasing complexity and cost. The development of soft-lithographic patterning techniques counters this trend, to some extent, by removing the need for cleanroom facilities.[1,2] Specifically microcontact printing (μCP) is a potentially cheap, easy, and versatile representative of the soft lithography family that has received much attention in recent years.[1−4] Nevertheless, with decreasing feature sizes, ever more challenging demands are posed specifically upon the mechanical properties of soft lithography masks (stamps), which have to be met by materials that are by definition soft and flexible.[2,5−16] Consequently, considerable research effort is being directed into using micrometer-sized mask features for the creation of even submicrometer patterns. This approach allows for taking advantage of the inherently favorable mechanical properties and the ease of mask fabrication and handling of such mask designs. Edge lithography encompasses a host of techniques that utilize the edges of larger pattern features to determine the resultant much smaller structures. Examples include near-field phase-shifting photolithography, topographically directed etching, edge transfer lithography, and controlled undercutting.[17−22] Within this set of edge lithography techniques, edge transfer lithography (ETL) takes a special place, as it offers the possibility of local *chemical* surface modification (as opposed to mere topographical surface alteration) in a single step (as opposed to the multistep techniques mentioned above). It is a technique that, conceptually, allows dynamic control over the transferred feature dimensions. In its original form, however, the latter cannot easily be realized because dynamic control over feature sizes implies ink mobility and thus the difficulty to confine the ink to the recessed areas of the soft lithographic stamp, which is a key step in the ETL process.[21] Notably the system of alkanethiol patterns on gold, which is the most extensively studied system, is deemed incompatible with ETL. Nevertheless, there exists a strong desire to overcome this limitation, which is mirrored in a recent advance in edge lithography named edge-spreading lithography (ESL).[23−25] It addresses this problem by decoupling the ink source from a relief structure that acts as the physical guide for the ink. This decoupling, however, renders the technique a multistep technique once again and relies on a prepatterning step that in the worst case demands cleanroom facilities, thereby negating the advantages of soft lithography.

Here we report on two successful approaches to extending the use of ETL to, but not limited to, alkanethiol inks without the loss of the inherent advantages of soft lithography and particularly those of μCP. The first approach addresses the incompatibility of alkanethiol inks with the earlier described ETL system due to the high ink mobility in the poly(dimethylsiloxane) (PDMS) stamp material. The second

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10.1021/nl0607885 CCC: $33.50
Published on Web 05/04/2006

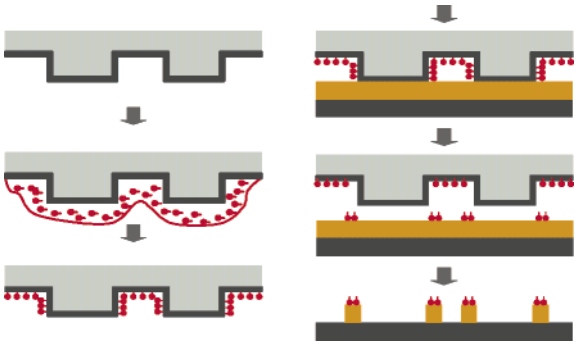

Figure 1. Scheme of an ETL process that employs a surface-modified elastomeric stamp (gray) rendered impermeable and repellent to the applied ink by an applied surface barrier layer (black). The molecules of the dried ink (red) accumulate in the recessed areas of the stamp pattern and are transferred to the substrate surface exclusively via the vertical edges of the elevated features. This initial surface pattern is transferred into the substrate gold layer (yellow) by wet-chemical etching.

approach also solves the problem of a limited ink reservoir, which is inherent to a patterning scheme relying on ink deposition exclusively onto and from the stamp surface.

Recently, we demonstrated a versatile entry to PDMS surface modification, with the specific aim of making it impervious to a variety of inks.[26] Here we show that this approach can be put to use to the problem of ETL with good result, hereby opening ETL to a host of different inks and allowing feature size control while retaining all the positive attributes of soft lithography. Figure 1 summarizes the principle of this first improved ETL method. The key step is the modification of the stamp surface that renders it impermeable and repellent to the applied ink. The ink molecules thus accumulate in the recessed area, from where they are transferred to the substrate along the edges of the elevated features.

