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Microfabrication of cavities in polydimethylsiloxane using DRIE silicon molds

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Abstract

We present a novel method to create cavities in PDMS that is simple and exhibits wide process latitude allowing control over the radius of curvature to form shallow concave pits or deep spherical cavities.

Polydimethylsiloxane (PDMS) is a silicon-based polymer exhibiting tunable mechanical, chemical and optical properties that are widely leveraged in microfluidic and biotechnology applications. Its clear optical properties are especially advantageous for spectroscopic analysis through lab-on-a-chip devices.^{1–4} Its compliant properties are exploited to perform large area lithography on non-planar surfaces⁵ and to form variable-focus microlens arrays.^{6–8} PDMS is inert and non-toxic, making it well suited for cell culture and tissue engineering applications.^{9,10} PDMS stamps are used to spatially pattern antibodies, enzymes, protein ligands and cells onto sensors and other material surfaces using the micro-contact printing technique.^{11–15} PDMS stamps are typically fabricated by reverse replication of features formed in a silicon wafer mold.

The most widely used PDMS elastomer is Dow Corning Sylgard 184 (1 part catalyst : 10 parts base by weight) which is degassed prior to filling the mold. This material has a high elongation at break (160%) and a relatively low modulus (1.8 MPa).¹⁶ Features molded in PDMS are typically rectilinear forms, including squares, rectangles, cylinders and composite geometries combining these. More complex shapes (spheres and ellipsoids) that are needed to form, for example, microlens arrays require innovative process development. Some recent examples include photoresist thermal reflow processing,^{17,18} gel trapping,⁸ mechanical deformation of elastomeric mold,¹⁹ liquid-filled cavities²⁰ and surface tension extrusion.²¹

In this communication we report a new method to create smooth concave cavities in PDMS that allows control over the radius of curvature to form shallow pits or deep spherical cavities. While these structure are useful for microlens molding, our interest is to create microbio-reactor arrays. Leveraging novel fluidic flows and affinity capture methods, cells can be sorted into spatially distinct reactors of different sizes, where they can be maintained on-chip for research purposes or until needed for therapeutic use.^{10,22,23}

Our method, outlined in Fig. 1, utilizes standard lithographic processing to create a silicon wafer mold comprised of deep reactive ion etched (DRIE) trenches (Fig. 1A). An SEM image of a typical wafer mold containing linear arrays of DRIE trenches measuring $95 \times 95 \times 350 \mu\text{m}$ is illustrated in Fig. 2A. These trenches were fabricated using the Bosch process that

consists of sequential SF₆ etching and C₄F₈ passivation steps.²⁴ The passivation step deposits a hydrophobic fluoropolymer coating that protects against side wall erosion as etching proceeds deeper into the silicon wafer. Normally, the hydrophobic passivation layer is removed prior to subsequent processing steps using oxygen plasma. Our method for molding cavities retains the hydrophobic coating, which exhibits a water contact angle of ~107°. The PDMS prepolymer is mixed and cast directly onto the hydrophobic DRIE mold. The PDMS is set at room temperature for 15 min to allow for passive degassing (Fig. 1B). Complete degassing of the prepolymer by vacuum is *not* done. PDMS is then cured at 100 °C for 2 h (Fig. 1C). After curing, we observe formation of spherical cavities (Fig. 2B and Fig. 3A–D) or shallow concave pits (Fig. 3E), rather than the anticipated reverse (negative) replication of mold features. To achieve reverse replication, the viscous PDMS prepolymer must infiltrate into the deep trench features. In general, liquid infiltration depends on surface tension and capillary action to draw the liquid in. Formation of cavities following passive application of the viscous PDMS prepolymer suggests that wetting of the hydrophobic trench is poor and that hydrostatic pressure is insufficient to overcome surface tension. Our studies indicate, however, that cavity formation depends on many factors and under certain conditions, described below, reverse replication is possible. Critical factors that effect the size and shape of cavities that form include mold hydrophobicity, residual air in the prepolymer, curing temperature, PDMS film thickness, as well as the size, shape and spatial orientation of the trench openings in the mold.

Cavity formation was attempted on a hydrophilic DRIE silicon wafer mold prepared using an oxygen plasma (water contact angle of <10°). Passive application of the viscous PDMS prepolymer yielded irreproducible cavity formation after curing at 100 °C for 2 h. Moreover, attempts at releasing the PDMS resulted in torn cavity openings, due to PDMS bonding to the hydrophilic mold. To achieve reproducible cavity formation and to preserve the integrity of cavity openings, a hydrophobic coating is required. Studies find that molds can be used 4–5 time before the hydrophobic coating deteriorates. Hydrophobic coating can be applied by immersing a used or hydrophilic mold into 10 mM FDTS (Gelest SIP6720.5, perfluorododecyl-1H, 1H, 2H,2H-triethoxysilane perfluorotetradecyl 1H,1H,2H,2H-triethoxysilane mixture) solution in heptane for 10 min at room temperature. Alternatively, the mold can be ultrasonicated in the FDTS solution for 10 min. Following silane treatment, the mold is immediately dried under a stream of N₂ gas and heated at 100 °C for 20 min. These FDTS coating procedures produce water contact angles of ~80° and ~100 °C, respectively. Both coating procedures enabled unhindered release of PDMS from the mold and intact cavity formation; however, the more hydrophobic mold yielded consistent cavity formation over a wide range of trench openings (40, 60, 80, and 100 μm diameters). How ultrasonication enhances FDTS deposition is unknown but it likely aids in dispersing the molecules in solution so that a more uniform and higher surface coverage layer can form.²⁵ Solution temperature did not increase substantially during the ultrasonic coating procedure.

