OFFSET PRINTING OF LIQUID MICROSTRUCTURES FOR HIGH RESOLUTION LITHOGRAPHY

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ABSTRACT

We have investigated the direct printing of polymer solutions from a chemically patterned stamp onto a hydrophilic target substrate as a new high-throughput alternative to optical lithography. The patterns on the stamp, which are typically in the micron size range, define regions of alternating wettability. They are produced by patterning a hydrophobic self-assembled monolayer previously deposited onto a hydrophilic surface, typically a glass slide or silicon wafer with a natural oxide coating. Polar liquids or aqueous polymeric solutions are then deposited only onto the hydrophilic surface patterns by dip-coating the stamp in a liquid reservoir. The deposited film thickness depends critically on the speed of withdrawal and the feature size and shape. For vertically oriented hydrophilic stripes dipped in a reservoir containing a polar liquid, we have developed a theoretical model whose prediction for the maximum deposited film thickness agrees exceptionally well with experimental measurements. After deposition, the wetted stamp is pressed against a target substrate by means of a motion controlled press. In this way we have so far printed 5μm wide polyethylene oxide lines onto a silicon wafer.

INTRODUCTION

The production of low–cost large–area electronics requires the development of new fabrication techniques that are considerably less expensive and allow higher throughput than conventional photolithography. The offset printing of materials for electronic device fabrication is one such approach under investigation. This type of contact printing, also known as lithographic printing, is heavily used in the graphic arts industry for the fast reproduction of newspapers, magazines, and other high–volume products. Ink is confined in regions of alternating wettability on the plate roller, which is then pressed onto a blanket roller. The desired ink patterns are then transferred from this soft roller surface onto the desired medium, such as paper. Since the layers that define the wetting and non–wetting regions are microscopically thin, the entire surface can be regarded as truly planar and only the surface chemical heterogeneities determine the ink placement. Pattern fidelity upon transfer to the target surface is achieved even at high roller speeds. Alternative techniques for ink confinement which also allow for high resolution reproduction, like gravure printing, depend instead on geometric constraints such as etched grooves. Extending the conventional offset process for use in microelectronics fabrication requires advances and optimization of three key steps. The resolution of the stamp pattern must be scaled down to the micron range. This first step is rather easy to accomplish given the number of self assembling monolayer treatments that have been introduced to produce substrates of tunable wettability at length scales down to the nanometer range [1]. Secondly, a simple but rapid deposition process is required so that the volume of liquid deposited and printed can be accurately controlled. Finally, it may be necessary to develop new inks that are compatible with the first two steps and useful for device fabrication, such as etch resists or insulating and conducting materials. In this paper, we focus on preparation of offset printing plates with micron–size features and the inking and printing of liquids with such plates.

EXPERIMENT

Printing Plate Fabrication

The stamps used in our study of offset printing are fabricated by patterning the surface of a hydrophobic self–assembled monolayer which resides on the surface of a hydrophilic substrate. Since the monolayer is molecularly thin, on the order of 3 nm, while the feature sizes of the imprinted pattern are on the micron scale, the stamp surface can be regarded as flat. The only deviations from the flat profile are the liquid microstructures deposited during the printing process.

