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Process Simulation for Contact Print Microlithography

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ABSTRACT

Using a combination of experiment and simulations, we have studied the conformation of liquid microstructures on both flat and corrugated, chemically heterogeneous substrates. The artificial surface patterns, which define regions of different surface energy, induce deformations of the liquid-solid contact line, which can either promote or impede capillary break-up and the formation of bulges. We study numerically the influence of the adhesion energies on the hydrophilic and hydrophobic surface areas, the pattern geometry and the deposited fluid volume on the liquid surface profiles. Moreover, we investigate the transfer of these microscopic ink patterns from the stamp surface to the target substrate during the printing process.

Keywords: Microlithography, Offset Printing, Intaglio, Liquid Microstructures, Surface Pattern

1 INTRODUCTION

In the last ten years several attempts have been made to find alternatives [1–3] to conventional photolithography for the fast, parallel and low-cost fabrication of patterns in the micrometer size range. For example, Mikami *et al.* [3] have developed a gravure-offset printing technique to fabricate fully functional electronic devices.

Optimization of the stamp pattern design and the ink transfer process for the fabrication of electronic structures requires knowledge of the liquid's equilibrium conformation on a patterned surface. For liquid elements in the micron range, the surface to volume ratio is very large. Thus, the energetics associated with the boundary surfaces completely determine the overall shape and stability of liquid microstructures. By understanding to which extent the various parameters affect the final shape, the edge resolution and pattern fidelity can be improved.

2 EXPERIMENTS

The samples were cut from standard silicon wafers and coated with a self-assembled monolayer of octadecyltrichlorosilane (OTS), which serves as the hydrophobic layer. The contact angle of water on OTS is about 112°. Subsequently, the OTS layer was removed locally by exposure of the samples to deep-UV radiation from an ArF excimer laser through a chromium mask. The regions where the OTS was removed by photocleavage [4] are rendered hydrophilic, since the SiO_2 underneath the OTS is now exposed. The experiments have mainly been performed with glycerol, because of its low volatility. Additional details of the experimental procedures can be found in Ref. [5].

3 NUMERICAL SIMULATIONS

The numerical calculations presented in this article were performed with the Surface Evolver [6] software taking into account the liquid's surface tension γ_{lv} and the liquid-solid contact energy. Due to the small scale of the investigated structures, the Bond number defined as $\mathrm{Bo} = \rho g R^2/\gamma_{lv}$ is much smaller than one and hence the influence of gravity can be neglected. ρ is the ink density, g the gravitational acceleration and R the relevant length scale.

The surface of the ink droplets is discretized by means of a triangular mesh and the total energy of the system is expressed as a function of the node coordinates. The numerical methods of steepest descent and conjugate gradients are implemented for the minimization of the total energy. Constraints can be applied to vertices, edges, facets and volumes and boundary condition parameters can be included in the optimization process.

4 INK ON FLAT SURFACES

An ink droplet on a homogeneous surface assumes the shape of a spherical cap, which exhibits a constant contact angle with the solid surface all around its perimeter. If the surface is hydrophilic, the contact angle θ is below 90°, if the surface is hydrophobic, θ exceeds 90°. In the latter case, the droplet tries to minimize the solid-liquid contact area, whereas in the first case it has an incentive to maximize it, in each case to the maximum extent compatible with the magnitude of the liquid's surface tension γ_{lv}.

If the surface is heterogeneous with both hydrophilic and hydrophobic patches, the contact angle is no longer a constant, but is position dependent. The ink will try to reside only on the hydrophilic parts of the surface and to recede from the hydrophobic areas. In this way, liquid can be confined to certain imaging areas by chemical surface modifications, which is the basis of the classical offset printing technique. [8]

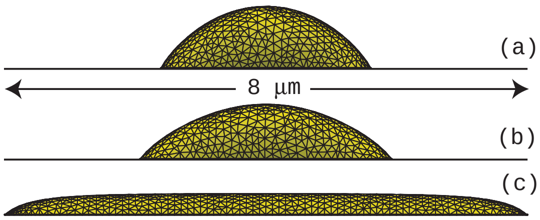

Figure 1: Influence of an insoluble surfactant. The side views correspond to an ink droplet with a contact angle of 60° (a), to the same droplet with a surfactant which reduces the surface tension by 20% (b) and by 50% (c).