An effective seal against various inks can be created by surface oxidation of PDMS followed by covalent attachment of 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (PFDTS).[26] With use of such a stamp that was inked by immersion in an ethanolic *n*-octadecanethiol ink solution prior to printing onto gold substrates, no etch protection was observed by optical microscopy. This indicates that ink was indeed repelled from the contact areas and replenishment from the bulk was prevented. There were, however, also no edge structures observed. When a stamp that was inked by applying the ink solution directly onto its surface was allowed to dry, with its feature side pointing upward in order to ensure an ink presence on its surface, etch protection was only conveyed in those regions, in which the recessed areas of the stamp had unintentionally contacted the substrate due to roof collapse of the microstructures.[9,10] Again, no edge structures were observed.

It is important to note that instrumental to the properties of the PFDTS layer is its low surface energy ($\gamma_{PFDTS} = 12.7 \times 10^{-3}$ J/m^2).[27] The ink that was used, *n*-octadecanethiol (ODT) was reported to have a higher surface energy ($\gamma_{ODT} = 22.0 \times 10^{-3}$ J/m^2).[27] Young's equation (eq 1) relates, assuming liquid behavior of ODT, the surface energies and

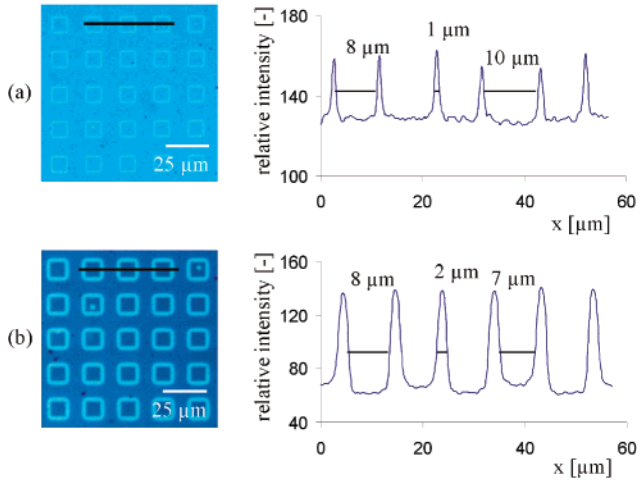

Figure 2. Optical micrographs of gold samples after printing with a surface-inked (ODT, 10 mM solution in ethanol), oxidized PDMS stamp bearing a surface relief pattern and etching. The pattern in image (a) resulted after a contact time of 15 s. The average width of the edge structures is approximately 1 μm. The pattern in image (b) resulted after a contact time of 165 s. The average width of the edge structures is found to have increased to approximately 2 μm. The black lines indicate the trajectory of the measured intensity profile as displayed in the graphs adjacent to the micrographs.

an interfacial energy through the contact angle θ_{eq}. From eq 1, it follows the likelihood that ODT, due to the very low surface energy of PFDTS, dewets the PFDTS layer ($\theta_{eq} > 90°$, i.e., $\gamma_{Interface} > 12.7 \times 10^{-3}$ J/m^2) and, therefore, does not spontaneously migrate along the stamp edges.

$$\gamma_{PFDTS} = \gamma_{Interface} + \gamma_{ODT} \cos(\theta_{eq}) \qquad (1)$$

A feasible ETL scheme, therefore, calls for a surface energy of the passivating layer that is sufficiently high, in addition to a negligible contribution of ink from the bulk of the stamp.

Another convenient route to create a transfer barrier, specifically for hydrophobic inks such as ODT, is the mere oxidation of the PDMS surface without further postprocessing.[26] Oxidized PDMS is thought to have a relatively high surface free energy. Because of hydrophobic recovery, i.e., the spontaneous reverting, from hydrophilic to hydrophobic, of an oxidized surface, its surface free energy cannot be determined accurately.[28,29] From measurements on hydroxyl-terminated monolayers that are tethered on PDMS, however, it can be estimated to be larger than 53×10^{-3} J/m^2.[30] Moreover, oxidized PDMS may be expected to allow spreading of ODT across their surfaces, judging from the fact that silica beads are used as physical guides in an existing ESL scheme.[23]

