Spreading of 16-Mercaptohexadecanoic Acid in Microcontact Printing

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Spreading in microcontact printing refers to the process or processes by which the ink molecules end up in the parts of the substrate that are adjacent to the contacted areas but which are not contacted themselves. This has been investigated for different inking concentrations of 16-mercaptohexadecanoic acid (MHDA). Spreading of MHDA takes place with retention of a well-defined demarcation. Feature sizes can be controlled by varying the contact times. Spreading, however, only takes place beyond a certain threshold concentration. For low ink concentrations the edges of stamp features dominate the ink transfer. For these low concentrations the extent of this edge dominance depends strongly on ink concentration rather than on contact time. These observations indicate a dominant role of the stamp surface in the processes of pattern formation and spreading.

Introduction

Self-assembled monolayers (SAMs) are ordered molecular assemblies that are formed spontaneously on the surface of a substrate by the adsorption of a surfactant with a specific headgroup affinity for a substrate material. Because of their ease of preparation, SAMs formed from alkanethiols on gold have become archetypal.[1–3] They are stable in, and shield the underlying substrate against, various etching solutions.[4,5] A primary interest in the patterning of SAMs is, therefore, their use as etch masks for the generation of microstructures in electronics or related industries. Microcontact printing (μCP) is a process in which suitable molecules are transferred from an elastomeric stamp with a surface relief structure to a substrate upon intimate contact. It has proven to be a fast and simple technique for patterning SAMs on surfaces.[6–9]

As a prerequisite for their ability to self-assemble, alkanethiols and other molecules that form ordered SAMs (hereafter denoted "*inks*") exhibit a significant mobility on the surface of a substrate. Consequently, there is always some loss of spatial control due to spontaneous reorganization and/or spreading beyond the intended regions. On the other hand, however, clever use of the spreading phenomenon may allow for the fabrication of structures that would otherwise be very difficult to reproduce by printing due, for instance, to their small spacing.

The focus of this study is the spreading behavior of 16-mercaptohexadecanoic acid in order to gain a better understanding of spreading processes in μCP as a whole.

Experimental Section

Materials. 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. 16-Mercaptohexadecanoic acid (MHDA, 90% purity) was purchased from Sigma-Aldrich and used as received. Ink solutions were prepared by dissolution of MHDA in ethanol. Solutions with concentrations of 1, 2, 4, 6, 8, and 10 mM were prepared and used within 2 weeks following preparation. Ethanol and heptane (both p.a. grade) were purchased from Merck. Gold was evaporated on silicon for use as a substrate (20 nm of gold on a 5 nm adhesion layer of titanium, on top of ∼250 nm of thermal silicon oxide). Prior to usage the substrates were sequentially rinsed with ultrapure water (resistivity >18 MΩ), ethanol, and heptane. They were thereafter exposed to Tepla 300E microwave argon plasma (300 W, 25 mbar Ar) for 5 min.

Characterization. Stamps were equilibrated overnight in the corresponding ink solutions. Prior to printing, they were rinsed briefly with neat ethanol and dried in a stream of nitrogen. Printing usually followed within 10 min. Frequently the spontaneous evolution of conformal contact was expedited by manually applying a light pressure to the back of the stamp during only the initial stages of contact. This was done in order to obtain more well-defined contact times. Without this initial light pressure, the contact times of various parts of a single substrate could vary by minutes due to the inclusion of air pockets. Optical micrographs were taken of etched patterns. A standard thiosulfate-based etch bath, to which octanol was added in order to decrease the sensitivity for pinholes, was used.[4,10] The length scale can be derived from the small squares that have a repeat distance of 20 μm and nominal size (without spreading) of 10 μm × 10 μm. Patterned images that were not etched were imaged

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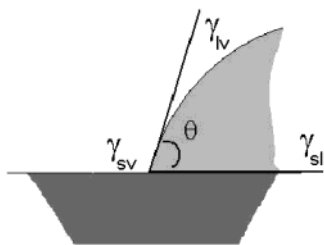
Figure 1. Schematic drawing of a droplet of liquid (ink) on a surface. The interfacial energies γ_{sv}, γ_{lv}, and γ_{sl} correspond to the substrate/vapor, the liquid/vapor, and the substrate/liquid interface, respectively. In equilibrium they are related to the contact angle θ_{eq} through Young's equation: $\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos(\theta_{eq})$.

