Supplementary Material (ESI) for Lab on a Chip
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# Supplementary Information

# High-speed Multiphoton Absorption Polymerization: Fabrication of microfluidic channels with arbitrary cross-sections and high aspect ratios

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## Experimental procedures

**Substrate functionalization**. Substrate cleaning was performed by placing substrates in an $O_2$ plasma cleaner (Harrick Plasma PDC-32G) for 2-3 min. Plasma-cleaned substrates were then placed in a 10% (v/v) solution of aminopropyltriethoxysilane (Fluka, 97%) in methanol (Sigma Aldrich, 99%) for 4 hours, after which they were washed/rinsed twice in methanol prior to being dried at 100 °C for an hour.

**Photoresist preparation**. SU8 2150 was used as received. To make FLUOR-SU8, a 1 wt% solid mixture of FLUOR in EPON SU8 was dissolved (for a period of 24 hrs) in cyclopentanone to yield a solution with a 0.5 wt% FLUOR concentration. This solution was filtered twice with 0.2 µm nylon filters. After filtration, the solution was held at 95 °C for 10 min and then at 110 °C for 20 min. This baking process reduces the solvent concentration and increases the viscosity of the final mixture. After baking, the mixture was held at 95 °C for 5 min, then at 65 °C for 5 min, and then finally cooled to room temperature. All heating was performed in an oven. This specific formulation was designed to use a minimal amount of the PAG and to have a viscosity that is appropriate for spin coating a resist film of the desired thickness. Formulations with a greater wt% of PAG were found to work equally well, and by changing the amount of residual solvent the viscosity of the resist can be changed to accommodate spin coating of layers of different thickness. However, because MAP is a 3D technique, the thickness of the photoresist is much less important than in conventional photolithography.

**Photoresist film preparation and development**. Photoresist films 100 µm to 200 µm thick were formed on substrates by spin-casting at 1500 – 1800 rpm for 40 s. These films were prebaked at 65 °C for 10 min and then at 95 °C for 50 min, with no cool-down between the heating steps. Prebaking removes some of the residual solvent, making the film more viscous. The films were cooled gradually from 95 °C, being held for 10 min at 65 °C before being allowed to reach room temperature.

After exposure, photoresists were postbaked at 65 °C for 5 min and then at 95 °C for 20 min. The postbake at 65 °C permits a relatively gradual anneal from room temperature to 95 °C, while the heating at 95 °C facilitates crosslinking of the epoxide monomers in the exposed regions of the resist. Films were held at 65 °C for 5 min prior to being cooled at room temperature.

**Sample position control**. The position of the sample with respect to the laser focal point was controlled by computer using the focusing drive of the microscope and a motorized stage (Ludl BioPrecision). The motorized microscope stage permitted control of the sample position in the plane perpendicular to the beam propagation direction, while the focusing drive of the microscope facilitated sample positioning along the beam propagation axis. A camera (Cohu 4195 High Performance CCD Camera) was used to monitor the sample image in real time. A long-pass filter (Edmund Optics LP 435) placed between the microscope illumination source and the sample prevented any single-photon polymerization from this source.

**Monitoring the fabrication process**. Because SU8 cross-linking generally occurs during a heating step that is undertaken after exposure, there is little to no refractive index change during exposure. Thus, it is difficult to distinguish between exposed and unexposed areas of the resist prior to post-exposure heating. However, we find that FLUOR-SU8 exhibits a significant change in refractive index upon exposure. As a result of this refractive index change, the exposed and non-exposed regions in a FLUOR-SU8 film are easily identified during MAP (Fig. s1).

FLUOR-SU8 films emit fluorescence upon 2PA of the 800 nm light used for MAP fabrication (Fig. s1). This fluorescence can be limited to a region at or near the focal point of the 800 nm laser beam by using appropriate beam powers. Under these conditions, the fluorescence emission from a FLUOR-SU8 film only occurs when the focal point of the fabrication beam resides within the film. This fluorescence can therefore be used to determine the film thickness and the location of the resist-substrate interface. We used the aforementioned refractive index change and the 2PA-induced fluorescence to locate the resist-substrate interface and to ensure that microstructures were anchored to the substrate.