Indeed edge structures could be obtained using plasma oxidation of PDMS stamps to create a barrier layer (Figure 2). Structures were obtained over the full surface area of 1 $\times$ 2 cm^2 gold substrates and for different shapes and sizes of the contact areas (not shown). Oxidation of PDMS renders its surface silica-like and brittle. Cracks in this blocking layer can constitute ducts for ink transport and impair the results of the ETL process.[26] This, however, could be largely

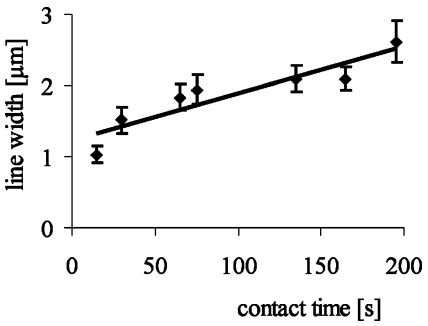

Figure 3. Contact time dependence of the size of the surface structures created on gold substrates by ETL and wet-chemical etching, as determined by optical microscopy. A 10 mM ODT ink solution was used to ink the used surface-oxidized PDMS relief stamps.

avoided by careful handling of the stamps and by using a rigid glass support for the stamp to limit deformation during manipulation.

Figure 2 shows the lines circumscribing square 10 × 10 μm^2 filled stamp features as observed after printing and etching of the gold substrates. The widths of the edge features could be controlled by varying the contact times between stamp and substrate (Figure 3). Although the inner diameter of the etched square frames remained constant, the distance between them decreased upon an increase of contact time as a result of increasing edge widths (Figure 2). This indicates that spreading indeed is directed from the edges of the contacted features outward into the noncontacted areas. To the best of our knowledge, this is the first time that control over ETL feature sizes by means of controlling the contact time is demonstrated.

The observation of an ETL feature width of 1 μm obtained after 15 s of contact and the requirement for another 150 s of contact for the growth of an additional feature width of 1 μm indicate an onset in edge width. This is consistent with observations of McLellan et al. who interpret this onset in terms of the diffusion front of ODT being fluidlike.[23] They identified the ink concentration to be a key parameter in decreasing this onset and for increasing control over the feature width.

An important disadvantage of the above ETL technique is the restriction to inks that are compatible with the modified stamp surface, from which they should not dewet. Furthermore, the amount of ink available at the stamp surface is limited by the size of the recessed feature areas, which serve as the ink reservoir. In contrast, in conventional μCP, the ink reservoir is formed by the bulk of the stamp. This much bigger reservoir allows for a large number of prints without the need for reinking and makes the ink transfer independent of the geometry of the surface pattern.

To combine these beneficial ink transfer properties of conventional μCP with the high resolution of ETL, we have now developed stamps that are suitable for the selective edge transfer of ink molecules ultimately from the bulk of the stamp material. Such stamps comprise a blocking layer only on their horizontal surfaces, those that are coplanar with the substrate surface (Figure 4).[31,32] For this purpose, we

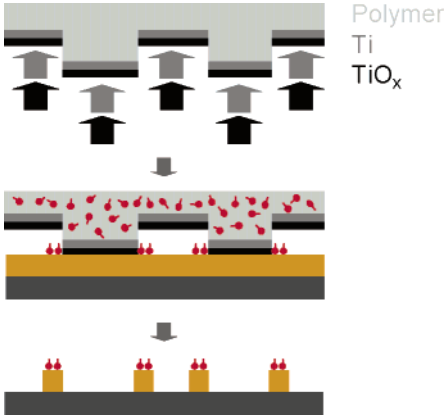

Figure 4. ETL with anisotropically modified stamps and etching. Only the horizontal layers of the stamp, those that are coplanar with the substrate surface, are covered with an ink-blocking TiO_x layer deposited by anisotropic ($\alpha = 90°$) evaporation in the presence of oxygen. A titanium layer may be deposited underneath this top layer. Ink molecules (red) are transferred selectively from the bulk of the inked stamp to the gold substrate (yellow) along the unmodified edges of the elevated stamp features.