using a Nanofilm "I-Elli 2000" imaging ellipsometer. The thiol content in PDMS was determined by ion chromatography, preceded by so-called Wickbold combustion, in which the bound sulfur was converted to sulfate. In preparation of the measurements, pieces of PDMS with minimum dimensions of approximately 1 cm were equilibrated for 2 weeks in thiol solutions of the appropriate concentration. The self-diffusion coefficient of apolar organic molecules in PDMS was found by Muzzalupo et al. to be on the order of magnitude of 1×10^{-10} m²/s.[11] It is likely that the diffusion of MHDA, however, is much slower due to the presence of the polar carboxyl group. Nevertheless, the 2 weeks equilibration time would be sufficient for an ink to penetrate 1 cm into PDMS even if its diffusion coefficient differs by 1 order of magnitude. The ink concentrations were determined separately for inked PDMS and the corresponding inking solutions. The concentrations of the latter were determined in the same way as the ink concentration in PDMS except for the 1 and 2 mM concentrations, which were determined using inductively coupled plasma optical emission spectrometry. X-ray photoelectron spectroscopy (XPS) measurements were performed using Physical Electronics' "Quantera SXM", which has an information depth in polymeric materials of about 5 nm and a detection limit of approximately 0.1 atom %. The XPS device operates at 10^{-9} Torr. To arrive at such low pressure and to avoid contamination of the sample chamber, inked stamps were kept in a separate vacuum lock under continuous pumping for approximately 2 h prior to insertion in the XPS.

Software for Analysis. Images were analyzed using "ImageJ", a public domain image processing program by the U.S. National Institutes of Health (NIH),[12] and Nanotec's "WSxM" a freeware data acquisition and processing program for scanning probe microscopy.[13]

Results and Discussion

The interest in the spreading behavior of MHDA arises from the assessment of Whitesides et al. that spreading is driven by an interfacial energy imbalance (reactive spreading).[5,14] In thermodynamic equilibrium, the interfacial energies are balanced by the contact angle θ_{eq} (Figure 1). The formation of a monolayer alters the surface energy of the substrate. The system can, therefore, not be in equilibrium, as long as a monolayer is being formed. For the case of imbalance, with $\theta > \theta_{eq}$, the line where the three phases connect (the *triple phase line*) will tend to shift outward, thereby increasing the solid/liquid interface at the expense of the solid/vapor interface (thus enhancing spreading). Conversely, for the case when $\theta < \theta_{eq}$, the triple phase line will tend to move inward, thereby opposing the spreading of the liquid. The interfacial energies can be tuned by changing one of the phases, e.g.,

by printing underwater instead of in air in order to enhance spreading of hydrophobic monolayers.[5] Similar reasoning suggests that printing in air using *hydrophilic* thiols, such as MHDA, will lower the equilibrium contact angle and, therefore, will enhance spreading as well.

MHDA patterns were printed using varying ink concentrations and contact times. For high ink concentrations, the lateral dimensions of the printed features were found to increase with increasing contact time (Figure 2). Consistent with prior observations (but crucial for a description of spreading) the width of the structures remained constant once the contact was terminated.

The concentration dependence of the spreading of MHDA shows, however, some peculiar features (Figure 3). Most strikingly, spreading cannot be observed for ink concentrations up to 6 mM. Furthermore, when spreading is not apparent, the smallest line width for each studied concentration increases with increasing inking concentration, as can be seen in Figure 3 by an increase in the line offset upon an increase in inking concentration. At a thiol concentration between 6 and 8 mM in the inking solution, spreading becomes contact time dependent.

In the concentration range below 6 mM, where spreading is not apparent, it is furthermore observed that the etch resistance of the monolayer near the edges of the contacted areas is significantly better than that of the monolayer in the center of the same area (Figure 4). This "*edge dominance*" is most apparent for, but not exclusive to, larger contact areas.