One of the most elementary geometries comprises a hydrophilic rectangular patch on a hydrophobic plane. If a very small quantity of ink is deposited on the hydrophilic channel, the droplet will assume a spherical cap shape, if its contact angle is above 0°. If the volume of the droplet is increased, the base radius of the spherical cap increases until it senses the channel boundaries. If the volume is increased further, the previous spherical cap shape will deform and extend itself along the channel. The side view of an ink droplet on a 1 μm $\times$ 8 μm channel with a contact angle of $\theta = 60°$ is presented in Fig. 1(a). As can be seen, the liquid does not spread along the entire channel, but concentrates in a bulge. This behavior is undesirable for printing, since instead of the designed 1 μm $\times$ 8 μm line only a much shorter pattern would be transferred.

There are two ways to overcome this problem. One is to increase the surface energy of the hydrophilic channel such that the contact angle of the ink is reduced. A value of 30° is low enough to provide for complete wetting of the entire channel. In principle the SiO_2 regions provide a sufficiently high surface energy to bring the contact angle for water or glycerol close to zero. Unfortunately a high energy surface also attracts organic contamination, which can increase the contact angle significantly.

A second possibility is the addition of surfactants which reduce the surface tension of the ink. If the surfactant is insoluble, it will not affect the liquid-solid contact energy and hence effectively reduces the ink's contact angle, leading to complete wetting of the channel. In Fig. 1(a), the droplet shape corresponding to a certain value of the surface tension γ_{lv} and a contact angle of $\theta = 60°$ is compared with the cases when the surface tension is reduced by 20% [Fig. 1(b)] and 50% [Fig. 1(c)]. In the latter case, the channel is completely wetted.

If the surroundings of the channel are only weakly

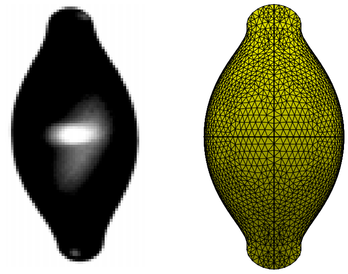

Figure 2: Top views of an experimental and calculated droplet shape of glycerol on a hydrophilic channel. The liquid forms a bulge which leaks into the hydrophobic surroundings.

hydrophobic, the droplet may not be confined to the channel, but leak out of it in order to minimize the liquid-vapor interface area. This situation is depicted in Fig. 2, where an optical micrograph of a droplet of glycerol on a 14 μm wide hydrophilic channel on a weakly hydrophobic surface is compared with a simulation.

In microelectronic devices, large and small patterns are frequently connected. An example are bonding pads and the current leads running to and from them. Since smaller length scales are inherently equivalent to a higher surface-to-volume ratio, the liquid will try to avoid the narrow parts and concentrate on the broader hydrophilic regions. As an example we present an ink droplet on a hydrophilic region which consists of a narrow rectangle of dimensions 1 μm $\times$ 4 μm, which is connected to a broader rectangle of size 6 μm $\times$ 3 μm in Fig. 3.

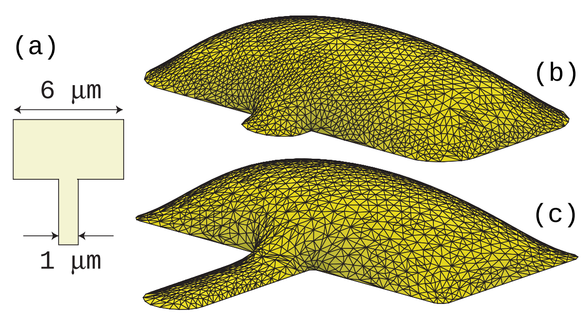

Figure 3: Effect of disparate length scales of the hydrophilic pattern (a) on the distribution of ink with contact angles of (b) 30° and (c) 10°.

In Fig. 3(a), the contact angle of the ink was assumed to be 30° whereas it was 10° in Fig. 3(b). In the first case, the liquid wets only a small fraction of the narrower channel. In the latter case it wets the entire narrow line, however, the height profiles of the liquid are very uneven. Upon printing only the broad rectangle would be transferred. For a more detailed discussion including the influence of topological and chemical defects the reader is referred to Ref. [5].