We have prepared two types of printing plates as illustrated in Fig. 1, each with distinct advantages. The first type of substrate consists of a patterned monolayer of octadecyl-trichlorosilane (OTS) on a silicon wafer or hexadecane thiol (HTD) on a gold film deposited against a chromium adhesion layer on a silicon wafer. In each case, areas coated with the monolayer are strongly hydrophobic while areas which expose the silicon oxide or gold surface are completely hydrophilic. These surfaces can be rapidly patterned by microcontact printing [2] or deep UV photo–cleavage [3]. The second type of printing plate we have used is prepared by first depositing a thin film of gold, approximately 50 nm, above a 5 nm adhesion layer of chromium on an oxidized silicon wafer and then patterning the gold and chromium using photolithography and wet chemical etching. After patterning the metal layers, an HDT monolayer is deposited selectively on the gold surface from a 1 mM ethanolic HDT solution. This renders the gold coated areas hydrophobic and leaves the exposed silicon dioxide surfaces hydrophilic. Because the metal layer is much thinner than the pattern feature size, this structure is functionally equivalent to the first type of printing plate. This design has two advantages. Not only is the wettability pattern easily refreshable by monolayer removal and redeposition but it is optically visible because of the difference in reflectivity between gold and silicon surface. This allows direct observation of the degree of pattern fidelity between the imposed surface pattern and the areas of liquid pickup and ink transfer. Silicon wafers ([100]-oriented p-type doped) were used as the base substrate because they are very smooth and flat which allows good contact between the two surfaces for printing macroscopically large areas.
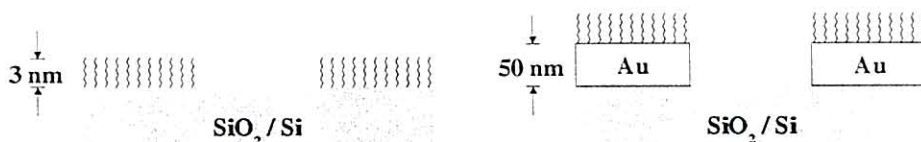

Figure 1: Two printing plate structures with surface wettability patterns defined by hydrophobic self–assembled monolayers. (a) A patterned monolayer formed on an unpatterned substrate. (b) A monolayer formed selectively on a patterned gold film on a substrate. In both case, the thickness of the monolayer or gold and monolayer combination is negligible in comparison to the patterned microscale features.

Liquid Deposition and Printing

The first step of the printing process is the deposition of liquid "ink" onto the printing plate. We accomplish this by selective dip coating, in which the patterned printing plate is withdrawn at constant velocity from a bath of liquid which preferentially wets the hydrophilic areas of the plate, generating liquid microstructures. We have studied the stability of liquid microstructures on such patterned surfaces in Ref. [4]. Inks used in this study were glycerol, tetraethylene glycol (TEG), and aqueous solutions of 15 wt% poly(ethylene oxide)

(PEO, mol. wt. 100 kg/mol). The first two liquids have no significant evaporation on the time–scale of the experiments because of their low vapor pressure. Water does evaporate from the PEO solution but the residual polymer is left only on the hydrophilic portions of the dip-coated sample. The viscosity, η, of glycerol and TEG, both Newtonian liquids, was measured with a capillary viscometer which gave 975 mPa·s and 51 mPa·s, respectively. Glycerol is a hygroscopic liquid and this value indicates the presence of absorbed water. Measurement of the viscosity versus shear rate behavior of the PEO solution using a cone-and–plate rheometer confirmed Newtonian behavior up to a shear rate of approximately $30 s^{-1}$, with a limiting viscosity of 1970 mPa·s. The liquid surface tensions, measured with a platinum Wilhemy plate, were determined to be $\gamma_{\text{glycerol}} = 63.0$ mN/m, $\gamma_{\text{TEG}} = 41.4$ mN/m, and $\gamma_{\text{PEO}} = 53.5$ mN/m. The height of each liquid structure formed by dip-coating was measured by interferometry. Microstructures were visualized using a reflected light microscope equipped with a green bandpass filter whose transmittance peak was centered about 550 nm. The inter–fringe spacing was of the order of 200 nm. The exact value depends on the liquid index of refraction.

The second step in the printing process is the transfer of ink from the printing plate to an unpatterned (hydrophilic) substrate. A motion controller was used to contact the inked printing plate with the target substrate (an oxidized silicon wafer) and to separate the plates.

RESULTS

Dip Coating

Landau and Levich analyzed the dip coating of a Newtonian liquid onto a homogeneous wetting plate withdrawn normal to the surface of a liquid reservoir [5]. Their analysis is valid for Newtonian liquids in the lubrication regime at low capillary number; the film thickness is small relative to the plate dimensions, and surface and viscous forces are dominant over inertial forces. The analysis relies on matching the curvature of the deposited film far above the liquid bath to the curvature in the meniscus region, which for small capillary numbers assumes its static shape. The final film thickness, h_{∞}, is determined to be

$$h_{\infty} = 0.946 \left(\frac{\gamma}{\rho g}\right)^{1/2} \left(\frac{\eta V}{\gamma}\right)^{2/3} \tag{1}$$

where ρ is the liquid density, g is the gravitational constant, and V is the plate withdrawal speed. The capillary number $\text{Ca} = \eta V/\gamma$.

