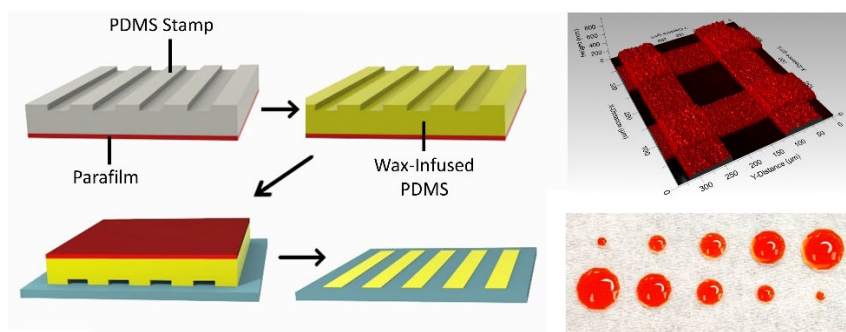




Hydrophobic surface patterning with soft, wax-infused micro-stamps

Soroosh Torabi¹, Zhuoyun Cai², Jonathan T. Pham², Christine A. Trinkle^{1*}

¹Mechanical Engineering, University of Kentucky, Lexington, KY, 40506, United States

²Chemical and Materials Engineering, University of Kentucky, Lexington, KY, 40506, United States

*Corresponding author: 277 Ralph G. Anderson Building, University of Kentucky, Lexington, KY 40506-0503, United States. Phone: 859-218-0640. E-mail: c.trinkle@uky.edu

Abstract

Hypothesis: Waxy hydrocarbons diffuse freely in polydimethylsiloxane (PDMS), and this capability can be leveraged to generate inexpensive surface micropatterns that modify adhesion and wetting.

Experiments: Patterns are created by placing a waxy Parafilm sheet on the back of a PDMS stamp containing microscale surface features. When heated, the paraffin liquefies and diffuses through the stamp, creating a thin liquid layer on the micropatterned stamp surface; when placed in contact with a target surface, the layer solidifies and is retained on the target when the stamp is removed. Micropatterns were generated on different materials and surface topographies; pattern geometry was evaluated using optical profilometry and changes in wetting were evaluated using contact angle goniometry. Diffusion of paraffin through PDMS was evaluated using XPS.

Findings: Wax micropatterns have submicron lateral resolution and thickness ranging from 85–380 nm depending on contact time. By using XPS analysis to track paraffin diffusion within the PDMS stamp during this process, we estimate the diffusion coefficient to be $5.3 \times 10^{-7} \text{ cm}^2/\text{s}$ at 65°C . This means that the paraffin layer at the stamp surface replenishes in less than a second after stamping, so it can be used multiple times without re-inking to deposit complex, multi-layer paraffin patterns.

Keywords

Hydrophobic patterning, Polydimethylsiloxane (PDMS) stamp, Paraffin diffusion, Microcontact printing.

Introduction

Waxy hydrocarbons are an important class of materials that offer hydrophobic character, semi-solid feel, and biocompatibility. Hence, paraffinic waxes are found in a host of daily-use applications, from candles and artistic sculptures to cheese coatings and children's crayons. Moreover, paraffin wax is an inexpensive material that is widely available to researchers. Hence, using wax as a material for hydrophobic micropatterning may offer a simple and easily accessible route to tune surface properties for a broad range of advanced applications, from patterning cells to controlling wetting and adhesion.

To create hydrophobic micropatterns, several approaches currently exist. Topographical modification of the primary surface itself can be done by plasma exposure [1, 2] or etching [3, 4] to selectively change local surface roughness. Additive approaches can also be used to create micropatterns by selective deposition of a secondary material onto the primary surface using a variety of methods, with microcontact printing being the most widely used. In microcontact printing, various materials have been selectively added to a surface to create distinctive hydrophobic and hydrophilic regions, including self-assembled monolayers (SAMs) [5, 6], biomolecules [7], and polymers [8]. However, these methods typically require pre-modification of the target surface before deposition and/or the use of expensive chemicals or solvents, which is typically undesirable. Using a material that does not require pre-modification can offer a route for higher throughput.

By contrast, paraffin wax is low-cost and widely available, can be deposited onto a variety of surfaces without prior chemical modification, and the patterns can be easily removed and reprinted indefinitely. The moderate melting temperature (42-80°C [9]) of paraffin wax also makes it compatible with a wide range of fabrication techniques. For example, Carlen et al. [10, 11] deposited a 3-10 μm thick paraffin film using thermal evaporation and patterned it using reactive ion etching (RIE). 2-10 μm thick films have also been deposited using spin-coating and patterned using lift-off [12], wet etching, or dry etching [13]. While these methods are capable of micrometer-scale resolution, they require access to advanced and expensive equipment or use of harsh chemicals. Moreover, the patterns are relatively thick (in the range of micrometers). Another patterning method is paraffin inkjet printing, broadly used in paper microfluidics [14] and more recently in hydrophobic patterning of glass and plastic surfaces [15]. This method can generate patterns quickly—making it useful for prototyping—however it also requires access to specialized equipment and is best suited for lower resolution ($\sim 30\mu\text{m}$) patterns.

On the other hand, microcontact printing has been a common method for patterning surfaces because it is a relatively easy process. In conventional microcontact printing, a structured, polydimethylsiloxane (PDMS) stamp is first prepared through photolithographic methods. The structured side of the stamp is then put into contact with the desired ink, transferring the ink to the top of the stamp structures. The stamp is then brought into contact with the target surface, printing the ink. However, re-inking is typically required to create multiple patterns, and there is little to no control over the thickness of the deposited layer. Moreover, it can be challenging to create thin patterns of waxy, highly viscous materials. For example, Kuo et al. [16] used dip-coating of a PDMS stamp to transfer molten paraffin wax patterns onto glass and aluminum surfaces, but with thicknesses of close to 5 microns. Hence, a simple process that enables repeat printing without re-inking, combined with the ability to tune sub-micron pattern thicknesses, would be beneficial.

