Patterning of polymers: precise channel stamping by optimizing wetting properties

Ralf Seemann, Edward J Kramer and Frederick F Lange

Mitsubishi Chemical Center for Advanced Materials, University of California, Santa Barbara, CA 93106, USA
E-mail: ralf.seemann@physik.uni-ulm.de

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Abstract. Channel stamping is a soft lithography technique that can be used to fabricate small structures of polymeric materials. This technique is cheap and easy but a considerable drawback is the fact that reproduction of the patterns of the stamp is often imprecise due to the wetting properties of liquid and stamp. In this paper, we report on experiments that reveal the parameters governing the behaviour of liquids in grooves and on edges. Optimizing these parameters leads to better-quality channel-stamped structures and enables the design of sophisticated structured polymeric materials, allowing channels as small as about 100 nm to be fabricated. Moreover, we show that it is even possible to build up a freestanding three-dimensional structure by stamping line patterns on top of each other.

Polymeric materials that are structured on a small length scale are gaining increasing interest in modern science and technology, e.g. for lab-on-chip technologies, organic microelectronics or for holographic data storage devices. Various methods have been developed in the last few years to structure polymeric materials in an easy, cheap and reproducible manner. Most of them can be summarized as ‘Soft Lithography’. In particular, the group of Whitesides contributed significantly in developing and perfecting soft lithography techniques (see [1] and references therein). The best-known technique is ‘micro-contact printing’. In this case, a PDMS rubber stamp is used similar to a conventional stamp, where the ink is transferred from the ridges of the stamp to the substrate. As ink, special molecules are used to create a self-assembled monolayer (SAM) on top of the substrate. Using this method, a chemical wetting in contrast with lateral feature sizes down to about 100 nm can be printed on a surface. To print small but elevated structures, techniques such as channel stamping [2, 3], also called micro-transfer-moulding in the literature [1], are applied. These techniques use the inverse pattern of the stamp—the grooves—to print small elevated features. In this case, the grooves are filled with a special liquid, usually

1 Present address: Max-Planck-Institute for Flow Research, Bunsenstrasse 10, 37075 Göttingen, Germany.
Preparing the stamp: pour PDMS prepolymer over master
cure, peel off

Filling the stamp: prepolymer
remove excess material

Stamping: place on the support
cure with UV-radiation, lift off

**Figure 1.** Liquid Sylgard 184 (Dow Corning) is moulded against a silicon master. After curing the PDMS, the stamp is removed from the master. The stamp can be filled by spin coating or dip coating. The filled stamp is placed on a support. The prepolymer is cured via UV radiation within a few seconds. The stamp is lifted off from the stamped structure.

UV-curable prepolymer^2^ or inorganic precursors [2, 3]. After placing the stamp on a support and solidifying the liquid, the stamp is removed and the inverse pattern of the stamp is transferred to the substrate. The process is shown in figure 1. A clear advantage of channel stamping over micro-moulding in capillaries, solvent-assisted micro-moulding [1] or imprinting [4, 5] is that the printed structures are free from excess polymer and that even free-standing polymeric structures can be printed see (figure 2(c)).

**Figure 2.** Polymer structures that were printed from only partly filled grooves. (a) Continuous ridges were transferred pressing the stamp on to the substrate during solidification. (b) Capillary forces drained the liquid from some regions after placing the stamp on the support. (c) Scanning electron micrograph (SEM) of free-standing polymer ridges fabricated by two subsequent printing processes perpendicular to each other.

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^2^ The (UV-)curable polymers and their sources are listed below: SK-9 and J-91 were purchased from Summers Optical; Vitralit 6127 from Panacol-Elosol GmbH; UV-901 from Optum International Ltd; XERT CF, XERT 50SP, XERT 50, XERT 25 and KOA 300 from Kemxert Corp. York; KCD-308, KCD-308K and KCD-308L from Nippon-Kayaku Co.; Sylgard 184 from Dow Corning.
would not reproduce exactly the form of the stamp. After placing the stamp on the support, the liquid morphology has to change its shape to correct for the missing liquid volume. The capillary forces lead to complete filling in some places and drainage from other places. As depicted in figure 2(b), a broken ridge is transferred to the substrate. Pressing the stamp onto the support during solidification can reduce the volume of the groove after filling. Continuous channels are printed to the substrate, but due to the deformation of the stamp, the height and shape of the stamped ridges are poorly controlled, as can be seen in figure 2(a). For free-standing structures, an additional effect might occur provided too much of liquid volume is not missing. The prepolymer forms arches to spare some volume of liquid. The excess material from overfilled grooves will be squeezed out and the areas between the stamped structures will be wetted with polymer. The aim of this paper is to study the parameters that govern the wettability of liquids in grooves to optimize channel-stamping techniques.