5 INK ON INTAGLIO SURFACES

The second main technique besides offset printing is gravure or intaglio printing, where the ink fills trenches and grooves in the stamp surface. In this case the surface morphology helps to confine the ink. The grooves provide a significant local increase of surface area, which makes spreading energetically more favorable than the formation of bulges - even for comparatively large contact angles. In Fig. 4 we present a direct comparison of the ink conformations on an offset [Fig. 4(a,b)] and an intaglio plate [Fig. 4(c,d)], where the hydrophilic region has a rectangular shape and dimensions 1 μm $\times$ 4 μm. The depth of the groove is 1 μm.

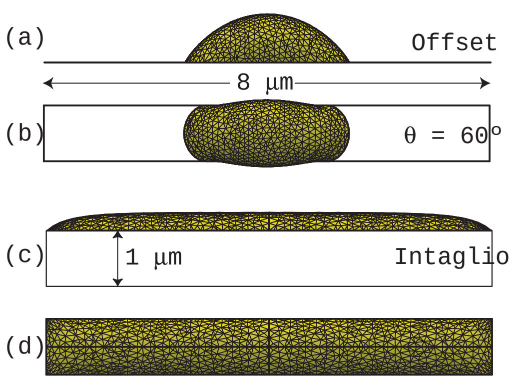

Figure 4: Comparison of ink droplets on an offset and an intaglio printing plate for a contact angle of 60°. (a) and (c) are side views, (b) and (d) are top views. The volume of the droplet on the offset plate and the excess ink volume on the intaglio plate are equal.

Whereas the ink droplet concentrates in a bulge in the center of the hydrophilic patch on the offset plate, the liquid spreads along the entire trench in the case of an intaglio geometry. The contact angle was assumed as $\theta = 60°$. Thus the introduction of grooves and trenches has a similar effect as the usage of surfactants. However, in the case of loops and corners, intaglio does not provide an advantage over offset printing.

6 INK TRANSFER

Figure 5(a) shows the equilibrium shapes of the ink meniscus between stamp and target surfaces for increasing plate separations $d = 0.5$, 1, 1.5 and 2, stated in units of $\sqrt[3]{V}$, where V is the ink volume. The contact angle on the stamp surface is assumed to be $\theta = 60°$, whereas it is $\theta = 45°$ on the target surface. In this case no lateral confinement of the contact lines due to chemical heterogeneities is taken into account. As the plate separation increases, the neck-radius of the ink meniscus becomes smaller and smaller and at some critical value, the meniscus breaks into two separated droplets on the two plates.

Fig. 5(b) shows the volume fraction of ink transferred from the stamp to the target surface as a function of the contact angle on the target substrate for two values of the contact angle θ on the stamp surface, 30° and 60°. When the contact angles on both surfaces are equal, the transfer ratio is 50% as dictated by symmetry. When the two contact angles are disparate, the transfer ratio changes rather rapidly either towards almost complete transfer or towards almost no transfer of ink to the target substrate. As is clearly visible, the surface with the smaller contact angle retains the bulk of the ink volume.

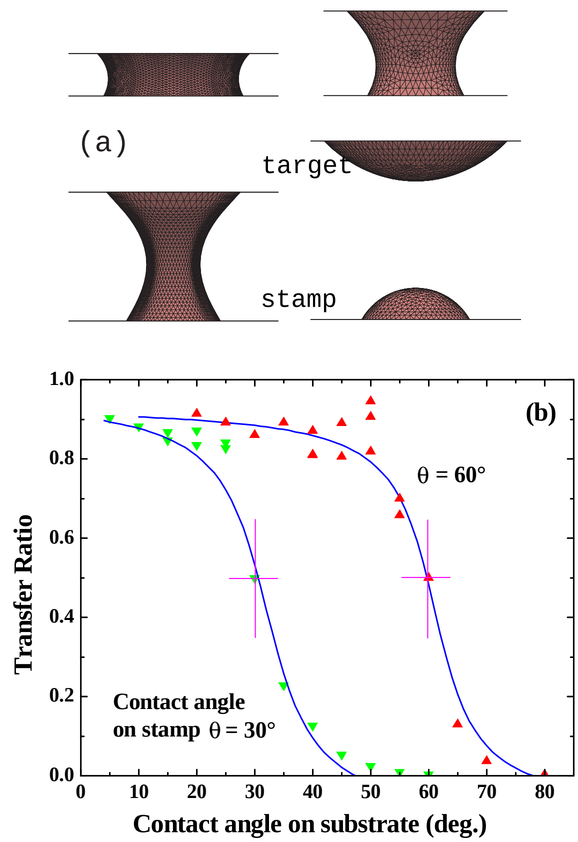

Figure 5: (a) Meniscus shape of a fixed volume of ink between parallel plates of different composition. The corresponding plate separations are 0.5, 1, 1.5 and 2 in units of $\sqrt[3]{V}$, where V is the ink volume. The contact angles on the stamp and target surface are $\theta = 45°$ and $\theta = 60°$, respectively. (b) Transfer ratio of the liquid ink from the stamp to the target surface for contact angles of $\theta = 30°$ and $\theta = 60°$ on the stamp. The solid lines are guides to the eye.