Close inspection reveals that the outer demarcation of the dominant edges is well-defined and closely follows the contours of the stamp features. The inner demarcation is, however, less well defined and often, specifically in the corners, a gradual decrease in gold feature quality is observed after etching. An ellipsometric study of the printed monolayer before etching (Figure 4D), clearly indicates that this is an effect of monolayer density rather than an etch artifact. Ellipsometry is very sensitive to surface coverage and film thickness. Lateral variations thereof are the cause of the observed contrast. In the presented image the brightness (intensity) is in a first approximation inversely proportional to the ink coverage. The gradient levels out toward high overall coverage for increasing ink concentrations (Figures 4C and 5).

Edge dominance was also observed by Delamarche et al. in the case of low inking concentrations and short contact times of eicosanethiol.[15] In their interpretation, a diffusive front of thiols advances from the vertical noncontact surface parts of the stamp into the contact region resulting in a net ink diffusion from the edges toward the inside. In the case of such a diffusion mechanism, an influence of the contact time would be expected. Considering the experimental error in the here presented study, this dependency could not be established for contact times between 15 and 195 s. There was found, however, a pronounced effect of ink concentration (Figure 5).

The above observations may be rationalized by a model, in which during the period of contact thiol transport originates mainly from the *surface* of the stamp with only a negligible contribution of diffusion from the bulk. This is a viable assumption considering the effect of ink concentration that clearly supersedes that of contact time. The penetration depth δ for bulk diffusion ($\delta(t) = (4\pi Dt)^{1/2}$, D denotes the bulk diffusion coefficient), which is proportional to the amount of MHDA that can be transferred, scales with the square root of the contact time t. For bulk

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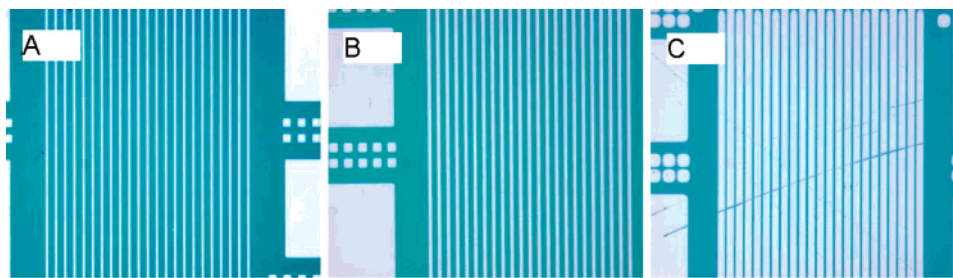
Figure 2. Optical micrographs of etched patterns created using a 10 mM MHDA inking solution after (A) 15 s, (B) 105 s, and (C) 195 s contact time. The white features correspond to nonetched gold. The average line widths in these examples were found to be 4.5 (equal to the nominal line width), 5.7, and 10.5 μm, respectively.
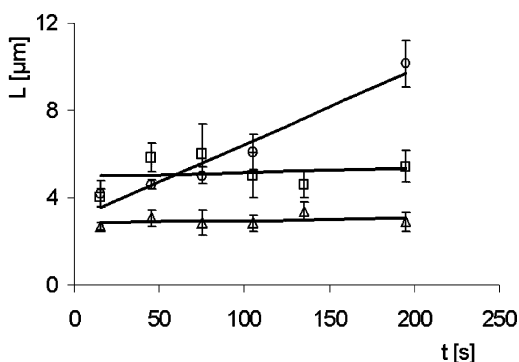

Figure 3. Concentration dependence of the rate of spreading for MHDA. t and L denote the contact time and the line width. Circles, squares, and triangles depict the lines corresponding to 10, 6, and 2 mM inking concentrations, respectively. The width of the features on the stamp was 2.5 μm.
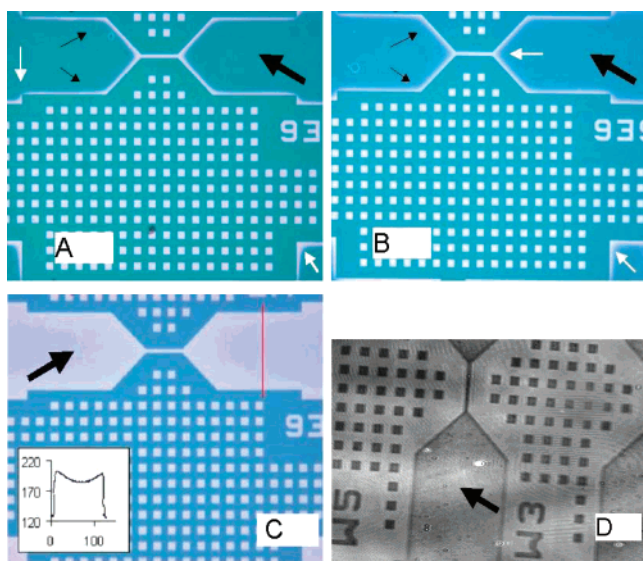