First, we will describe the wetting properties of certain parts of stamps, namely edges and wedges. Then, we will evaluate experimentally the possible morphologies small liquid volumes exhibit when put on patterned substrates. With this knowledge, we will then be able to tailor a system of stamp material, groove size and liquid that allows us to generate structures that reproduce exactly the morphologies of the stamp.

The characteristic features of topographically structured substrates are edges and wedges: liquids prefer to wet wedges than planar surfaces, provided that the intrinsic contact angle is sufficiently small. Wedge wetting occurs for wedges with an opening angle $\alpha$ if the contact angle $\theta$ of the liquid is below $90^\circ - \alpha/2$. Here, wedge wetting extends to its entire length.

For larger contact angles, the liquid forms isolated droplets that are confined to a finite length of the groove \[6, 7\]. In the particular case of grooves having a triangular cross-section and an opening angle $\alpha = 90^\circ$, as shown in figure 3, wedge wetting occurs for liquids below a critical contact angle $\theta = 45^\circ$.

On a smooth substrate, the contact angle of a liquid droplet in mechanical equilibrium is given by the Young–Dupré equation $\sigma_{lv} \cos \theta = \sigma_{sv} - \sigma_{sl}$, where $\sigma_{lv}$, $\sigma_{sv}$ and $\sigma_{sl}$ are the interfacial tensions of the liquid–vapour, solid–vapour and solid–liquid interface, respectively \[8\]. The shape of droplets having dimensions that are well below the capillary length, but still large when compared with the interaction length of long-range wetting forces is governed only by interfacial energies. As sketched in figure 4, the contact angle of a liquid is well defined at the left and on the right side of the edge. However, right at the edge, the equation of Young and Dupré is not valid. The liquid is free, within $\alpha - 180^\circ$, to form any angle between the contact angles of the left and the right side of the edge. As to the example shown in figure 4 for an edge with an opening angle of $270^\circ$, the ‘contact angle’ with respect to the right side can take up any value between...
Figure 4. A sketch of liquid wetting an edge with an opening angle of $\alpha = 270^\circ$. Left: the contact angles on the left and right sides of the edge are well defined. Right: the contact angle at the edge can vary in between the contact angle of the left and right sides.

$\theta$ and $\theta + 90^\circ$. Hence, the contact line may be pinned down for certain liquid morphologies on topographic substrates.

Laplace derived an expression for the pressure difference across a curved interface in terms of surface tension and mean curvature. The Laplace pressure $P_l$ is given by

$$2\sigma_{lv}M = P_l - P_v,$$

where $P_l - P_v$ is the difference in bulk pressures between the liquid and vapour phases. The mean curvature $M$ is defined as the sum of both principal curvatures of the surface of the liquid–vapour interface in equilibrium: $M = (1/r_1 + 1/r_2)$. Therefore, a positive mean curvature refers to a positive pressure contribution and vice versa. Due to Laplace pressure, only interface morphologies with constant mean curvature can be mechanically stable. If we, for instance, connect two droplets of different size placed on a plane substrate through a liquid channel, we observe that the smaller one is drained into the larger one immediately due to the different surface curvatures. This means that, for wetting morphologies in grooves, the cross-section of an extended liquid morphology spreading in the direction of a groove has to be a segment of a circle or two equal parts in case of wedge wetting. In particular, the mean curvatures of the liquid spreading along the wedges and the liquid spanning the whole width of the groove can be the same and, if so, the two morphologies can coexist in equilibrium. Hence, for a topographic substrate, the Laplace pressure of small and large liquid structures might be the same. From these basic considerations, we recently derived a morphological diagram for liquid morphologies in grooves with a rectangular cross-section by minimizing the free energy of a liquid morphology for a given geometry, a given contact angle and a given liquid volume [9].