In this work, we present an easy and accessible stamping method that can be used to deposit hydrophobic paraffin wax patterns with sub-100 nm thickness on a variety of surfaces. This method relies first on the diffusion of paraffin into a PDMS stamp, followed by a contact-printing process (Fig. 1a). The wax-infused

stamp serves both as the patterning mechanism and as a reservoir for the paraffin, which allows for reuse without re-inking; once a stamp is prepared, it can be stored in a heated environment virtually indefinitely and used to generate a pattern in only a few seconds. Master molds for PDMS stamps are fabricated using a commercially-available 3D printer, which avoids the need for a cleanroom environment. Wax-infused patterning of paraffin enables high resolution hydrophobic patterns on multiple substrate materials, on flat or curved surfaces, and it can even be used to generate complex multi-layer patterns on the same surface (Fig. 1 b, c). Unlike traditional microcontact printing, the thickness of our deposited paraffin layer is a function of the contact time and can be tuned to values between 80 nm and 350 nm. This allows the user to quickly and easily tune the pattern thickness without requiring additional equipment, such as a spincoater. Ultimately, the wax-infused PDMS stamping method offers a quick and reliable route to pattern hydrophobic surfaces with minimal infrastructural requirements, and is expected to be easily accessible to a wide range of researchers.

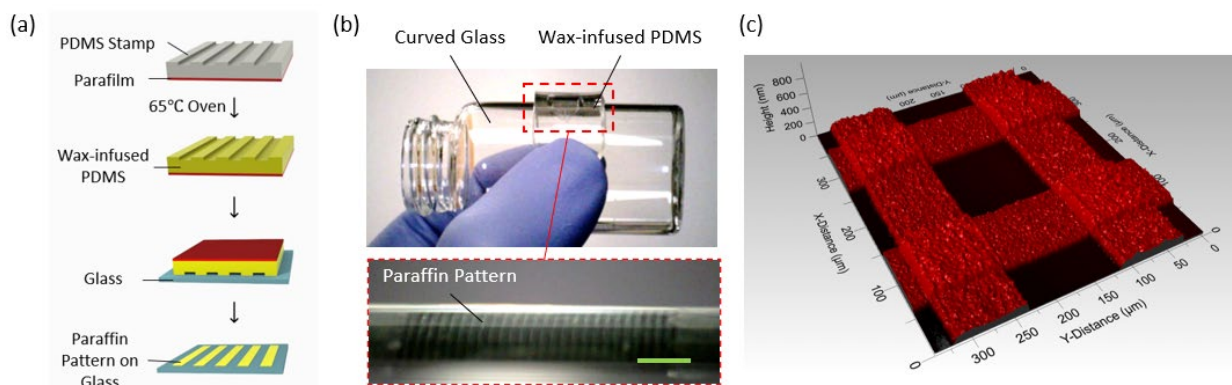


Figure 1. a) Wax-infused patterning of paraffin. Scale bar = 1 mm; b) paraffin pattern on curved glass; c) optical profilometry scan of a multi-layer pattern created by stamping multiple times on glass. Scale bar = 1 mm.

Methods and materials

Stamp fabrication

The master molds for the PDMS stamps were made using either 3D printing or photolithography. For 3D-printed molds, a stereolithography-based 3D printer (Form 3, Formlabs) was used to print master molds. Following printing, the parts were thoroughly washed and sonicated in an isopropyl alcohol (IPA) bath (FormWash, Formlabs) for 10 min. The parts were then blow dried with compressed air to remove excess IPA and allowed to air dry at room temperature for 30 minutes. The parts were then placed in a UV oven (FormCure, Formlabs) for 30 min at 60 °C temperature. After curing, a thin layer of mold release (Ease Release® 200, Mann Release Technologies) was sprayed on the 3D printed parts to facilitate peeling of the PDMS after curing.

For master molds made via soft lithography, one layer of SU-8 photoresist (SU-8 3050, MicroChem) was spincoated onto a clean silicon wafer (1500 rpm for 30 s), followed by a 1 min baking step on a hotplate at 65 °C, followed by a second spincoated layer of SU-8 (1000 rpm for 30 s)—resulting in a total thickness of 200 μm. Then the SU-8/silicon wafer was heated on a hotplate for 1 min at 65 °C, followed by 25 min at 95 °C. The wafer was then exposed to UV through a patterned photomask and then post-exposure baked on a hotplate for 1 min at 65 °C followed by 5 min at 95 °C. After cooling to room temperature, the uncross-linked SU-8 was removed by vigorously agitating the wafer for 5 min in SU-8 developer. The wafer was then rinsed in isopropyl alcohol (IPA 70% in water, Sigma-Aldrich) and dried with nitrogen gas. To

create a hydrophobic surface, the wafer was exposed to trichloro(1H,1H,2H,2H-perfluorooctyl)silane (Sigma-Aldrich) under vacuum for 40 min. Acrylic sheets (McMaster-Carr) were laser-cut and clamped to the silicon wafers in order to form sidewalls for the molds.

The PDMS stamps were made by mixing polydimethylsiloxane base and curing agent (Sylgard 184, Dow Corning) in a 10:1 ratio and degassing under vacuum for 1 h. The degassed PDMS mixture was poured into either a 3D printed or SU-8 master mold and placed in a 65°C oven for 2 h. The molds were then removed from the oven; after the assembly cooled to room temperature, the cured PDMS stamp was peeled from the mold.

Wax-infused stamping

For wax-infused stamping, a layer of Parafilm was placed on a glass slide, and then the PDMS stamp was placed on top, with the back of the stamp—the surface opposite the patterned surface—in contact with the paraffin (Fig 1a). The assembly was then placed in a 65°C oven for 24 h to saturate the PDMS with paraffin. To transfer the wax pattern to a target surface, the stamp was removed from the oven and the patterned surface of the PDMS was placed against the target substrate for 5 seconds at room temperature. When using the saturated stamp for multiple consecutive patterns, the stamp was reheated in the 65°C oven for approximately 3 min after each stamping step. Resulting patterns were measured using 3D optical profilometry (Profilim 3, Filmetrics).

Paraffin diffusion characterization

Blocks of unpatterned PDMS (8 mm x 4.5 mm x 1.5 mm) were cast using methods similar to that in the Stamp Fabrication section. A layer of Parafilm was placed on a glass slide in a 65°C oven for 10 min. Then, the PDMS blocks were placed on top of molten paraffin for either 20 minutes to capture transient diffusion of the paraffin into the PDMS, or for 96 h to create fully paraffinated PDMS. After the incubation time, the blocks were removed from the oven and allowed to cool to room temperature. X-ray Photoelectron Spectroscopy (XPS) (K-Alpha, Thermo Scientific) was used to trace atomic percentages of silicon, oxygen and carbon on the side surface of the PDMS cubes. Additionally, a plain PDMS block was analyzed to capture the PDMS XPS signal without paraffin.