Figure 4. A, B, and C are optical micrographs of etched patterns using MHDA inking solutions and contact times of 2 mM and 75 s, 2 mM and 195 s, and 6 mM and 15 s, respectively. The large black arrows indicate large contact areas, the small black arrows indicate the dominantly present edges. The white arrows point to examples of a poorly defined inner demarcation. In image C, the insert shows the intensity profile along the vertically drawn line. D is an ellipsometry image of a patterned substrate (1 mM, 135 s contact) that was *not* etched.

diffusion, the amount of MHDA that can be transferred in a fixed time interval, however, scales linearly with the initial concentration. The effect of a 2-fold increase in concentration with respect to some reference should, therefore, be similar to a 4-fold increase of the contact time with respect to the same reference. The absence of such correlation in the observed spreading behavior as
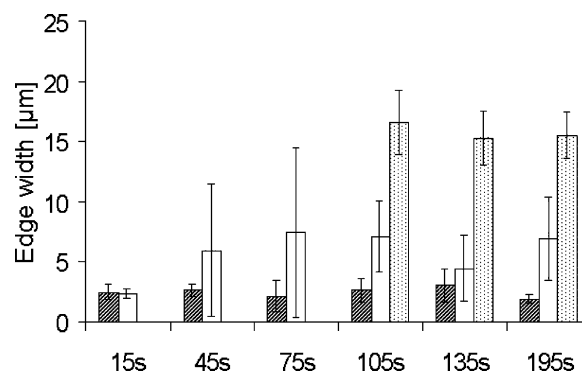

Figure 5. Contact time and concentration dependence of the edge dominance phenomenon. Shown, from left to right, are the edge widths for 1, 2, and 4 mM ink concentrations. Edge widths are defined as the full width at half-maximum of the intensity profile. For the 4 mM ink solution, the width of the edges at contact times of 15, 45, and 75 s could not be determined because of the intensity profiles beginning to overlap. This overlap for the short contact times is a matter of coincidence, governed by the rather large scatter. Because of the increasing overlap, the edge widths could also not be determined for the ink concentrations higher than 4 mM.

well as in the behavior of the edge width variations indicates a subservient role for the bulk diffusion in the transfer of ink. This, in turn, emphasizes the importance of the stamp surface, or its bulk/surface interface, for this ink transfer.

To complement the model it is furthermore hypothesized that the surface presence of thiol is facilitated at the corners (edges) of the stamp features, causing the previously discussed concentration gradient (Figure 6A). Upon an increase of inking concentration, buildup of surface thiol originates at these corners. Possible reasons for this will be discussed below. Since it is assumed to reflect a stable situation in the stamp, as opposed to a dynamic process on the surface of the substrate that becomes effective during printing, it explains the observed contact time independence of the gradient (constant width of the edges).

Parallel with the leveling out of the gradient upon an increase in inking concentration, there is an increase in the minimum measured width (offset) of patterned features, which is, within experimental error, independent of contact time (Figure 3). Assuming that the effective contact area remains constant, this indicates a short period of mobility, the length of which is governed by the inking concentration. This is feasible considering that the patches of the ink on the edges of the stamp constitute finite reservoirs (Figure 6B). When these reservoirs deplete within the first instances of the experiment, the scatter in the measurements masks spreading. Instead it will give rise to an observed increase in offset.
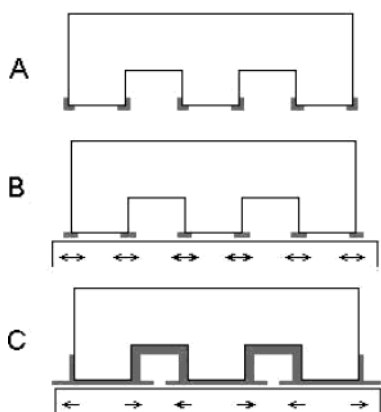
Figure 6. Schematic representation of the hypothesis for edge dominance and spreading. Picture A represents the situation for a stamp with low inking concentration and which is not in contact with a substrate. The gray blocks on its corners represent higher surface concentrations of ink, which constitute finite ink reservoirs. Picture B shows the situation in which the stamp is in contact with a substrate and in which only a limited amount of spreading is allowed until depletion of the reservoirs occurs. Picture C shows a comparable situation in which, however, the ink concentration is sufficiently high for the ink reservoirs to interconnect.

