

Supporting Information for

Dead-end filling of SlipChip evaluated theoretically and experimentally as a function of the surface chemistry and the gap size between the plates for lubricated and dry SlipChips

Liang Li, Mikhail A. Karymov, Kevin P. Nichols, Rustem F. Ismagilov

Department of Chemistry and Institute for Biophysical Dynamics, The University of Chicago,
929 East 57th Street, Chicago, IL, 60637

Experimental Section:

Fabrication of glass devices

The procedure for fabrication of SlipChip from glass was based on previous work.¹ The soda-lime glass slide with chromium and photoresist coating was aligned with a photomask containing the design for the wells and the ducts, and AZ 1500 positive photoresist was exposed using standard exposure protocols. The glass plate was immersed in 0.1 mol/L NaOH immediately after exposure to remove the areas of the photoresist exposed to UV light. The exposed chromium layer was removed by applying a chromium etchant (a solution of 0.6:0.365 mol/L HClO₄ / (NH₄)₂Ce (NO₃)₆). The glass plate was then rinsed with Millipore water and dried with nitrogen gas. The back of the glass plate was taped with PVC sealing tape, and then the glass plate was immersed in a glass etching solution (1:0.5:0.75 mol/L HF/NH₄F/HNO₃) to etch the exposed glass surface where chromium coating was removed in the previous step. The etching speed was controlled by the etching temperature.

The glass plate with etched wells was thoroughly rinsed with Millipore water. To make “micropatterns” with ~ 2.5 μm depth, the UV-exposure and etching process described above was repeated with a different mask (10 μm by 10 μm transparent square with 10 mm spacing on 1.5” by 3” black background) and a shortened etching time (~ 2 minutes), respectively; followed by thorough ethanol rinsing and blow drying with nitrogen gas.

The glass plate was oxidized in plasma cleaner for 100 seconds and then immediately transferred into a desiccator. 50 μL of (Tridecafluoro-1,1,2,2 -tetrahydrooctyl) trichlorosilane was injected into the desiccator and vacuum was then applied in the desiccator to perform gas phase silanization for 3 hours. The silanized glass plates were incubated in 120° oven for 30 minutes and cleaned with a fluorocarbon, FC-3283, and then dried in 65° oven. Through holes were drilled in the top plate as an inlet for all designs. For devices used for quantification of gap size, dichlorodimethylsilane was used to perform gas phase silanization.

Fabricating glass molds. A glass mold was prepared by glass etching (Figure S1). The glass plate (3 mm thick) with chromium and photoresist coatings (Telic Company, Valencia, CA) was covered by a photomask containing the SlipChip design (patterns were shades on clear background) and was exposed to UV light for 1 min. Immediately after exposure, the glass plate

was developed by immersing it in 0.1 mol/L NaOH solution for 2 min. Only the areas of the photoresist that were exposed to the UV light dissolved in the solution. The exposed underlying chromium layer was removed using a chromium etchant (a solution of 0.6:0.365 mol/L HClO_4 / $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$). As a result, the patterns in the design were still covered by chromium and photoresist coatings. The plate was thoroughly rinsed with Millipore water and dried with nitrogen gas, and the back of the glass plate was taped with PVC sealing tape (McMaster-Carr) to protect the back side of glass. The taped glass plate was then carefully immersed in a plastic container with a glass etching solution (1:0.5:0.75 mol/L $\text{HF}/\text{NH}_4\text{F}/\text{HNO}_3$) to etch the bare glass surface of the plate (areas on the plate where both photoresist and chromium coatings were removed). A 40 °C constant-temperature water bath shaker was used to control the etching speed. By controlling the etching time (~55 min), the etching depth was 60 μm . The photoresist and chromium coatings that covered the patterns were then sequentially removed by ethanol and the chromium etchant. Consequently, the non-etched patterns stood as 60 μm -high pillars (Figure S1). The glass plate with positive patterns was then coated with another chromium layer. An array of holes (5 μm by 5 μm) was formed by ablating the chromium layer using a Resonetics RapidX 250 excimer laser operating at 193 nm. The fluence was adjusted to ablate a 150 nm layer of Cr in a single pulse, without affecting the glass. The glass was subsequently etched with HF using the Cr as an etch mask. Resulting holes become posts in the hot embossed plastic piece, which significantly increases the contact angle.

Surface tension and contact angle measurements

The surface tension of aqueous solution in fluorocarbon was measured as previously reported with some modifications.² Briefly, droplets of a lubricating fluid of interest were formed at the end of a disposable droplet extrusion tip. The tip was assembled by using quick-set epoxy to glue polyimide-coated glass tubing to one 10 μL disposable pipette tip, which was first plasma cleaned for 5 minutes. The tip was immersed vertically in an aqueous solution contained in a 1 mL cuvette. The polyimide tubing was connected to a 50 μL Hamilton Gastight syringe by using 30-gauge Teflon tubing. The syringe was pre-filled with the lubricating fluid. The formed droplets were imaged using Model 250 Standard Digital Goniometer & DROPimage Advanced software (Rame-Hart Instrument Co).