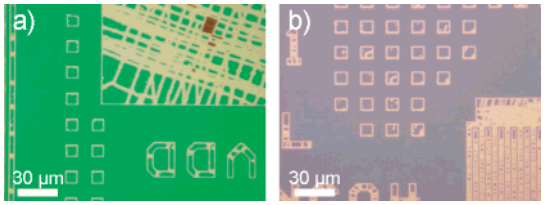

Figure 5. Optical micrograph of gold substrates (10 nm thick gold layer) after printing (15 s contact time) with an ODT-inked, anisotropically modified PDMS stamp bearing a surface relief pattern and etching. The PDMS stamp was oxidized isotropically in an oxygen plasma prior to the deposition of a 10 nm thick layer of titanium oxide selectively onto the feature areas that were oriented coplanar with the substrate surface. Stamps were inked by immersion into the ink solution for 1 h (a) or by contact inking from the backside with an ink-loaded flat PDMS stamp for 12 h (b) followed by drying in the ambient (4 h).

considered anisotropically deposited titanium to constitute a suitable barrier, due to its generally good adhesion to polymer surfaces.[33−37] To minimize undesired interactions of the evaporated titanium barrier layer with the thiol ink on one hand and with the gold surface of the substrate on the other hand, a titanium oxide layer was formed as a top coat either by surface oxidation of the deposited titanium layer with an oxygen plasma or by anisotropic titanium deposition in the presence of oxygen. Depending on the stamp material, the initial deposition of a titanium layer could even be omitted without compromising the final printing results. A pretreatment of the polymeric stamp surface with an oxygen plasma was found to be important for a good adhesion to the titanium-based barrier layer. Remarkably, the isotropic nature of the initial plasma treatment did not affect the ink transfer properties of the final stamp, probably due to a sufficiently fast (<24 h) hydrophobic recovery of the vertical surfaces of the stamp pattern.[28,29]

Figure 5a displays a micrograph of an etched gold substrate that was printed with a so modified PDMS stamp, after immersion inking in an ODT solution and subsequent surface

rinsing and drying. The elevated bright gold lines in the substrate pattern circumscribe the original contact areas of the elevated square stamp features, indicating selective ink transfer from the vertical walls of the stamp pattern onto the gold substrate. Particularly in the larger contact areas, ink transfer was not entirely restricted to the edges, which is again ascribed to the stress-induced formation of cracks in the brittle barrier layer thereby opening an undesired additional path for ink transfer from the bulk reservoir.[26] In an attempt to reduce the mechanical stress imposed onto the barrier layer due to the swelling of the stamp material during immersion inking and the subsequent crimping upon solvent evaporation, stamps were inked by contacting them on their flat backside with a dry, flat, ink-loaded PDMS stamp overnight.[38,39] This inking procedure was unfortunately found not to improve the print quality significantly (Figure 5b); the experiment, nevertheless, proves that the PDMS bulk serves as the ink reservoir. Crack formation thus appears to result mainly from the stress induced by the mechanical handling of the stamps, as already discussed for the above-described ETL scheme. The introduction of a buffering, more ductile gold layer sandwiched between the titanium layer and the top titanium oxide coating did, however, not result in a significant reduction of the number of crack-induced print defects.

A significant improvement of the pattern quality was achieved by substituting the regular PDMS stamp material (Sylgard 184, $E = 1.8$ MPa)[40] with hard PDMS, which has a higher Young's modulus ($E = 15-20$ mPa),[6] or even better with poly(butylene terephthalate-*co*-tetra(methylene oxide)) (PEE, Arnitel EM400, $E = 50$ MPa),[41] which provides a matrix with a very similar ODT compatibility when compared to regular PDMS ($c_{stamp}/c_{solution}$(PEE) = 0.71 (Figure S1), $c_{stamp}/c_{solution}$(PDMS) = 0.86).[42] With an anisotropically modified PEE stamp bearing a titanium/titanium oxide barrier layer stack, essentially defect-free ETL patterns could be transferred onto gold substrates for contact areas not exceeding some 10 μm in diameter (Figure 6). The average line width (fwhm) obtained upon 5 s of stamp−substrate contact and etching was determined to be 0.35 ± 0.15 μm by atomic force microscopy. As expected, increasing stamp−substrate contact times resulted in a linear increase of the obtained feature width yielding 1.57 ± 0.15 μm wide lines upon 120 s of contact (Figure S2).

