Supporting Information

Experimental Investigation of the Impact of Mixed Wettability on Pore-Scale Fluid Displacement: A Microfluidic Study

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Mixed Wettability Micromodel Fabrication

The microfluidic devices were fabricated fully in-house utilizing state-of-the-art semiconductor processing technology at the KAUST Nanofabrication Core Lab. The fabrication process was based on our recently developed innovative technique AlOmier et al. (2024), which utilizes selective wettability modification via photolithography and molecular vapor deposition (MVD) of perfluorodecyltrichlorosilane (FDTS), allowing for precise alteration of surface wettability at the pore-scale. The workflow, as depicted in Figure S1, outlines the fabrication process of micromodels designed to achieve mixed wettability features. The methodology required two layers of photolithography. Layer-1 focused on the fabrication of the actual microfluidic flow domain, while Layer-2 was dedicated to wettability alteration to achieve the mixed wettability characteristics. This process consisted of four main steps, all of which were performed in a class 100 cleanroom.

1. Layer-1 Photomask Fabrication

In this step, the predesigned micromodels (see Figure 2) were printed onto a physical photomask. The photomask was fabricated using a 5-inch blank photomask (Nanofilm, United States). The blank mask consisted of a 2.5 mm thick, rectangular, soda lime glass plate which was coated with 100 nm of chromium and 500 nm of baked photoresist. A DWL 66+ (Heidelberg Instruments, Germany), high-resolution laser lithography system was deployed to transfer the digital designs of micromodels onto the photoresist by precise laser-based exposure. Post-writing, the photomask was developed in AZ 726 MIF (MicroChemicals GmbH, Germany) developer solution to remove

the photoresist from the exposed areas. The photomask was then wet etched to remove the exposed chromium layer using a TechniEtch Cr01 (MicroChemicals GmbH, Germany) metal etchant solution. Following this, the remaining photoresist was stripped from the mask, and the mask was cleaned in piranha solution (3:1 mixture of sulfuric acid (H□SO□) and hydrogen peroxide (H□O□)) at 115 °C for 10 minutes. The final mask pattern featured areas coated with chromium and transparent pore patterns. This design allowed light to pass through the unmasked transparent areas while being blocked by the chromium-covered regions, thereby defining the required features.

2. Layer-1 Micromodel Fabrication

A 4-inch silicon wafer (MSE Supplies, United States) was used as a base for fabrication. At first, the substrate was cleaned by sonication in solvents and piranha solution. Then, the substrate surface was vapor-primed using hexamethyldisilazane (HMDS) to promote photoresist adhesion. AZ ECI 3027 (MicroChemicals GmbH, Germany) positive photoresist was spin-coated on top of the substrate (4 µm thick layer at 1750 rpm) and soft baked at 100 °C for 60 seconds on a hot plate. The fabricated layer-1 photomask (see step-1) was aligned on the top of the substrate and exposed to UV light with an exposure dose of 200 mJ/cm^2 using an EVG 6200 (EV Group, Austria) high-resolution mask aligner. The light shines through the unmasked transparent areas while being blocked in the covered areas, allowing the designed flow patterns to transfer to the substrate. The exposed photoresist was then removed by immersing it in an AZ 726 MIF (MicroChemicals GmbH, Germany) developing solution for one minute. The openly exposed substrate was patterned by Deep Reactive-ion Etching (DRIE) to obtain the desired channel depth. DRIE by the Bosch process was carried out using a Plasma lab 100 – ICP 380 (Oxford Instruments, United Kingdom) dry etching tool.

This cyclic anisotropic etching process involved deposition cycles of a polymeric passivation layer for sidewall profile control with the following parameters: chamber pressure of 30 mTorr, table bias power of 5 W, ICP power of 1300 W, C_4F_8 flow of 100 sccm, and SF_6 flow of 10 sccm at a temperature of 0 °C for 5 seconds. The etching cycles were performed in SF_6 dominated plasma under the following parameters: chamber pressure of 30 mT, table bias power of 30 W, ICP power of 1300 W, C_4F_8 flow of 5 sccm, and SF_6 flow of 100 sccm at a temperature of 0 °C for 7 seconds.

After etching, the remaining photoresist was stripped off, and the final micromodel was thoroughly cleaned using piranha solution.

3. Layer-2 Photomask Fabrication

In this step, a second photomask was fabricated to create the wettability patterns. All predesigned wettability scenarios (see Figure 3) were transferred onto this photomask, to be aligned on top of the micromodels. The fabrication process followed that of the first photomask (Step 1), where designs were written onto a 5-inch blank photomask using a laser writer. After photoresist development, the chromium layer was wet etched to expose the desired areas, and the remaining photoresist was stripped off using piranha solution. The final mask featured areas coated with chromium, which subsequently targeted for wettability alteration.

4. Layer-2 Wettability Alteration

The fourth step involved altering the surface wettability of the micromodels. The patterned substrate was first vapor primed with HMDS and then spin-coated with AZ nLOF 2070 (MicroChemicals GmbH, Germany) negative photoresist. After the photoresist was soft baked at 110 °C for 60 sec, the wettability patterns were imprinted on the top of the etched substrate by exposing the layer-2 photomask to UV light (200 mJ/cm^2 exposure dose) utilizing the same mask alignment system mentioned earlier. Precise alignment was ensured using predesigned high-precision alignment marks to accurately place the wettability patterns at the desired locations. After exposure, the photoresist was post baked at 110 °C for 60 sec. Since a negative photoresist was used in this step, the developing solution removed the resist only from the unexposed areas covered by the wettability mask. Meanwhile, the exposed areas of the micromodels remained coated with photoresist, leaving the targeted regions uncovered for wettability alteration. The substrate was then uniformly coated with hydrophobic FDTS using a MVD 100 (Applied Microstructures, United States) tool. Subsequently, the remaining photoresist was lifted off using n-methylpyrrolidone (NMP) solvent, restoring the original silicon surface wettability in the non-coated regions. Finally, the micromodels were diced and bonded to a thin layer of polydimethylsiloxane (PDMS) to create the final microfluidic chips.