Contact angles were measured following the same protocol reported previously.^{3,4} Briefly, 4 μL of a solution to be measured was pipetted on the substrate of interest. The contact angle of the droplet on the substrate was then measured by using an optical contact angle meter (Ramé-Hart Instrument Co., Model 500).

Viscosity measurement

Viscosity was measured by using the Cannon-Fenske calibrated viscometers manufactured by Cannon Instrument Company (State College, PA). The instructions accompanying the product were followed to take the measurements. The viscosity of the less viscous aqueous solution of green dye was measured on a M2/6 viscometer $(1.04 \pm 0.01) \times 10^{-3}$ Pa-sec and was close to

viscosity of water at room temperature. The more viscous aqueous solution of 10% w/v PEG 8000 in water was measured on M4/13 viscometer from the same manufacturer and was $(3.28 \pm 0.07) \times 10^{-3}$ Pa·sec.

Measuring and controlling the gap between two plates of a SlipChip

Gap measurements were done on a DMI6000 epi-fluorescence microscope (Leica, Germany) equipped with a digital cooled CCD camera (Hamamatsu, Japan). This cooled camera has linear response on light intensity, which allows for precise intensity measurements. The gap between the slides was measured using mineral oil (Fisher Scientific, NJ) stained with green fluorescent quantum dots (QDs) (1% QDs in toluene, Ocean Nanotech, AR). The original QDs solution was filtered through 0.22- μ m microcentrifuge Amicon filters (Millipore, MA) and sonicated in an ultrasonic bath (Fisher Scientific, NJ) for 10 min. A 10% solution of QDs in mineral oil was thoroughly vortexed and kept for at least 10 min under vacuum before filling the device.

The stained mineral oil was deposited between the two plates of the SlipChip; excess oil was removed by rinsing the assembled device sequentially with chloroform, acetone, and ethanol. The two plates were clamped with 8 paper clips as described in “Device Assembly” and “Filling Solutions” in the Experimental Section of the main text, and kept for at least 1 hour under pressure before taking measurements. Image acquisition, image processing, and measurements were done using Metamorph software (Universal Imaging Corporation). Images were acquired at reduced field of illumination to avoid leaching of fluorescent light from the much brighter features used as a reference to relatively dim surrounding areas. Fluorescence images were treated according to a standard procedure, which include subtracting the background camera noise and compensating for the uniformity of field of illumination. SlipChip has features of known depths, allowing for the estimation of the depths of unknown features, including the gap between the slides, by simply comparing fluorescence intensities from these features. To determine precise distance between the slides we applied a self-recursive procedure according to the formula: $d_{i+1} = (w + d_i) \times I_s / I_w$. Here w is the depth of the known feature (such as a well), $d_0 = 0$; d_i is the gap size, I_s and I_w are intensities acquired from the surrounding surface and from the well. We usually conducted $i = 1-2$ iterations to obtain reliable distance.

To validate this procedure and check for linearity we performed fluorescence measurements from a series of wells of known depths. These reference wells were made on a Laser Ablation System (Resonetics, NH). Depths of all features were measured by using a profilometer (Dektak 150, Veeco, CA). Fluorescence intensities acquired from the wells were found to be linear with the well depth. Distances obtained with both techniques were within ~5% of one another. Therefore, we can use fluorescence intensities to measure gaps between the SlipChip plates.

To control the gap between the slides, we used fluorescent silica beads of two different sizes. In particular, we used beads with diameter of 1.5 μ m and 3.86 μ m respectively (Corpuscular Inc., NY). These beads were silanized before use to make them compatible with the hydrocarbon oil. Silanization was performed as follows: beads were rinsed and sonicated with

acetone three times; 5% dichlorodimethylsilane was added to beads in acetone and exposed for 30 min at room temperature. Beads were rinsed once with acetone and twice with chloroform. The appropriate amount of beads was added to fluorescently stained hydrocarbon oil to obtain relatively uniform bead distribution. The gap between the SlipChip plates was measured as described above for each case. Results of gap measurements are shown in Table S1 below.

Table S1. Measured gap sizes resulting from differently sized beads.

Bead size (μm)	No beads	1.5	3.86
Gap (μm)	1.2 ± 0.1	1.9 ± 0.1	4.6 ± 0.2

Imaging

Images of the SlipChip were acquired by using fluorescence stereomicroscope, MZ 16 (Leica, Germany), equipped with Spot Insight color camera, model 3.2.0 (Diagnostic Instruments Inc., MI).