In Ref. [6] this analysis is extended to a plate patterned with a vertical wetting stripe. The curvature perpendicular to the vertical stripe modifies the static meniscus profile changing the final exponent in Eq. (1). The maximum deposited film thickness is instead given by

$$h_{\infty} \propto W \left(\frac{\eta V}{\gamma}\right)^{1/3} , \tag{2}$$

where W is the (hydrophilic) stripe width.

Figure 2(a) presents experimental data for the height of a liquid line deposited on a hydrophilic stripe versus velocity of withdrawal for a stripe 40 μm wide withdrawn from a bath of glycerol. The data shows excellent agreement with the theoretical prediction of a 1/3 exponent. Further study has also confirmed the linear dependence on the width W [6]. Figure 2(b) shows the effect of varying the azimuthal angle of the hydrophilic stripe on the deposited liquid height. The data points represent experimental measurements at 40 μm/s withdrawal velocity for a line width of 40 μm. The deposited film thickness changes little for angles less than approximately 45° but rises steeply by a factor of 2.3 for larger angles. For the larger angles, the effective line width increases, which modifies the meniscus shape
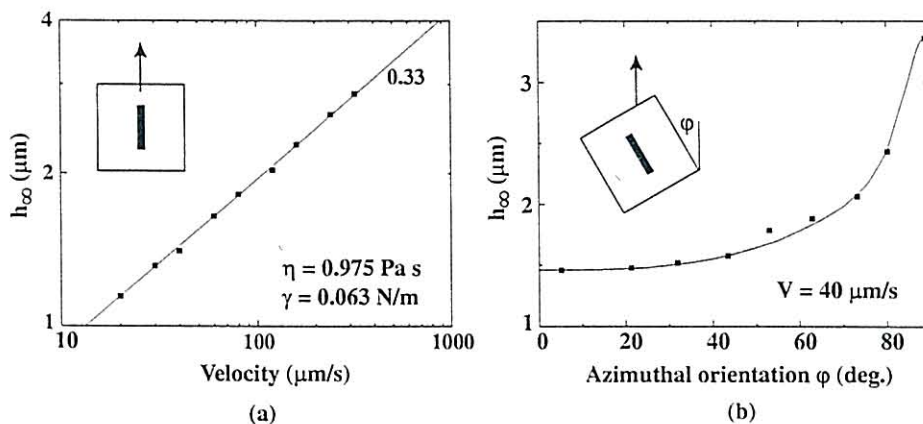
Figure 2: The thickness of a liquid film deposited on a wetting stripe on a hydrophobic surface by dip coating. Measurements were conducted using a 40 μm wide wetting line. (a) The thickness as a function of velocity of withdrawal. Points are experimental measurements, the line is the analytical 1/3 power law prediction. (b) Film thickness as a function of azimuthal angle of the wetting line. Points are experimental measurements made at 40 μm/s withdrawal velocity, the curve is a guide to the eye.

in such a way as to increase liquid pickup. The effective withdrawal velocity along the stripe direction also increases.