Results and Discussion

Pattern formation, transparency, and stability

Our wax-infused patterning method relies on the fact that liquid paraffin can freely diffuse into a solid PDMS structure. This makes it possible to saturate a PDMS stamp with paraffin and use the same stamp numerous times without re-inking. Saturating the PDMS with paraffin is performed by placing a PDMS stamp with a Parafilm backing in a 65°C oven—just above the melting temperature of the paraffin wax. The molten paraffin diffuses into the PDMS stamp, and it reaches the outer boundaries of the stamp and wets those interfaces. When the stamp is removed from the oven and placed on a target substrate at room temperature, the outer molten paraffin layer temperature drops below the melting point and solidifies on the surface. When the stamp is removed, the solidified paraffin pattern is retained on the target substrate. Because the paraffin is sourced only through the stamp and there is minimal molten paraffin present at the stamping interface, there is no distortion or blurring of the transferred pattern.

This results in high fidelity hydrophobic patterns on the substrate that are nearly optically transparent, as shown in Fig. S1.

Due to the elasticity of the PDMS stamp, it can be bent to create conformal contact with non-flat surfaces, even when saturated with paraffin wax. To demonstrate this, we wrapped a 1.6 mm thick paraffin-saturated stamp around a 27.4 mm diameter glass vial, as shown in Fig. 1b. The resulting pattern transferred without any observed defects, indicating good contact during the transfer process.

Multi-layer paraffin patterns can also be achieved by consecutive patterning on the same target substrate. Because of the short contact time, this method can be applied multiple times on a single substrate without disrupting the previous pattern(s). Fig 1.c shows a multi-layer paraffin pattern created by two consecutive stamping steps, where the stamp was rotated by 90° between the first and second contact. This makes it possible to create complex paraffin geometries by layering sequential patterns of one or more PDMS stamps.

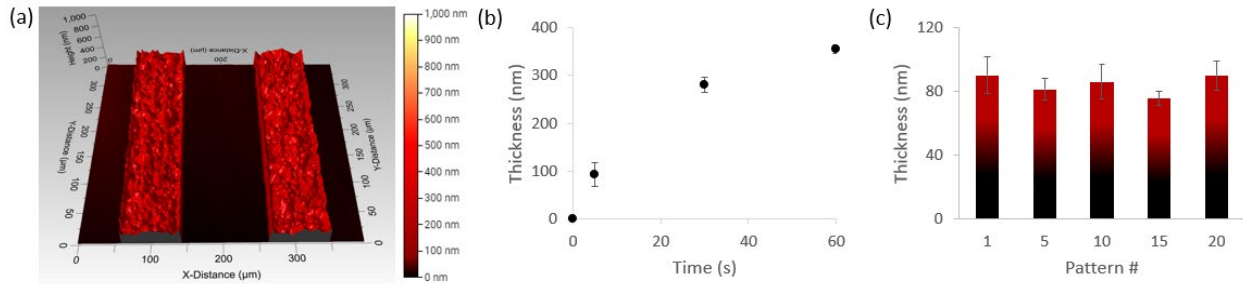


Figure 2. a) 3D topography of paraffin patterns deposited using our wax-infused stamping method after 60 seconds of contact; b) thickness of deposited paraffin pattern thickness vs contact time; c) thickness of deposited paraffin for 20 consecutive patterns using the same stamp (5 second contact time).

The average thickness of the paraffin layer was $355 \text{ nm} \pm 9.6 \text{ nm}$ (mean $\pm$ standard deviation), when the stamp and target surface were in contact for 60 seconds (Fig. 2a). By contrast, patterns created using microcontact printing for the same amount of time have been reported as being $4.5 \text{ }\mu\text{m}$ thick [16]. The difference in pattern thickness between the two methods implies that there is a smaller paraffin volume present on the surface of the wax-infused stamp compared to the microcontact printing stamp during contact.

The nature of the paraffin deposition makes it possible to adjust the paraffin thickness by changing the amount of time the stamp remained in contact with the target surface. As shown in Fig. 2b, the thickness of the deposited paraffin can be as thin as $84 \text{ nm} \pm 18 \text{ nm}$ for 5 seconds of contact time and up to $355 \text{ nm} \pm 9.6 \text{ nm}$ for 60 seconds of contact. 5 seconds is the minimum practical time for manual stamping, but it may be possible to achieve thinner layers by reducing the contact time in a more controlled fashion. The ability to make controlled submicron thickness patterns could be useful in applications where very fine pattern resolution is required, and thicker layers would create fragile, high-aspect-ratio paraffin structures. Additionally, while solid paraffin is white in color and opaque, the submicron paraffin patterns here are transparent, which avoids any optical interference when imaging (Fig. S2).

The geometry of the deposited paraffin patterns matches that of the original PDMS stamp with very high fidelity. This is significant because PDMS swells with absorption of many of the liquids to which it is permeable [17-19]; however, Dangla et al [20] reported no significant swelling of PDMS upon absorption of liquid paraffin, which allows the fully infused PDMS stamp in our method to remain close to its original

geometry. To verify this, we imaged microscale features on the PDMS stamp optically before saturation with paraffin and compared it to the resulting pattern deposited using the same stamp (Fig. S1); the geometry of the two is virtually identical. In order to characterize this more precisely, we measured PDMS micropatterned surfaces using 3D optical profilometry before and after paraffin saturation and found that features increased from $79.4 \pm 0.6 \mu\text{m}$ (unparaffinated) to $81.9 \pm 0.7 \mu\text{m}$ (paraffinated), or an increase of $\sim 3\%$.

Using paraffin-saturated stamps also makes it possible to reuse the same stamp multiple times without needing to re-ink. We demonstrated this by repetitive stamping using a single PDMS stamp; the stamp was briefly reheated in between consecutive stamping steps (~ 3 min in a 65°C oven) and brought into contact with a fresh, untreated glass surface each time. The resulting patterns were measured and showed no significant variation in feature height (Fig. 2c) even after 20 consecutive stamping events, demonstrating that the PDMS stamp functioned as an adequate reservoir without noticeable depletion of the paraffin wax.

To test the stability of the paraffin micropatterns in solutions relevant to biological studies, patterned surfaces were submerged in either cell culture media or 70% ethanol at 37°C for 4 days. Inspection of the patterns submerged in media showed no significant loss of pattern coverage during this time, although the surface roughness of the patterns increased (Fig. S3). The results of the media tests are significant, given that paraffin wax has been used in cell culture previously [15, 16]—so the ability of these patterns to withstand typical incubator conditions for several days supports its use in generating surfaces for selective cell adhesion and manipulation.