To explore the various liquid morphologies experimentally, we performed wetting experiments with grooves of a rectangular cross-section. The cross-section was chosen to resemble the shape of a typical stamp used for channel stamping. The grooves were fabricated in silicon by standard photolithography methods. A positive photo-resist was spin-coated on the silicon substrate and exposed to UV radiation through a chromium mask. For very small feature sizes, the exposure was performed by an interference technique leading to a holographic grating with structure dimensions down to about 100 nm. The photo-resist structures were developed and the silicon samples—decorated with a photo-resist pattern on top—were etched in a pulsed-ion
gas etcher. After etching the grooves, the remaining photo-resist was removed by immersing the sample in organic solvents. By this procedure, grooves with a width of 400 nm–3 µm and a depth of 100–900 nm were fabricated in silicon, leading to an aspect ratio of depth/width of 0.04 : 0.6. The surface energy was tailored by covering the surface with a SAM of semi-fluorinated trichlorosilanes (F(C₂F)₈(CH₂)₂SiCl₃, purchased from Gelest, Tullytown, PA, USA). Before coating, the silicon wafers were degreased by ultrasonic cleaning in ethanol, acetone and toluene. Residual hydrocarbons were etched away by a 30 min dip in a fresh 1 : 1 H₂SO₄ (concentrated) / H₂O₂ (30%) solution. Subsequently, the acids were removed by thoroughly rinsing in hot Millipore™ water. Cleaning and coating were performed in a class 100 clean room. For fine-tuning the wettability, an oxygen plasma treatment was performed for a certain additional time (Harrick PDC-32G). Liquid structures on these substrates were created by exposing the substrates for 6–48 h to oversaturated vapour of short-chained polystyrene (polystyrene: \( M_w = 2 \text{ kg/mol, } M_w/M_n = 1.06 \), purchased from Pressure Chemical Company, Pittsburgh, PA, USA; \( M_w = 1.89 \text{ kg/mol, } M_w/M_n = 1.06 \), from Polymer Standards Service, Mainz, Germany). During this exposure time, the polystyrene vapour condenses on the substrate, creating liquid morphologies. Owing to the slow evaporation process, we assume the liquid structures to be in equilibrium. Lowering the temperature below the glass transition temperature, the former liquid structures can be easily analysed by scanning force microscopy (SFM) or scanning electron microscopy (SEM). Previous SFM studies have shown that the morphology of the liquid is conserved by cooling without any detectable change [10]. Figure 5 depicts three characteristic wetting morphologies. Some liquid surfaces exhibit positive mean curvature and others negative mean curvature. In an extended study [9], we show that they are in agreement with analytical calculations and numerical simulations. For two types of morphologies, the liquid is confined to the groove and spreads along the groove (figures 5(b) and 5(c)). These morphologies are especially important for the channel-stamping technique. Because of its prominent shape, we call these liquid morphologies ‘liquid channels’. The length of a liquid channel depends on the amount of liquid in the groove. Droplet-like morphologies, similar to the one shown in figures 5(a) and 5(d), are mechanically unstable. They are not confined to grooves and spread on top of the ridges. Unstable morphologies occur for very shallow grooves or for very large contact angles. For smaller contact angles and deeper channels, the liquid forms ‘lemon-shaped’ droplets. The length of the ‘lemon’ increases due to a decrease in the contact angle or an increase in the aspect ratio of the groove. This finally leads to metastable liquid channels that are confined to grooves and that exhibit a positive Laplace pressure (cf figures 5(b) and 5(e)). If we continue to lower the contact angle or to increase the aspect ratio, the Laplace pressure of the liquid morphologies decreases and finally changes its sign, forming liquid channels with a negative mean curvature as shown in figures 5(c) and 5(f). These liquid morphologies are mechanically stable. Owing to the rectangular cross-section of the groove, wedge wetting occurs for contact angles below 45°. Hence, the liquid channels or droplet-like morphologies are in coexistence with liquid spreading along the wedge of the groove.

In general, a rich variety of mechanically stable, metastable or unstable liquid morphologies can be found, depending on the contact angle and geometric details of the grooves. Similar liquid morphologies can be found on chemically structured substrates [11]–[16]; however, on topographically structured surfaces, the number of possible wetting morphologies is clearly larger [9]. One particularly attractive aspect of liquid condensates in wedges or grooves is that their surface can exhibit a negative mean curvature. This allows for stabilization of liquid structures in contact with a large reservoir at zero pressure, or in the presence of vapour close to saturation.
Figure 5. Scanning force micrographs of liquid morphologies on topographically structured substrates. (a) Aspect ratio $a = 0.062(1)$, contact angle $\theta = 52(1)^\circ$; the droplet morphology is not confined to the groove. (b) $a = 0.067(1)$, $\theta = 22(2)^\circ$; the liquid channel shows a positive Laplace pressure $P_l > 0$ in coexistence with a liquid wedge. (c) $a = 0.17(1)$, $\theta = 18(2)^\circ$; the liquid channel with $P_l < 0$ in coexistence with a liquid wedge. (d)–(f) show the horizontal cross-sections of the respective SFM image on top of it taken at the middle of the image. Wedge wetting is clearly visible in (f).