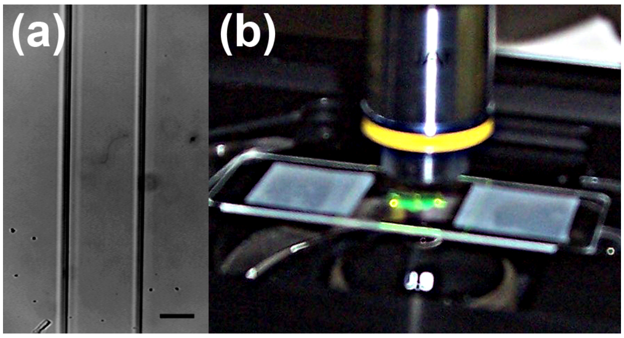

**Fig. s1** (a) An optical image captured immediately after 800 nm exposure of FLUOR-SU8 to produce two 10-μm-wide walls. The walls are 200 μm high, and the scale bar is 50 μm. The exposed regions are markedly darker than the unexposed regions. (b) FLUOR-SU8 fluorescence (green light in image) produced when short-pulsed, 800-nm light is focused in a FLUOR-SU8 film. This fluorescence is also clearly discernable on the CCD camera used to monitor fabrication.

**PDMS molding**. PDMS microfluidic systems were molded in a well that was also composed of PDMS. The well was molded from a piece of metal by pouring a degassed PDMS mixture (a 10:1 mass ratio of elastomer base to curing agent) onto this metal piece and curing at 95 °C for 25 min. The surface of this PDMS well was functionalized by first $O_2$ plasma-cleaning (< 300 mTorr $O_2$ for 2 min) the well and then placing it in an evacuated chamber with a watch glass containing a few drops of (tridecafluoro-1,1,2,2-

tetrahydroctyl) dimethylchlorosilane. The PDMS well was held in this chamber for 24 hours to permit the vapor deposition of the silane.

To make a mold of a master structure, a 10:1 mass ratio mixture of silicone elastomer base to curing agent was poured into the functionalized PDMS well. This mixture was then degassed by placing the PDMS well in an evacuated chamber (< 300 mTorr) for a few minutes. The face of the glass substrate in contact with the master was placed in the PDMS mixture by resting the edges of the glass slide on the walls of the PDMS well. This procedure keeps the other face of the slide free from contact with the PDMS mixture and facilitates the separation of the mold and master following PDMS curing. The PDMS mixture was cured at 95 °C for 25 min.

**Bonding**. Bonding involved oxidizing a glass substrate and a PDMS mold in an $O_2$ plasma for ane minute, and then bringing the substrate and mold into conformal contact. Holding this arrangement of an oxidized mold in contact with a glass substrate at 95 °C for 5 min results in a strong seal between the mold and substrate.

## Maximum achievable packing densities for high-aspect ratio structures

High-aspect-ratio blocks with relatively uniform cross-sections are readily fabricated at high speeds using FLUOR-SU8 (Fig. s2). Generally, fabrication of such microstructures requires a resist thickness of several hundreds of µm. During conventional lithographic exposure through a mask, UV absorption can lead to significant variations in the photoresist exposure with depth because the intensity of the incident light decreases due to absorption as the light travels through the film. These variations can lead to high-