However, when the same paraffin patterns were exposed to static culture in an 70% ethanol solution, they degraded significantly during the 96-hour timeframe. Because the ethanol is able to successfully break up the paraffin layer, this makes it an ideal candidate for intentional removal of paraffin patterns. By rinsing the substrate with 70% ethanol and wiping off the liquid with a KimWipe, patterns can be completely removed—leaving no trace on the substrate—and a new pattern can be deposited on the same spot (Fig. S4). The contact angle of water on the glass surface was measured before paraffin deposition, after patterning, and again after the pattern had been removed. The contact angle before paraffin deposition and after paraffin removal were $47.0^\circ \pm 3.7^\circ$ and $45.5^\circ \pm 3.8^\circ$, respectively; thus patterns can be successfully changed multiple times in this way without any detectable residue.

Quantifying paraffin diffusion into PDMS stamps

Other researchers have used absorption of molten paraffin into PDMS to control PDMS transparency [21], small molecule and gas permeability [17], and surface energy [22]; but saturation was mostly achieved by submerging the PDMS in a liquid wax bath [21, 22]. This ensures absorption of paraffin into all PDMS surfaces, but a thick, non-uniform paraffin layer is formed around the block after removal from the bath. By contrast, our mechanism only places the original paraffin source into contact with the PDMS surface opposite of the patterned features. When the surrounding temperature is raised, the paraffin melts and follows a unidirectional diffusion path through the PDMS from the source side to the surface containing the micropatterned geometry.

As the paraffin diffuses along this path, it alters both the optical transparency of the PDMS and the material's carbon content, making it possible to track diffusion optically or by using XPS analysis. To measure this diffusion, we prepared a series of PDMS blocks with the same geometry (8 mm x 4.5 mm x

1.5 mm) and incubated some of them in a 65°C oven with Parafilm on one surface for either 20 minutes or 96 hours. Other blocks were not exposed to any paraffin to provide a negative control. Brightfield images of the three sample types are shown in Fig. 3a, and demonstrate a clear gradient that forms after only 20 minutes of exposure to liquid paraffin. After 96 hours, the samples are uniformly opaque.

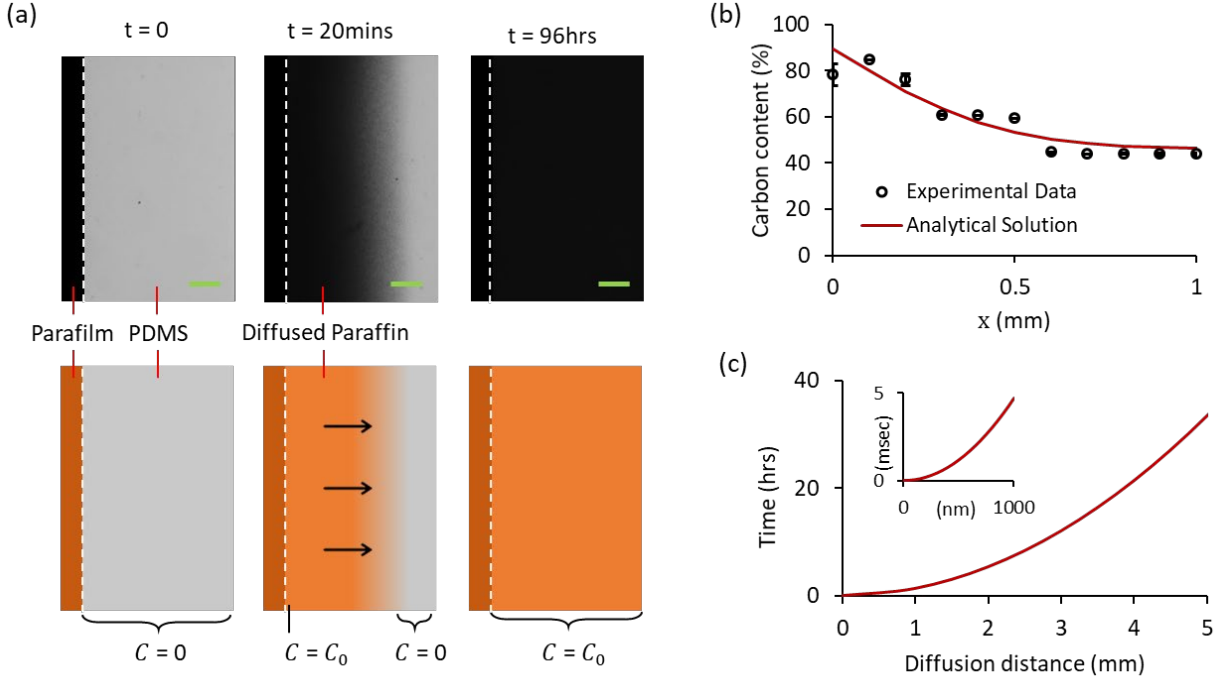


Figure 3. Paraffin diffusion in PDMS. a) Schematic view (top), and microscopic images (bottom) of the paraffin diffusion in PDMS; scale bar = 200 μm . b) XPS measurements of carbon content as a function of distance from the paraffin source in PDMS after 20 minutes of diffusion compared to analytical solution of 1-D diffusion where $D = 5.3 \times 10^{-7} \text{ cm}^2/\text{s}$. c) Estimated saturation time for given PDMS stamp thickness based on $D = 5.3 \times 10^{-7} \text{ cm}^2/\text{s}$.

This data qualitatively follows what is expected in 1-D diffusion from an infinite source at constant concentration. To test this in a more quantitative manner, we measured the samples using XPS at a number of discrete points at specified intervals from the source boundary. The resulting carbon content measurements, shown in Fig. 3b, show a similar gradient trend that was observed in the optical inspection. If we model this diffusion as 1-D transient diffusion from a source that keeps the paraffin concentration just inside the PDMS surface at a constant concentration (C_0), the internal paraffin distribution (C) as a function of time (t) and distance from the source (x) would follow the solution to Fick's second law of diffusion under these conditions:

$$C(x, t) = C_0 \cdot \text{erfc}(x/\sqrt{4 \cdot D \cdot t})$$

By using a best-fit of our data to this curve, we estimate the diffusion coefficient of paraffin in PDMS as being $5.3 \times 10^{-7} \text{ cm}^2/\text{s}$.