References:

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- (2) Roach, L. S.; Song, H.; Ismagilov, R. F., *Anal. Chem.* **2005**, 77, 785-796.
- (3) Li, L.; Du, W.; Ismagilov, R. F., *J. Am. Chem. Soc.* **2010**, 132, 106-111.
- (4) Li, L.; Du, W.; Ismagilov, R. F., *J. Am. Chem. Soc.* **2010**, 132, 112-119.

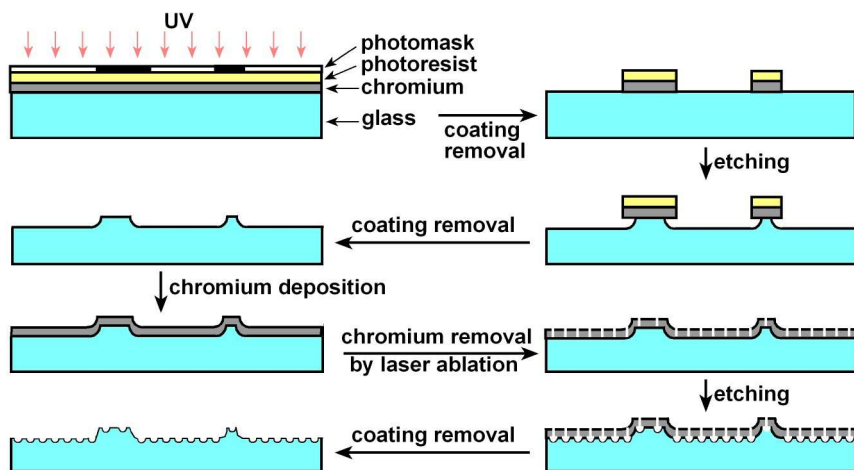


Figure S1: Procedures to make glass mold for fabrication of plastic device. See details in the text.

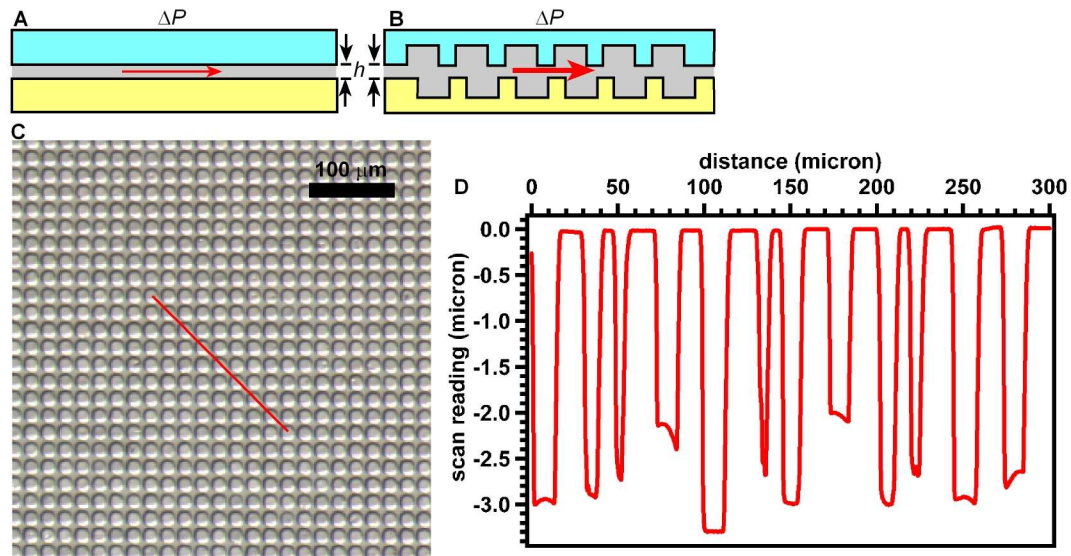


Figure S2: Use of “micropatterns” to facilitate LF dissipation. Within the same pressure drop (ΔP), LF flow rate was expected to be higher in devices with “micropatterns” (B) than without micropatterns (A), because the depression of the patterns increases the dimension of the flow path and reduces flow resistance. (C) A microphotograph of the pattern; (D) a diagonal scan (red line shown in C) of a 300 μm distance with a Veeco Dektak 150 profilometer.

Movie S1: Dead-end filling of the slip-chip.

The SlipChip used to generate this movie is slightly modified from the design shown in Figure 3: the ducts connecting the sample wells are curved, not straight. The movie was generated from a series of consequential images taken with 1 s time intervals (See Experimental Section). The time duration of the whole loading process is close to 117 s, or ca. 2 min. The green solution represents the sample, and the orange solution represents one reagent.