Even more possibilities for generating complex fluid microstructures can be envisioned by combining topographically and chemically structured patterns.

What did we learn from the study of the wetting properties of edges and wedges for optimizing channel stamping? To print polymeric structures on a support that resembles closely the shape of the stamp, we have to work in the wetting regime where the liquid forms elongated channels with negligible Laplace pressure. Figure 6 shows scanning electron micrographs of channel-stamped ridges from evenly filled grooves with feature sizes less than about 100 nm. The printed structures resemble closely the shape of the grooves of the stamp whereas the area between the ridges is free of polymer.

Moreover, we can print structures that are clearly smaller than the actual stamp structure. Working in a wetting regime with a low contact angle where the wedge wetting occurs (below 45° for grooves with rectangular cross-section), the wedges of the groove are wetted by liquid spreading along the entire length of the groove provided that the amount of liquid in the groove is of the right order of magnitude. The left side of figure 7 shows an example where two lines with a width of about 250 nm were printed by one groove with a width of about 1.8 µm. The
Figure 6. SEM micrographs of polymer (KCD-308L, Nippon-Kayaku Co.) structures fabricated by channel stamping on a glass substrate. The stamped structures clearly resemble the shape of the grooves with a rectangular cross-section and an aspect ratio (depth/width) of about 0.5. To fill the grooves almost evenly with UV-curable polymer, the PDMS stamp was immersed for about 5 min in the polymer before dip coating. Left: the channel width is about 1.8 µm. Right: the channel width is about 100 nm.

Figure 7. Channel-stamped polymer structures of KCD-308L (Nippon-Kayaku Co.) on a silicon substrate. The aspect ratio of the grooves is about 0.5. The stamp was immersed for about 30 min in the UV-curable polymer before dip coating. By this procedure, the contact angle could be lowered in order that the filled grooves exhibit a remarkable negative curvature. In contact with the support, the liquid channel breaks up into completely filled compartments and compartments in which only the wedges are wetted. The various compartments are in contact with each other. Right: optical micrograph; printed chains of consecutive liquid segments. Left: SFM micrograph; close up from the image on the right side. The right side of this micrograph shows two solidified liquid wedges printed from a groove that is only partly filled.
‘excess’ liquid in the stamp was drained by heavily spinning the stamp after filling the grooves by dip coating. Using wedge wetting for printing small features, the cross-section of the printed structure will be wedge-like. By curing the prepolymer while the stamp is still in contact with the support, we can transfer structures that exhibit the shape of a wedge. By removing the stamp from the support just before the prepolymer is cured or before it is cured completely, the liquid polymer is allowed to flow. Under these conditions, the stripe of prepolymer, which originally had a wedge-shaped cross-section in the groove, is transferred to the substrate and assumes a cross-section on this flat surface as a segment of a circle.

In the wetting regime of channels, the liquid forms consecutive liquid channels with finite length if the liquid volume is not sufficient to fill the entire groove. In the regime of contact angle and aspect ratio where liquid channels are formed (cf figures 5(b) and (c)), the liquid in a single groove forms several channels of finite length rather than one extended channel if the liquid volume is not sufficient to fill the entire groove. This chain of short liquid channels can be printed to a substrate. An example is shown on the right side of figure 7. The missing liquid volume defines the distance and the length of the separate segments.

It is even conceivable to print hollow structures by channel stamping: in case the aspect ratio of the groove is in an intermediate range and the contact angle of the liquid is small enough, the liquid might form a continuous wetting layer in the capillary, which is formed out of the groove and the substrate.

It is obvious that the morphologies of liquid in the grooves of the stamp must be precisely controlled to use channel stamping in a well-controlled manner. The wetting morphologies depend on the aspect ratio of the grooves and on the wettability of the substrate. To print various structures for a given aspect ratio, it is crucial to be able to tune the wetting properties of the stamp precisely. We will therefore explore techniques for manipulating the wettability of the stamp.