The predicted diffusion coefficient can be used as a basis to estimate the diffusion time to fully saturate the PDMS stamps for any given thickness (Fig. 3c). This makes it possible to estimate the time necessary for a PDMS stamp to be fully inked by paraffin. For example, for the 1.5 mm PDMS stamps used here, the

required saturation time was ~ 5 hours. Once the stamp is ready, each stamping deposits ~ 84 nm layer of paraffin on the substrate. Based on the predicted values in Fig. 3c, the time required to replenish the stamp interface after each stamp is $\ll 1$ s, which further validates the robustness of this method for rapid and consecutive patterning, as demonstrated experimentally in Fig. 2c.

Potential applications for paraffin micropatterns

The hydrophobic nature of paraffin patterns means that they can be used to confine small liquid droplets on a surface or to guide liquid motion. One of the most appealing applications for hydrophobic patterning is droplet isolation and manipulation in drug screening [23] and cell patterning [24, 25]. This is achieved by creating repetitive hydrophobic boundaries on a hydrophilic surface that can confine liquid droplets or cells to the hydrophilic regions. To illustrate this, we generated a 3D printed mold with circular features between 1 and 5 mm in diameter, cast a PDMS stamp from this mold, saturated the stamp with paraffin and used it to generate a paraffin pattern on an otherwise untreated glass surface. Paraffin formed the “background” of the pattern, leaving an array of hydrophilic circles on the glass. When aliquots of colored water with volumes ranging from 0.2 to 8 μ L were pipetted onto this surface, the hydrophobic pattern successfully confined the droplets to the pre-patterned regions, as shown in Fig. 4a.

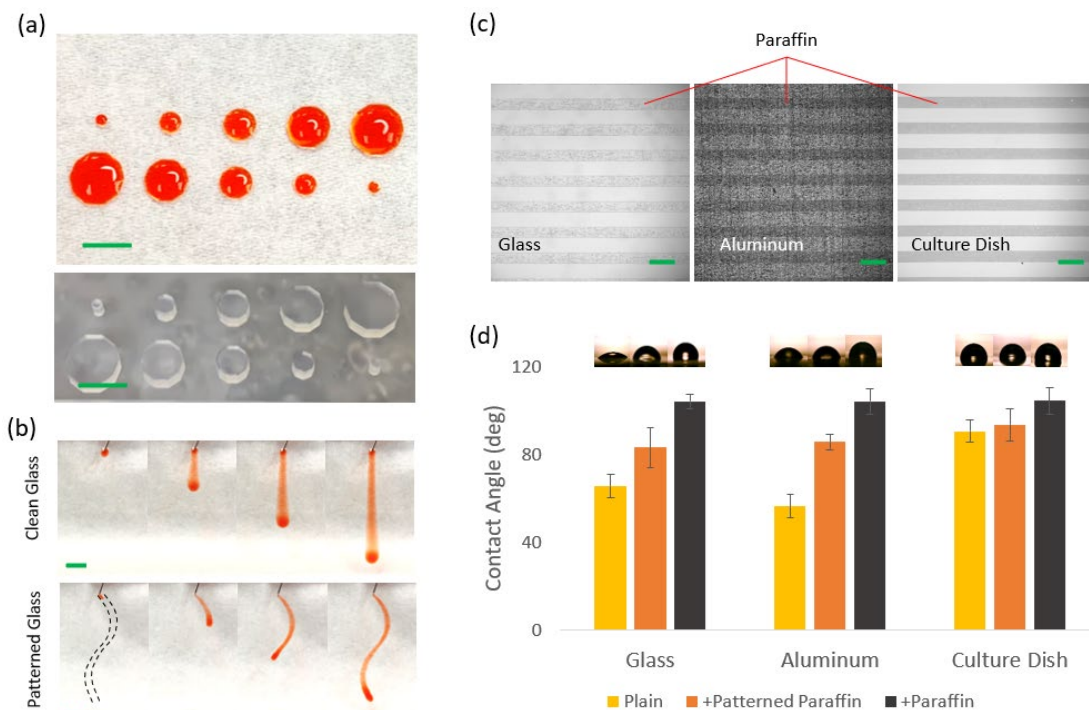


Figure 4. (a,b) Liquid confinement using paraffin patterns: a) colored water volumes of 0.2, 1, 3, 5, and 8 μ L confined by hydrophobic paraffin circles with respective diameters of 1, 2, 3, 4, and 5 mm (top) vs 3D printed master mold (bottom), scale bar = 5 mm, b) confined water flow on patterned glass (bottom) vs untreated glass (top), scale bar = 5 mm. (c,d) Modified contact angle on paraffin patterned surfaces: c) striped paraffin patterns on glass, polystyrene cell culture dish, and aluminum surfaces, scale bar = 200 μ m, d) contact angle of water on unpatterned surfaces, surfaces with uniform paraffin coating, and surfaces with striped paraffin pattern.

A similar method was used to guide liquid motion on a patterned surface. We created a 3D printed mold with a wavy-line feature to generate a wavy paraffin surface pattern on glass. Both the patterned glass and a clean glass slide were placed at an 80° angle and colored water was deposited at a rate of 200

$\mu\text{L}/\text{min}$ onto the upper region of the glass, as shown in Fig. 4b. On the plain glass surface, the water stream moves straight down the surface, as guided by gravity, and spreads out laterally as the liquid wets the hydrophilic surface. On the wavy patterned glass, the hydrophobic edges of the pattern create a surface energy barrier and force the water to remain confined to the paraffin-free regions and maintain a constant path width. These types of hydrophobic patterns can be used to guide liquid on macroscale surfaces [26, 27] and can also be used for applications like wall-less microfluidics [24, 28, 29] where liquid flow needs to be guided on a specific track.

Paraffin wax micropatterns can be applied to numerous different materials, and these patterns can be used to directly confine liquid as shown the previous experiments, or smaller features can be used to tune the apparent contact angle of the surface. We applied a pattern of $110\ \mu\text{m}$ width lines to glass, aluminum, and polystyrene surfaces (Fig. 4c). Then we measured the contact angle of a $10\ \mu\text{L}$ water droplet placed on untreated surfaces, surfaces with the $110\ \mu\text{m}$ paraffin patterns, and surfaces that had been stamped with a uniform layer of paraffin. The results, shown in Fig. 4d, display a significant change in the water contact angle between plain and fully paraffin-coated substrates; the value for the fully paraffin coated surfaces is also uniform across materials, demonstrating that the deposited paraffin layer is sufficient to mask the effects of the underlying substrate on contact angle.