Figure 3 shows typical liquid structures obtained by dip coating. Figure 3(a) shows three lines of glycerol 18 mm long, and 16 μm wide, separated by 7 μm. The length to width ratio exceeds 1000. Figure 3(b) shows a 3.5 μm wide line of PEO. The structures in Fig. 3(a) and (b) were both formed on the first type of printing plate (OTS/SiO$_2$). Liquid structures other than straight lines can also be produced by dip-coating, as illustrated in Figure 3(c), which shows a half–loop of glycerol formed on the second type of printing plate (HDT/Au/SiO$_2$). The line width of this half–loop is 100 μm not because of any fundamental limitations related to the shape, but because the printing plate was patterned from an inexpensive photolithographic mask made from a commercial image–setter [7]. Much smaller pattern features require the use of a more expensive chromium mask, as was used for other printing plates in our study.
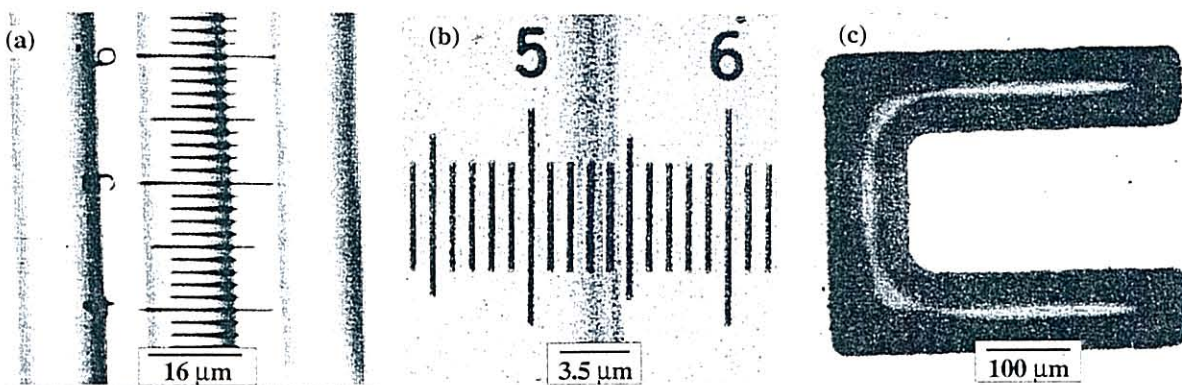

Figure 3: Materials deposited onto patterned printing plates via dip coating. (a) Three parallel lines of glycerol, each 16 μm wide with 7 μm interline separation. (b) A 3.5 μm wide PEO line. Both (a) and (b) were formed on an OTS/SiO$_2$ surface. (c) A half loop of glycerol with line width 100 μm formed on an HDT/Au/SiO$_2$ surface.

Liquid Printing

Polymer structures were printed onto unpatterned silicon wafer target substrates as illustrated in Fig. 4. The left panel shows a printed line 3 μm wide, while the right panel shows two printed droplets, each 4 μm wide. The height of the droplets was estimated from the interference fringes to be 190 nm, which corresponds to a volume less than 2 femtoliters.

Both the printed line and droplets display an asymmetry to the left. This effect is likely caused by a non–uniformity in the printing process. When the printing plate and the target substrate were drawn apart, one side of the substrates separated first, causing the polymer stripe which bridged the two substrates to undergo an instability similar to viscous fingering. For the case of a liquid sheet between separating solid substrates, the fingering instability can be analyzed in the Newtonian or perfectly–plastic limit [8]. The fingering wavelength, λ, is given by:

$$\lambda_{Newtonian} = \pi\sqrt{\frac{\gamma h^2}{\eta V}} \approx 26\mu m \tag{3}$$

$$\lambda_{plastic} = \pi\sqrt{\frac{2\gamma}{\tau_0}}h \approx 0.21\mu m \ , \tag{4}$$