The presented results were obtained under the assumptions of quasistatic printing, unconstrained contact line motion and perfectly flat and parallel surfaces. Thus they represent only the influence of the surface chemistry on the transfer process, regardless of the dynamic properties of the liquid. Chadov [9] and Yakhnin [10] have shown that for a speed of the plate separation fast as compared to the intrinsic velocities (resonance frequencies) of the liquid meniscus, the transfer ratio is always 50%, irrespective of the chemical composition of the plates. As the separation speed is reduced the transferred fraction gradually converges to the quasistatic value which is determined by the chemistry alone.

Figure 6(a) shows an ink meniscus between the stamp and the target substrate for equal contact angles of $\theta = 30°$ when a small tilt of 2° is present. This situation might arise when the parallelity of the plates is not strictly enforced by mechanical provisions during their separation. The ink on the stamp surface is confined to a rectangular hydrophilic pad of dimensions 1 μm × 4 μm, whereas there is no confinement on the target surface. Since a smaller separation corresponds to a smaller average curvature of the liquid's surface, which is energetically favorable, the ink meniscus is attracted to the region of minimum plate separation by capillary action.

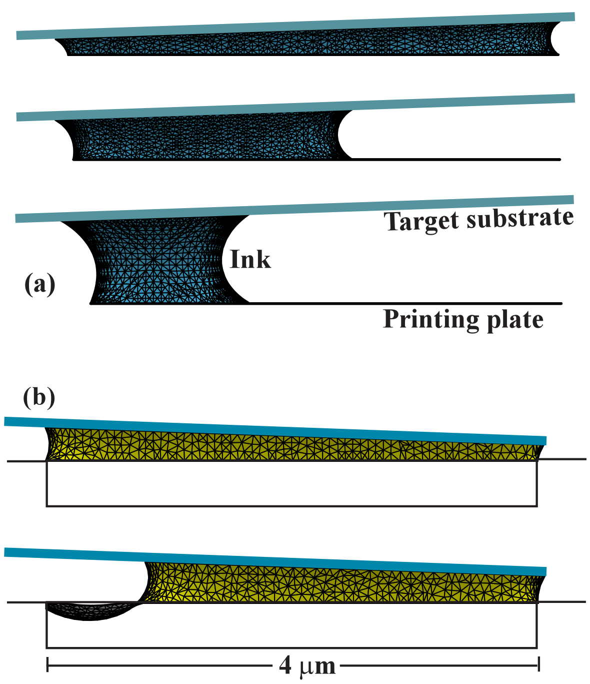

Figure 6: (a) Tilted offset printing plates. As the plate separation increases, the ink meniscus is attracted to the region of minimum plate separation. (b) Tilted intaglio printing plates. The liquid's contact line is pinned at the sidewall of the groove in the stamp, but free to move on the target surface. The contact angles on both plates were assumed to be (a) 30° and (b) 60°.

The analogous situation for intaglio printing is presented in Fig. 6(b). Equal contact angles on both stamp and target of $\theta = 60°$ were assumed. The groove has rectangular shape with dimensions 1 μm × 4 μm and a depth of 1 μm. The same tilt angle of 2° as in Fig. 6(a) is assumed with the tilt axis parallel to the shorter edge of the rectangle. Upon separation of the plates, the liquid's contact line is pinned to the sidewall of the groove, but it is free to move on the target surface. Thus again, the ink meniscus moves towards the zone of smaller plate separation.

This would induce a loss of pattern fidelity, which illustrates the necessity to provide for a mechanism to impede contact line motion on the target substrate. Such a pinning of the contact line could be achieved by surface initiated polymerization of an ink which contains monomers or oligomers, or by increasing the ink viscosity by means of a temperature induced phase transition (e.g. freezing) or chemical reaction with a thin layer of suitable material uniformly deposited on the target surface.

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