Coinciding with the disappearance of the edge dominance, significant spreading begins to occur. This again can be explained with the model of finite reservoirs at the edges of the stamp. When these independent reservoirs interconnect across the contact planes of the stamp (disappearance of edge dominance), they also interconnect at other parts of the stamp surface, thereby constituting a much larger ink reservoir to feed the spreading process (Figure 6C).

An important observation in the above is that the bulk presence of MHDA in the stamp is less significant in the transfer and spreading of the thiol molecules than its surface presence. The hypothesis implies a spontaneously occurring surface presence of the ink, which is, moreover, most pronounced along the edges of the stamp features. The mechanism for such surface presence, however, or even the existence of edge dominance, is far from understood. A host of hypotheses can be readily formulated, but experimental verification thereof is far from trivial. Several hypotheses will be discussed below.

The explanation provided by Delamarche et al. for the observation of dominant ink transfer at the edges of large contacted areas may possibly be extended to spreading of MHDA.[15] Due to its hydrophilic end groups, MHDA has a preference for residing at the surface of the hydrophobic stamp. In equilibrium, the surface coverage will be fairly uniform. Rinsing of the stamp prior to printing as described above, as well as the act of printing itself, however, disturbs the equilibrium. Especially in the latter case, the ink on the surface of the undisturbed receded areas of the stamp can contribute to the total ink transport toward the affected contact areas. If there is any such contribution, the ink will necessarily migrate from the edges inward, thereby enhancing edge dominance. If the transport of the ink across the stamp surface is significantly faster than ink transport from the bulk to the surface, the contribution of the receded areas to an enhanced edge dominance can also be significant. An extension of this model, however, is required to explain the relative contact time independence of the edge features. Cherniavskaya et al. have already described a system in which hydrophilic ink is

transferred in a controlled fashion from the edges of a PDMS stamp, of which the contact areas are devoid of ink.[16]

A different hypothesis takes into account the reactivity of the thiol ink. The high surface-to-volume ratio at the edges of stamp features expedites the diffusion of oxygen into the stamps. As thiols are prone to oxidation, and this oxidation is likely to affect their solubility in PDMS, it can be reasoned that the anisotropic diffusion of dioxygen into the stamp, oxidation of thiol, and subsequent expulsion of oxidized thiol cause the anisotropic surface presence of ink. Supporting this theory is the observation that inked stamps that have been stored in air for several months were found to grow small crystallites on their surface.[17]

XPS was used to verify the ink distribution on the stamp surface as well as its oxidation state for a stamp inked with a 2 mM MHDA ink solution. No sulfur could be detected. Using eq 2 (see below) and considering that hydrogen atoms are invisible in XPS, the effective sulfur concentration in the bulk of the stamp can be calculated to be approximately 10^{-3} atom %. This is far below the detection limit of the XPS apparatus of 10^{-1} atom %. It can be calculated that for the sulfur content to exceed the detection threshold, 2 molecule % of the probed volume should consist of MHDA. If all the ink is assumed to be located on the stamp surface, it can be shown that, with an information depth of 5 nm and assuming equal densities for MHDA and PDMS, the MHDA surface layer must have a thickness of at least 0.1 nm in order to be detectable by XPS. This is about 1 order of magnitude less than the thickness of a close packed monolayer (i.e., ~2 nm). Apparently, for the conditions used, the surface coverage is even less. This observation weakens the notion that transport across the stamp surface into the contact areas is the cause for the edge dominance. It may well be, however, that the absence of ink is an artifact brought about by the necessity of vacuum for XPS measurements. An anisotropic surface distribution of ink on the stamp surface could not be observed.