On all three materials, the contact angle of water on surfaces with the striped paraffin pattern lies between the value for the bare material and the fully-paraffin coated material. The apparent contact angle (θ_c) for a surface containing an alternating pattern of two regions with unique measured contact angles (θ_1 and θ_2) can be predicted using the Cassie-Baxter equation [30]:

$$\cos \theta_c = f(\cos \theta_1 - \cos \theta_2) + \cos \theta_2$$

Where f is the fraction of the surface area covered by the region with contact angle θ_1 . The paraffin stripes in the pattern used here had a width of $110\ \mu\text{m}$ and a gap of $90\ \mu\text{m}$ between them, resulting in a value of $f = 0.55$ for all surfaces. As shown in Fig. 4d, the values for θ_1 were 66° , 57° , and 91° for glass, aluminum, and polystyrene respectively, and θ_2 was measured to be 104° for paraffin coating on all substrates. θ_1 values were measured on unpatterned regions of the same surfaces (glass, aluminum, and polystyrene) and θ_2 was measured on each of the surfaces by using a flat PDMS stamp to apply a uniform layer of paraffin to each sample surface. Using the above equation, the predicted contact angle on paraffin-patterned glass, aluminum, and polystyrene surfaces (87° , 88° , and 98° respectively) matches the measured contact angle ($83 \pm 9^\circ$, $86 \pm 3^\circ$, and $94 \pm 7^\circ$ respectively) rather well. Therefore, it is likely that this method can be used to generate a wide of range water contact angles on a surface by changing the dimensions on the paraffin patterns.

Conclusions

In this work, we demonstrate that paraffin-saturated PDMS micropatterned stamps can be used to generate high-fidelity paraffin surface patterns with controllable, sub-100 nm thickness. Our method is solvent-free and does not require pre-modification of the target surface, in contrast to many deposition-based surface modification methods [31-34]. The ability to pattern without premodification makes this method compatible with a variety of target surfaces, including aluminum, glass, and polystyrene. Because the paraffin ink absorbs into PDMS, the stamp itself serves as an ink reservoir, such that the re-inking step in traditional microcontact printing is not required. Using XPS, we quantified the diffusion of paraffin wax

into PDMS and estimate the mass diffusivity (D) to be approximately $5.3 \times 10^{-7} \text{ cm}^2/\text{s}$, which is similar to the only other class of well-known PDMS soluble inks, n -Alkanethiols ($D = 4\text{--}7 \times 10^{-7} \text{ cm}^2/\text{s}$) [35].

The thickness of the deposited layer can be modified from 85 nm to 380 nm by controlling the contact time. The ability to easily and accurately control layer thickness is unique to our deposition method compared to other microcontact printing methods. The ability to control contact-deposited polymer thickness has previously required complex multi-step processes, such as depositing a patterned seed layer and then thickening this layer with post-hoc graft polymerization steps [36], transfer-printing of a multi-layer Langmuir film prepared using multiple inking steps [37], or modified hot-embossing of a polymer layer [38]. Even when saturated with paraffin, the PDMS stamps are flexible at both the macro- and microscale. This enables high-fidelity micropatterns to be stamped onto surfaces with macroscale curvature and to create unique, multi-layered patterns.

From an applications point of view, the hydrophobic/hydrophilic patterning allows for control over the wettability of macroscopic surfaces, the size of single droplets on a surface, and the transport path of single drops. Moreover, the paraffin patterns are relatively stable in cell culture media, showing promise for biological patterning applications [15, 16]. The PDMS master mold can be generated using traditional photolithography processes if submicron resolution is required, or lower resolution molds ($\sim 25 \mu\text{m}$) can be fabricated using standard 3D printing, which eliminates the need for a specialized cleanroom environment. The ease and versatility of our method makes it an attractive option for economical, rapid modification of surface energy and topography in a single process. Overall, we anticipate that the ease, versatility, and inexpensive nature of our process will make hydrophobic patterning more accessible to a wide range of researchers.

Acknowledgements

This material is based upon work supported by the National Science Foundation under Cooperative Agreement No. 1849213.

References

1. Kim, S.C., D.J. Sukovich, and A.R. Abate, *Patterning microfluidic device wettability with spatially-controlled plasma oxidation*. Lab on a Chip, 2015. **15**(15): p. 3163-3169.
2. Rashid, Z., et al., *Reversible switching of wetting properties and erasable patterning of polymer surfaces using plasma oxidation and thermal treatment*. Applied Surface Science, 2018. **441**: p. 841-852.
3. Yang, X., et al., *A twice electrochemical-etching method to fabricate superhydrophobic-superhydrophilic patterns for biomimetic fog harvest*. Scientific reports, 2017. **7**(1): p. 1-12.
4. Kim, H., et al., *Drop impact characteristics and structure effects of hydrophobic surfaces with micro-and/or nanoscaled structures*. Langmuir, 2012. **28**(30): p. 11250-11257.
5. Gorman, C.B., H.A. Biebuyck, and G.M. Whitesides, *Use of a patterned self-assembled monolayer to control the formation of a liquid resist pattern on a gold surface*. Chemistry of Materials, 1995. **7**(2): p. 252-254.
6. Rios-Carvajal, T., et al., *Specific ion effects on the interaction of hydrophobic and hydrophilic self-assembled monolayers*. Langmuir, 2018. **34**(35): p. 10254-10261.