In summary, it has been demonstrated that ETL can be extended to incorporate the use of mobile inks, such as octadecanethiol, given a proper stamp design. Key parameters of a patterning scheme that employs PDMS stamps bearing an isotropic silicon oxide blocking layer are the impermeability of this barrier, and the surface energy compatibility between the stamp surface and the ink. With this approach, large areas could be patterned in a single-step process with dynamic control over feature sizes. The applicability of the patterning scheme was further improved by introducing anisotropically modified PEE stamps, which even allow for taking advantage of the bulk material of the stamp as the ink reservoir, while still achieving a submicrometer resolution. The only concession made to the versatility of conventional μCP has been the need for careful handling of the stamp and, thus, the incorporation of a rigid support. This is, nevertheless, a small price to be paid for the possibility to print submicrometer structures with micrometer-sized stamp patterns.

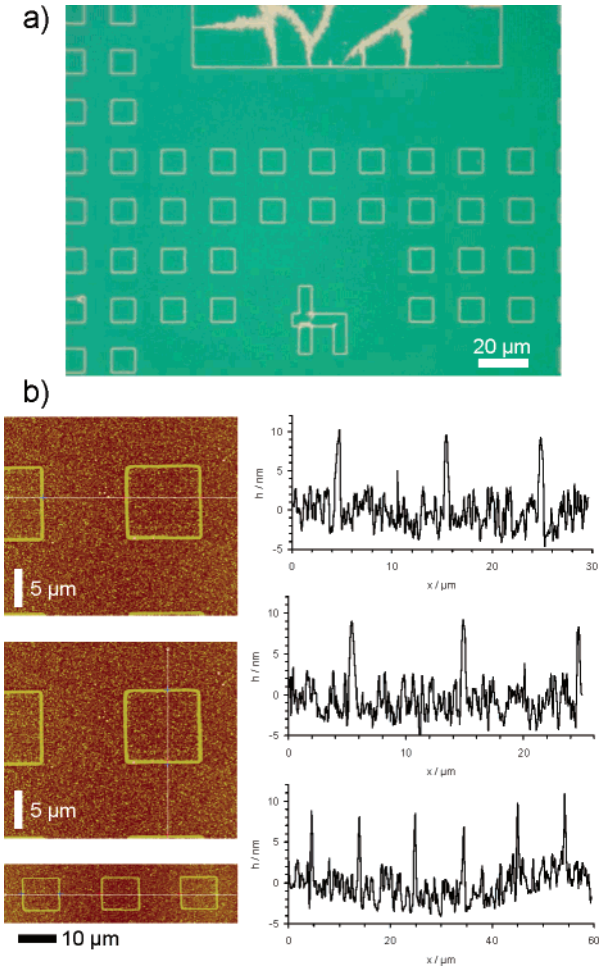

Figure 6. Optical micrograph (a) and AFM images and related height profiles (b) of gold substrates (10 nm thick gold layer) after printing (5 s contact time) with an ODT-inked (immersion in 10 mM ODT solution in ethanol and drying), anisotropically modified PEE stamp bearing a surface relief pattern, and etching. The PEE stamp was oxidized isotropically in an oxygen plasma prior to the deposition of a 10 nm thick layer of titanium selectively onto the feature areas that were oriented coplanar with the substrate surface. A top titanium oxide layer was created by exposure to an oxygen plasma. The average line width of the developed gold pattern was 350 ± 150 nm.

Acknowledgment. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM, financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and Philips Research). The presented work has been carried out as part of the "Lab Zonder Muren" program, partly at Philips Research Eindhoven, The Netherlands. R.S. and B.T. gratefully acknowledge the hospitality of the group "Bio-Molecular Engineering". The authors furthermore thank Jeroen P. W. G. van den Berg for ion chromatography analyses, Eric van den Heuvel for stamp fabrication support,

and Michel Decré and Dick Broer (all at Philips Research, The Netherlands) for many fruitful discussions.

Supporting Information Available: Figures showing concentrations of ODT in stamps after inking (Figure S1) and contact time dependence of the size of surface structures (Figure S2) and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL0607885