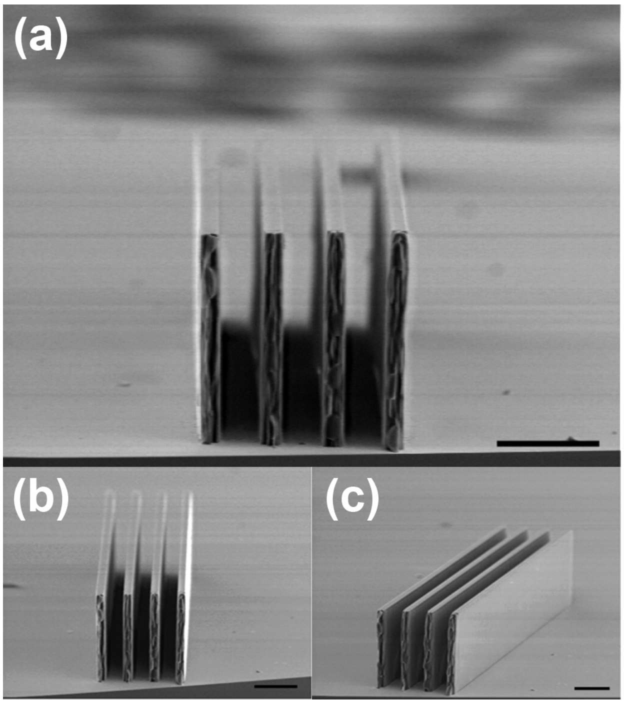

**Fig. s2** SEM images giving three different views of high-aspect-ratio, FLUOR-SU8 blocks fabricated using MAP. The separation between neighboring blocks, which are 1000 × 200 × 20 µm in dimension, is 50 µm. All scale bars are 100 µm.

aspect-ratio structures with unintended cross-sections, such as side wall profiles that are wedged instead of vertical. With MAP, the laser light focused into a resist is absorbed predominantly in the region around the laser focal point, and hence little to no exposure variation is created during fabrication. High-aspect-ratio structures are therefore easily created with MAP. The time required to make one of the 1000 × 200 × 20 µm blocks shown in Figure s2 is roughly 25 min, and 10 mm long blocks with the same cross-section can be fabricated in about 50 min.

The minimum spacing attainable between blocks made with FLUOR-SU8 increases with increasing aspect ratio. For example, the minimum spacings for 100- and 160-µm high blocks that are 20 µm thick are roughly 20 and 40 µm, respectively (Fig. s3). At spacings smaller than the minimum spacing, microstructures became attached to one another during development (Fig. s3). Solvent capillary forces experienced during solvent development can cause neighboring microstructures to come into contact, and such structures usually remain in contact after development. As the aspect ratio of microstructures is increased at a certain fixed spacing, the likelihood of this effect increases. Thus, it is the development step that currently limits the minimum spacing between high-aspect-ratio blocks and that therefore determines the maximum achievable packing density for these high-aspect-ratio structures.

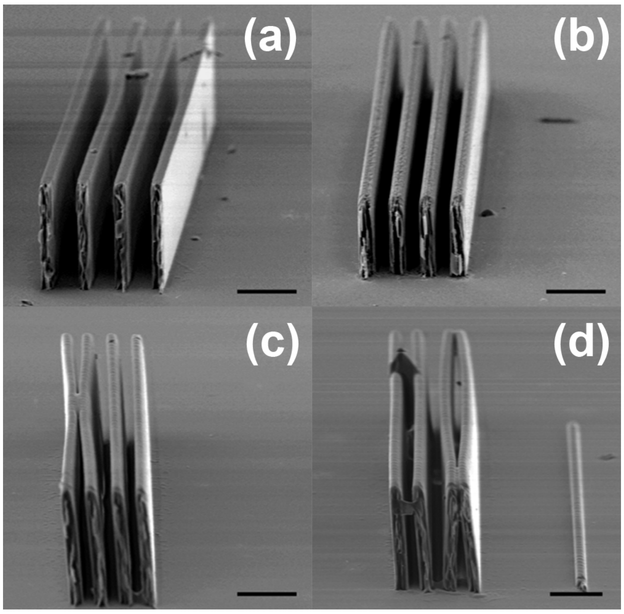

**Fig. s3** SEM images of sets of parallel walls. In (a), the spacing between neighboring 1000 × 160 × 20 µm FLUOR-SU8 walls was 40 µm. In (b), 100-µm-high FLUOR-SU8 walls were separated by 25 µm. At smaller spacings, walls tend to stick together during development. 160-µm-high blocks spaced by 25 µm exhibit such sticking during post-exposure processing ((c) and (d)). All scale bars are 100 µm.