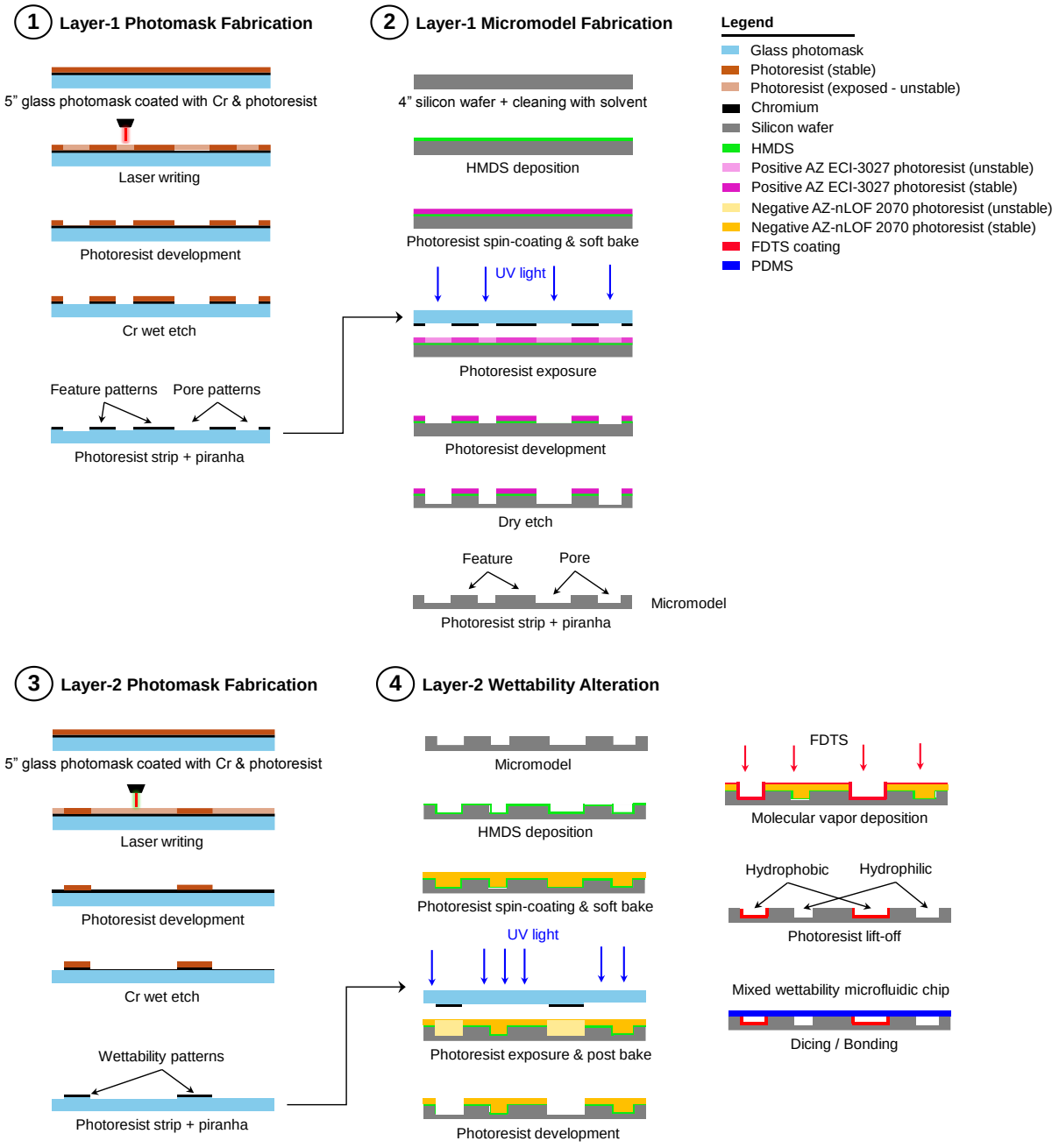

Figure S1: Mixed wettability micromodel fabrication procedure highlighting the major steps. (1) Fabricating layer-1 photomask: The design of the micromodels was transferred onto a chrome-coated glass photomask using high-resolution laser writing. (2) Layer-1 micromodel fabrication: The micromodel was fabricated using a photolithography process and shaped with DRIE technique. (3) Layer-2 photomask: The wettability patterns were created on a second photomask. (4) Layer-2 wettability alteration: Mixed wettability micromodels were fabricated by superimposing different wettability photomasks and selectively placing the FDTS hydrophobic coating. The chips were bonded to create final microfluidic devices.

References:

AlOmier, A., Cha, D., Ayirala, S., Al-Yousef, A., & Hoteit, H. (2024). Novel fabrication of mixed wettability micromodels for pore-scale studies of fluid–rock interactions. *Lab on a Chip*. https://doi.org/10.1039/D3LC01009K