where τ_0 is the yield stress for the plastic liquid. (Between the dip–coating and printing processes, much of the water evaporates from the PEO solution, leaving behind a semi-solid substance.) We estimated λ using $\gamma_{PEO} = 53.5$ mN/m (which assumes that the semi-solid PEO has a surface tension equal to that of the aqueous solution), $h = 0.5\mu$m, $V = 100\mu$m/s, and $\tau_0 = 11.7$ MPa [9]. The values obtained represent two possible limiting behaviors. The experimentally observed wavelength [Figure 4 (a)] is about 2μm, which lies inbetween the two estimates. Since the fingering process cannot be eliminated altogether, one possible solution is to increase the value of λ beyond the typical feature size, by increasing the film thickness or decreasing the plate separation velocity for Newtonian liquids. Alternatively, a post–processing step like annealing can eliminate some asymmetries or defects introduced during printing. Control of ink rheology is equally important in preventing filament formation (Fig. 4(b)), as well as ribbing and misting during the printing process [10].
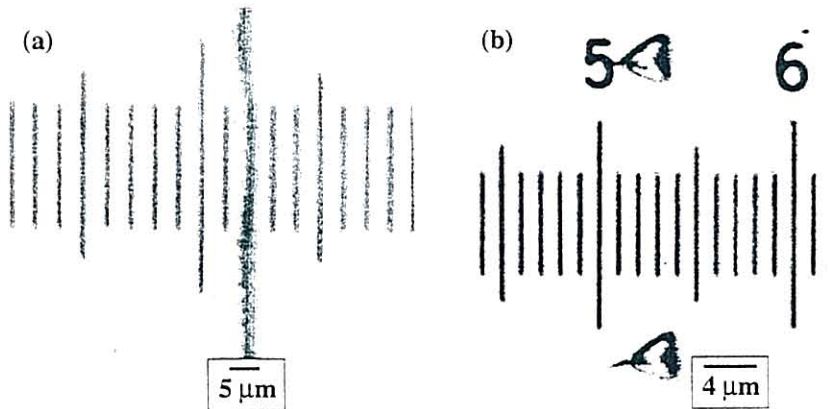

Figure 4: Polymer structures printed onto an unpatterned (hydrophilic) substrate. PEO was deposited from aqueous solution by dip-coating and then printed onto an SiO$_2$ surface. (a) A stripe of PEO 3.5 μm wide. (b) Two droplets of PEO printed onto a SiO$_2$ surface. The droplet volume is $\sim$ 2 femtoliters.

SUMMARY

Stable liquid and polymer structures can be formed by dip-coating chemically patterned substrates into a liquid reservoir and withdrawing at constant speed. The desired liquid shapes form on substrates coated with a pre-patterned self-assembled monolayer of OTS or HDT. Microscale feature sizes are easily obtained. For a dip-coated sample consisting of well spaced vertical hydrophilic stripes surrounded by hydrophobic regions, the maximum deposited film thickness scales as $W\,Ca^{1/3}$, where W is the stripe width and Ca the capillary number based on the plate withdrawal speed, a result well confirmed by experiment. This correlation is markedly different from the classic Landau-Levich result for the dip-coating of chemically homogeneous surfaces. The dependence on the stripe width, W, permits the deposition of very thin liquid layers. The liquid microstructures formed by dip-coating are then brought into contact with a hydrophilic surface to mimic an offset printing press. This techique has so far printed $5\mu m$ wide PEO stripes. Optimization of this process should lend itself to the rapid reproduction of liquid and semi-solid microstructure elements.

ACKNOWLEDGMENTS

REFERENCES

1. R. Moaz and J. Sagiv, J. Coll. Interface Sci. **100**, 465 (1984).

2. A. Kumar, H.A. Biebuyck, and G.M. Whitesides, Langmuir. **10**, 1498 (1994).

3. C.S. Dulcey, J.H. Georger Jr., V. Krauthamer, D.A. Stenger, T.L. Fare, and J.M. Calvert, Science. **252**, 551 (1991).

4. A.A. Darhuber, S.M. Troian, S.M. Miller, and S. Wagner, J. Appl. Phys. **87**, 7768 (2000).

5. L. Landau, and B. Levich, Acta Physicochimica U.R.S.S. **17**. 42 (1942).

6. A.A. Darhuber, S.M. Troian, J.M. Davis, S.M. Miller, and S. Wagner, J. Appl. Phys. *submitted*.

7. D. Qin and Y. Xia, and G.M. Whitesides, Adv. Mater. **8**. 917 (1996).

8. R.J. Fields, and M.F. Ashby, Phil. Mag. **33**, 33 (1976).

9. F.E. Bailey, Jr., and J.V. Koleske, ed. *Poly(ethylene oxide)*, (Academic Press, New York, 1976), p. 132.

10. J.E. Glass, and R.K. Prud'homme, in *Liquid Film Coating*, edited by S.F. Kistler, and P.M. Schweizer (Chapman Hall, London, 1997), pp. 137-182.