7. Lee, S.H., et al., *Multifunctional self-assembled monolayers via microcontact printing and degas-driven flow guided patterning*. Scientific Reports, 2018. **8**(1): p. 1-8.
8. Liu, Q., et al., *A polydopamine patterned perfluoropolymer-based substrate for protein microarray applications*. Sensors and Actuators B: Chemical, 2019. **287**: p. 306-311.
9. Slodowicz, M.P., et al., *Physicochemical properties and field evaluation of monolithic wax formulations for the controlled release of a forest pest pheromone*. Journal of the Brazilian Chemical Society, 2017. **28**(2): p. 348-359.
10. Carlen, E. and C. Mastrangelo. *Simple, high actuation power, thermally activated paraffin microactuator*. in *Transducers' 99 Conference, Sendai, Japan, June. 1999*.
11. Carlen, E.T. and C.H. Mastrangelo, *Surface micromachined paraffin-actuated microvalve*. Journal of Microelectromechanical Systems, 2002. **11**(5): p. 408-420.
12. Jing, G., et al., *Development of a microfluidic biosensor for detection of environmental mycobacteria*. Sensors and Actuators B: Chemical, 2007. **123**(1): p. 614-621.
13. Jing, G., et al., *Paraffin surfaces for culture-based detection of mycobacteria in environmental samples*. Journal of Micromechanics and Microengineering, 2004. **15**(2): p. 270.
14. Renault, C., et al., *Three-dimensional wax patterning of paper fluidic devices*. Langmuir, 2014. **30**(23): p. 7030-7036.
15. Tse, C.C.W., et al., *Utilising inkjet printed paraffin wax for cell patterning applications*. International Journal of Bioprinting, 2016. **2**.
16. Kuo, C.T., et al., *ParaStamp and Its Applications to Cell Patterning, Drug Synergy Screening, and Rewritable Devices for Droplet Storage*. Advanced Biosystems, 2017. **1**(5): p. 1700048.
17. Ren, K., et al., *Convenient method for modifying poly (dimethylsiloxane) to be airtight and resistive against absorption of small molecules*. Analytical Chemistry, 2010. **82**(14): p. 5965-5971.
18. Lee, J.N., C. Park, and G.M. Whitesides, *Solvent compatibility of poly (dimethylsiloxane)-based microfluidic devices*. Analytical Chemistry, 2003. **75**(23): p. 6544-6554.
19. Cai, Z., et al., *Fluid separation and network deformation in wetting of soft and swollen surfaces*. Communications Materials, 2021. **2**(1): p. 1-11.
20. Dangla, R., F. Gallaire, and C.N. Baroud, *Microchannel deformations due to solvent-induced PDMS swelling*. Lab on a Chip, 2010. **10**(21): p. 2972-2978.
21. Park, J.Y., et al., *PDMS-paraffin/graphene laminated films with electrothermally switchable haze*. Carbon, 2016. **96**: p. 805-811.
22. Yao, X., et al., *Temperature-Driven Switching of Water Adhesion on Organogel Surface*. Advanced Materials, 2014. **26**(12): p. 1895-1900.
23. Feng, W., E. Ueda, and P.A. Levkin, *Droplet Microarrays: From Surface Patterning to High-Throughput Applications*. Advanced Materials, 2018. **30**(20): p. 1706111.
24. Xu, K., et al., *Self-partitioned droplet array on laser-patterned superhydrophilic glass surface for wall-less cell arrays*. Analytical Chemistry, 2016. **88**(5): p. 2652-2658.
25. Efremov, A.N., et al., *Micropatterned superhydrophobic structures for the simultaneous culture of multiple cell types and the study of cell-cell communication*. Biomaterials, 2013. **34**(7): p. 1757-1763.
26. Hu, H., S. Yu, and D. Song, *No-loss transportation of water droplets by patterning a desired hydrophobic path on a superhydrophobic surface*. Langmuir, 2016. **32**(29): p. 7339-7345.
27. Tenjimbayashi, M., et al., *Droplet motion control on dynamically hydrophobic patterned surfaces as multifunctional liquid manipulators*. ACS Applied Materials & Interfaces, 2017. **9**(12): p. 10371-10377.
28. Soitu, C., et al., *Jet-Printing Microfluidic Devices on Demand*. Advanced Science, 2020. **7**(23): p. 2001854.

29. Walsh, E.J., et al., *Microfluidics with fluid walls*. Nature Communications, 2017. **8**(1): p. 1-9.
30. Milne, A.J.B. and A. Amirfazli, *The Cassie equation: How it is meant to be used*. Advances in Colloid and Interface Science, 2012. **170**: p. 48-55.
31. Schwartz, D.K., *Mechanisms and kinetics of self-assembled monolayer formation*. Annual Review of Physical Chemistry, 2001. **52**(1): p. 107-137.
32. Arkles, B., *Hydrophobicity, hydrophilicity and silane surface modification*. Gelest Inc, Morrisville, 2011.
33. Quist, A.P., E. Pavlovic, and S. Oscarsson, *Recent advances in microcontact printing*. Analytical and bioanalytical chemistry, 2005. **381**(3): p. 591-600.
34. Pujari, S.P., et al., *Covalent surface modification of oxide surfaces*. Angewandte Chemie International Edition, 2014. **53**(25): p. 6322-6356.
35. Balmer, T.E., et al., *Diffusion of Alkanethiols in PDMS and Its Implications on Microcontact Printing (μ CP)*. Langmuir, 2005. **21**(2): p. 622-632.
36. Jeon, N.L., et al., *Patterned polymer growth on silicon surfaces using microcontact printing and surface-initiated polymerization*. J Applied Physics Letters, 1999. **75**(26): p. 4201-4203.
37. Kim, Y.-K., et al., *Facile Transfer of Thickness Controllable Poly(methyl methacrylate) Patterns on a Nanometer Scale onto SiO₂ Substrates via Microcontact Printing Combined with Simplified Langmuir-Schaefer Technique*. Langmuir, 2008. **24**(24): p. 14289-14295.
38. Chen, L., P. Degenaar, and D.D. Bradley, *Polymer transfer printing: application to layer coating, pattern definition, and diode dark current blocking*. Advanced Materials, 2008. **20**(9): p. 1679-1683.

Supplementary Information

Estimation of Diffusion Coefficient

Diffusion in 1-D from an infinite source at constant concentration (C_0) follows the solution to Fick's second law of diffusion:

$$C(x, t) = C_0 \cdot \operatorname{erfc}(x/\sqrt{4 \cdot D \cdot t}) \quad (1)$$

Where $C(x, t)$ is the concentration at a given location (x) and time (t), and D represents the diffusion coefficient. This equation assumes that the initial concentration at all values of x is initially zero (i.e., $C(x, 0) = 0$). To apply this equation to our XPS measurements, we must account for the fact that there is a nonzero background signal caused by the carbon content of the PDMS (C_B):

$$C(x, t) = (C_0 + C_B) \operatorname{erfc}(x/\sqrt{4 \cdot D \cdot t}) + C_B \quad (2)$$

The value for C_B was obtained by measuring an unparaffinated piece of PDMS ($C_B = 46.3$). The value for C_0 can be obtained by observing that as $t \rightarrow \infty$, $C(x, t) \approx C_0$ for all values of x . We incubated a PDMS piece with paraffin for 96 hours and then measured carbon content using XPS at multiple locations; the value was found to be essentially the same at all locations, confirming that we had incubated the PDMS + paraffin system long enough to assume uniformity and could use this value in our equations ($C_0 = 89.2$). The experimental data shown in Figure 3(b) was obtained after 20 minutes of incubation ($t = 1200$ s). For a given value of D , the accuracy of the fit between equation (2) and the experimental data can be calculated using the coefficient of determination (R^2). The D value that produced the highest R^2 value was $D = 5.3\text{e-}7$ cm²/s, with an R^2 value of 0.874, thus we believe this to be a very good fit to our data.