Any anisotropic presence of MHDA on the surface is likely to be a consequence of a nonequilibrium process, such as, e.g., the evaporation of the solvent (i.e., ethanol). Another mechanism that was considered was, therefore, a time-dependent local supersaturation of the stamp that might occur as a consequence of solvent evaporation. Because of the high surface-to-volume ratio at the stamp edges, solvent depletion and hence any possible supersaturation will occur first at these stamp features. To investigate this further, the MHDA content in PDMS in equilibrium with the used inking solutions was determined as described above (Figure 7). No saturation of the stamp occurs up to a 10 mM inking concentration, which was also found to be the saturation point of MHDA in ethanol. (The employed ink solution was observed to contain MHDA precipitates.)

Upon inking, both ethanol and thiol are dissolved in the PDMS matrix. The weight of a $(2 \times 22 \times 22)$ mm^3 slab of PDMS that had been submerged overnight in ethanol was found to have increased from 0.77 to 0.82 g (i.e., the weight gain was ~6%). Since, from Figure 7, it can be seen that MHDA dissolves more readily in ethanol than in an ethanol/PDMS system, it may be expected that the presence of ethanol enhances the uptake capability of PDMS. To gauge the extent of this enhancement, it is assumed that the thiol content of the inked stamp is

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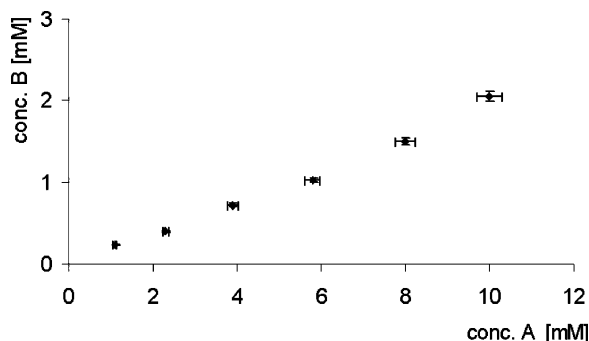
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Figure 7. The concentration of MHDA in the bulk of PDMS ("conc. B") when in equilibrium with varying concentrations of MHDA in ethanol ("conc. A").

distributed between an ethanol volume fraction x and a PDMS volume fraction $(1 - x)$ (Figure 8). The relative contribution of both fractions to the total ink concentration in the stamp [$thiol_{stamp}$] may therefore be expressed as

$$[\text{thiol}_{\text{stamp}}] = x[\text{thiol}_{\text{eth}}] + (1 - x)[\text{thiol}_{\text{PDMS}}] \quad (1)$$

In this equation [$thiol_{eth}$] and [$thiol_{PDMS}$] are the thiol concentrations of the ethanol and the PDMS fractions, respectively. From Figure 7 it is found that the total thiol content in the stamp, in a first approximation, can be derived from the concentration of the ink solution [$thiol_{ink}$].

$$[\text{thiol}_{\text{stamp}}] = 0.2[\text{thiol}_{\text{ink}}] \quad (2)$$

Assuming that the thiol concentration of the ethanol inside the stamp equals the thiol concentration of the ink solution, and substituting the ethanol volume fraction in the stamp for the relative weight gain of a stamp upon inking (i.e., $x = 0.06$), eq 1 can be solved in terms of ink concentration. This yields the relative contribution of the dissolved ethanol fraction x[$thiol_{eth}$] and that of the PDMS fraction $(1 - x)$[$thiol_{PDMS}$].

$$x[\text{thiol}_{\text{eth}}] = 0.06[\text{thiol}_{\text{ink}}] \quad (3)$$

$$(1 - x)[\text{thiol}_{\text{PDMS}}] = 0.14[\text{thiol}_{\text{ink}}] \quad (4)$$

From eqs 3 and 4 it follows that about 30% of the thiol content of an MHDA inked stamp may be attributed to the presence of the ethanol, which occupies only 6% of the stamp volume. From this it can further be deduced that [$thiol_{PDMS}$] at high inking concentrations exceeds [$thiol_{stamp}$] at the low inking concentrations, for which edge dominance is observed. For these low inking concentrations, the PDMS is therefore not likely to supersaturate upon evaporation of ethanol.