Usually, the stamp is fabricated from PDMS rubber owing to its favourable mechanical properties and the fact that it can be moulded easily against various masters. PDMS rubber is transparent and enables easy positioning of the stamp on the support. The transparency extends up to wavelengths of light of about 300 nm [17]. Hence, UV-curable prepolymer can be cured easily by illuminating the stamp with a typical wavelength of 365 nm, which is optimal for many commercial photoactive prepolymer. In the following, we will therefore restrict our attention to the wetting properties of PDMS surfaces. The wetting properties can be varied either by choosing from various liquid prepolymer with different wetting properties or by varying the wettability of the stamp by treatment of the PDMS surface. The wetting properties can be varied either by choosing from various liquid prepolymer with different wetting properties or by varying the wettability of the stamp by treatment of the PDMS surface. In figure 8, the contact angles of various commercially available UV-curable prepolymer on PDMS rubber are displayed. Those prepolymer having low viscosity (<300 Pa s) and low shrinkage (<4%) were selected so as to be appropriate for channel stamping. By choosing an appropriate prepolymer, we have access to most of the possible wetting morphologies in grooves with a rectangular cross-section. The accessible range of contact angle can be increased even further by the particular interaction of the prepolymer with the PDMS: most UV-curable prepolymer diffuse into the PDMS rubber. The contact angle of the prepolymer on the slightly swollen PDMS surface is decreased as a function of immersion time, reaching a plateau value for very long immersion times. As an example, the contact angles of various prepolymer after immersing the PDMS samples for 5 min in the respective prepolymer are shown on the left of figure 8. After 5 min, the contact angle is typically reduced by 10–15°. Immersion of the stamp for various time periods can be used to achieve a suitable contact angle on the stamp as long as the swelling does not significantly
alter its dimensions and mechanical properties. This can be done easily, e.g. by dip coating. The stamp will be withdrawn from the prepolymer reservoir after a certain soaking time rather than withdrawing immediately.

In cases where it is not possible to choose an appropriate prepolymer, e.g. because suitable candidates may swell the stamp, thus altering its dimensions and mechanical properties, it may be necessary to modify the surface of the PDMS.

To decrease the contact angle for prepolymers that barely diffuse into PDMS or for those whose saturation contact angles after long soaking times are still unsatisfactory, the PDMS surface can be oxidized by a very gentle treatment with UV-ozone. With increase in UV-ozone treatment time, the water contact angle is decreased, reaching a plateau value of almost zero, as can be seen on the right of figure 8. Ozone treatment converts the PDMS rubber surface partly into silicon oxide, whereas the mechanical properties of the underlying rubber are basically unchanged [18]–[20]. A silicon oxide surface on top of the PDMS enables the use of well-known surface chemistries to modify the wettability of glass or SiOx surfaces: e.g. SAMs can be formed on top of the partly oxidized PDMS surface. To increase the water contact angle to a value above the typical value known for these grafting methods on a glass or silicon surface, we can take advantage of the elastic properties of PDMS with a low Young’s modulus. The packing density of the monolayer and the contact angle can be increased by stretching the PDMS during the oxidation and grafting processes. After relaxing the PDMS rubber, a water contact angle of 130° with a very low wetting hysteresis can be achieved with semi-fluorinated trichlorosilanes (F(C2F)3(CH2)3SiCl3) [19]. This value is about 15° above the contact angle of water for the same molecules grafted on a rigid silicon substrate. All the above-mentioned techniques for modifying the contact angle permit access to a wide range of contact angles for a given liquid on a PDMS surface.

**Figure 8.** Left: contact angle of a sessile droplet of various UV-curable polymers on Sylgard 184 (Dow Corning). The measurements were performed with an optical goniometer. The upper data points depict the contact angle without preliminary soaking time. The lower data points give the contact angle after 5 min soaking time before contact angle measurement. Right: reduction of the water contact angle on Sylgard 184 as a function of the UV-ozone treatment time.
In conclusion, we show in this paper that we can use our knowledge of the family of morphological structures that are possible for a given liquid in a rectangular groove geometry to select and print-specific structures. The selection of a structure is done by adjusting two parameters, the contact angle of the liquid on the channel material and the aspect ratio of the rectangular groove. The former can be changed by the techniques mentioned above, e.g. UV treatment, and the latter by choosing a stamp morphology. Thus, structures that closely resemble the shape of the stamp can be printed. Moreover, small wedges with twice the periodicity of the stamp, chains of short channels and even free-standing ridges can be fabricated. Certainly, channel stamping can be used for any kind of liquid, provided its viscosity is low enough to reach equilibrium within a short time and it can later be solidified. Using materials with significant shrinkage or expansion during solidification, we can account for the change in volume, e.g. by over-filling or under-filling the grooves. Here, in contrast with materials with no volume change during solidification, it might be desirable to work in a wetting regime with a certain distance from the border where the curvature of the liquid surface changes its sign.

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