Estimation of Saturation Time

A reasonable approximation of diffusion distance of a species as a function of time can be given by the equation $x = 2\sqrt{Dt}$. Using this, we can estimate the time required for a species to diffuse a given distance as:

$$t = x^2/(4D) \quad (3)$$

This equation can be used as a rough estimate of how long it would take for paraffin to diffuse from one side of a PDMS stamp to the other: i.e., from the paraffin source surface to the patterning surface. This method, combined with the estimation of the diffusion coefficient was used to produce Figure 3(c).

Supplementary Figures

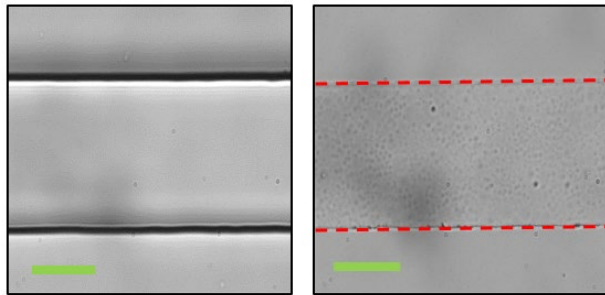


Figure S1. Optical images of PDMS stamp (left) and resulting patterned paraffin on glass (right). Dashed lines at paraffin boundary added to aid visualization. Scale bar = 50 μm .

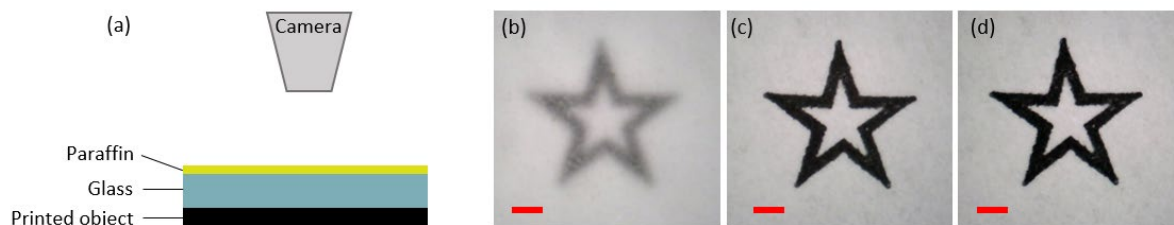


Figure S2. Transparency of paraffin layers. A layer of paraffin on glass was placed between the camera and printed image (a). Captured images of a printed shape through glass with a paraffin coating thickness of b) 180 μm , c) 84 nm, and d) bare glass, scale bar = 1 mm.

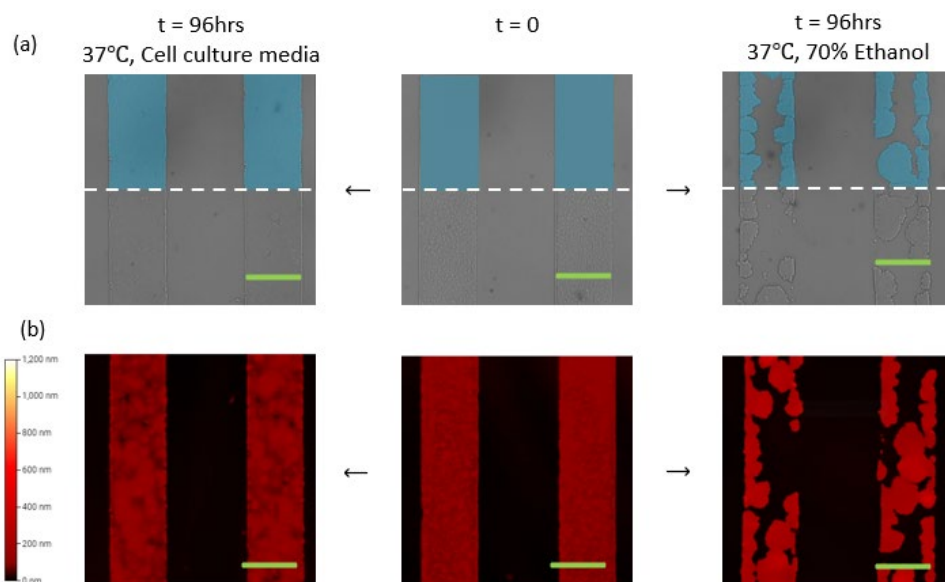


Figure S3. a) Optical (with blue false color added to highlight patterned areas) and b) profilometer images of submerged paraffin patterns in cell culture media and 70% ethanol after 96 hrs at 37°C, scale bar = 100 μm .

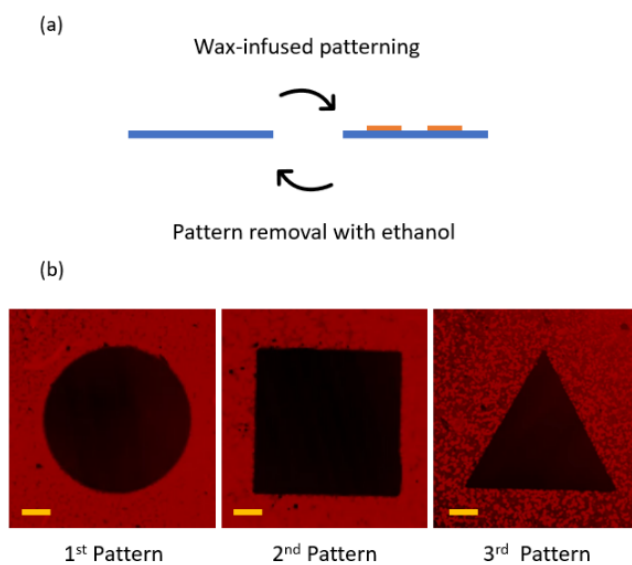


Figure S4. (a) Schematic view of the cyclic patterning process, (b) profilometer images of first, second and third patterns deposited on the same surface, scale bar = 200 μm .