Judging from the relatively high affinity of MHDA for ethanol with respect to its affinity for PDMS, evaporation of ethanol can induce a current of MHDA toward the surface with a rate profile concurrent with the evaporation-rate profile and a magnitude that scales with the inking concentration. Because of the relatively high surface-to-volume ratio at the edges, ethanol can be expected to evaporate with the highest rate at these stamp features, with a gradient in rate dropping toward the center of the stamp facets. Supersaturation of ethanol due to evaporation *at the surface* and subsequent precipitation of MHDA would lead to a surface concentration profile similar to the one observed. This is the most elegant model that combines a preorganization of the ink on the surface with the observed contact time and concentration dependence of the edge features.
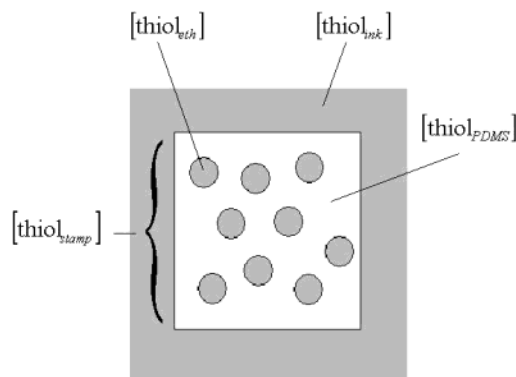

Figure 8. Schematic representation of an ink distribution configuration for a submersed stamp. In this configuration, the ethanol and the PDMS phases are discretely separated, each with a distinct thiol content. The gray areas of the figure represent the ethanol phase, whereas the white area represents the PDMS phase. The thiol concentration in the ethanol phase *inside* the stamp is denoted [$thiol_{eth}$] and is assumed to be equal to the thiol concentration in the ink [$thiol_{ink}$], i.e., the ethanol phase *outside* the stamp. The thiol concentration in the PDMS matrix is denoted [$thiol_{PDMS}$]. The thiol content of the PDMS matrix and the thiol content of the ethanol phase inside the stamp, together constitute the total thiol content of the stamp whose concentration is denoted [$thiol_{stamp}$].

Quite apart from an initial anisotropic ink distribution on the stamp, edge dominance may also be interpreted in terms of a pressure gradient on the contacting stamp facets during printing. Furthermore, the bulk transport properties of the stamp may be anisotropic due to, e.g., kinetic considerations in the curing process. Even surface energy effects resulting from differences in curvature may play a role.

Although the challenges are manifold, a better understanding of the behavior of ink on the surface of a stamp is well worth pursuing, for it offers the possibility of site selective inking. Specifically the edge dominance, observed in this and previous studies, may find applications in the microfabrication of isolated structures. These are structures that have a small footprint relative to their spacing (e.g., connecting wires in electronic structures) and are difficult to manufacture by μCP due to stability issues of the stamp. Inking only the edges of the stamp features would allow for a drastic increase of their footprint and thereby for an equivalent increase in stamp stability. This and related technological options are currently being explored.

Conclusions

During μCP with patterned PDMS stamps on gold surfaces, MHDA ink molecules spread with retention of a well-defined demarcation. Varying the contact times enables the control of feature sizes. Spreading, however, only takes place above a certain threshold concentration.

For low MHDA inking concentrations, the edges of the stamp are dominant in the transferred SAM pattern as detected by imaging ellipsometry analysis before, and optical microscopy measurements after etching of printed gold substrates. Furthermore, for low ink concentrations, spreading is found to be independent of contact time. The contact time independent line width, however, is found to increase with increasing inking concentration until at some discrete concentration spreading becomes contact time dependent.

The deviant morphology and spreading behavior may be qualitatively connected assuming that only ink that is

present on the surface of the stamp contributes to pattern formation and that this presence is facilitated at the edges of the stamp. The latter can be rationalized by a model, in which the evaporation of ethanol from an inked stamp induces a current of MHDA toward its surface with a rate profile concurrent with the evaporation-rate profile and a magnitude that scales with the inking concentration.

It is shown that for a proper understanding of the processes involved in μCP, the interactions of the ink with the stamp are significant but, as yet, poorly understood.

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