PDMS curing temperature also affects cavity formation. Curing non-degassed PDMS at room temperature (~25 °C) for 24 h does not yield cavities. Instead, incomplete reverse molding occurs resulting in formation of raised pillars on the PDMS surface that spatially correlate with the DRIE trenches (385 μm deep) however, the pillar height is smaller than the depth of the trench. Studies are in progress to investigate the effect of trench depth on pillar height following passive application of PDMS cured at ~25 °C. Complete reverse replication can be achieved using ultrasonication. Here PDMS prepolymer is applied to a hydrophobic mold and ultrasonicated for 15 min and cured at ~25 °C. This procedure enables reproducible reverse replication DRIE features, including high aspect ratio structures (Fig. 4). It suggests that ultrasonication helps dislodge air trapped in the trenches and/or provides sufficient energy to overcome surface tension, enabling the viscous PDMS prepolymer to infiltrate the trenches.

The effect of PDMS thickness on cavity formation was investigated over square trench openings ($95 \times 95 \mu\text{m}$) by casting thicker non-degassed prepolymer layers. Following curing at 100°C , the size of the cavity formed was observed to increase with thickness, as illustrated in Fig. 3A–D. The aspect ratio (diameter/depth) for each cavity was measured as a function of PDMS thickness (Fig. 5). Results show a slight dependence on thickness but they are nearly spherical (aspect ratio = 1). Interestingly, the volume of air in each cavity (calculated assuming spherical geometry) shows a strong dependence on PDMS thickness (Fig. 5). In each case, however, the cavity volume significantly exceeds the trench volume. This suggests accumulation of air from an additional source, *i.e.* residual air in the prepolymer. In fact, if the PDMS prepolymer is degassed prior to curing at 100°C , reverse mold replication results. Cavities only form when nondegassed PDMS is cured at high temperature. This suggests that cavity formation likely begins with expansion of gas trapped inside the DRIE features, which forces out any viscous prepolymer that may have infiltrated. This also initiates recruitment of residual air in the prepolymer to the site.²⁶ Room temperature is insufficient to expand the gas and curing at this temperature does not result in cavity formation. This phenomenon is consistent with results from a previous study in which gas bubble formation is observed when fluid is flowed over a heated substrate patterned with cavities.²⁷

In addition to the above, we observe that the size and shape of cavities that form depend on trench opening (area and shape) and their spatial orientation. For example, viscous prepolymer can infiltrate large circular trench openings ($600 \mu\text{m}$ diameter) forming a concave pit with a $40 \mu\text{m}$ raised edge (Fig. 3E). Spherical cavities (aspect ratio ~ 1) form over square trench openings, whereas more obtuse cavities (aspect ratio > 1) form over circular openings. Furthermore, cavity volume expansion is significantly impeded when the spacing between trench openings is less than $\sim 36 \times$ trench diameter (Fig. 2B). Quantification of these observations will be reported elsewhere.

In summary, we present a simple method to reproducibly fabricate microspherical structures in PDMS with process latitude to tailor the radius of curvature. To form concave cavity structures the passive application of non-degassed PDMS prepolymer must be applied to a hydrophobic mold and curing must be done at elevated temperatures. Experiments are in progress to fully quantify how the cavity dimensions depend on the trench parameters. Preliminary studies suggest that by varying the size of the trench opening, it may be possible to achieve mixed structures (concave shapes and conventional reverse molding) on the same wafer. Our particular interest is to develop cavities for microfluidic cell sorting and microbioreactor storage applications.²³ However, these structures should be of general interest to other research areas, such as microlens array fabrication.

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Fig. 1. Schematic of cavity process. A hydrophobic silicon wafer with DRIE features (A) is obtained and PDMS prepolymer is poured onto the wafer (B). After curing, spherical cavities are formed in the PDMS (C).

Fig. 2. (A) SEM image of silicon mold showing orientation of DRIE trenches on wafer surface and side view of trench cross section. (B) Top view of spherical PDMS cavity array formed elsewhere on the mold pictured in (A) illustrating effect of trench spatial orientation on cavity size.

Fig. 3. Cross section of the microcavities formed by varying the thickness of PDMS: 2.0 mm (A), 3.0 mm (B), 3.1 mm (C), and 4.3 mm (D), bar = 95 μm . Note that cavity volume increases and distance between adjacent cavities decreases with increasing PDMS thickness (A–D). It is also possible to form concave cavities with raised edges from larger sized openings (E).

Fig. 4. SEM image showing an array of reverse molded PDMS pillars (3 μm wide by 50 μm tall) formed using ultrasonication.

Fig. 5. The aspect ratio (diameter/depth, or b/a) of cavities with varied PDMS thickness ≈ 1 ($\blacktriangle$). PDMS thickness increases the size of the cavity that is formed ($\blacksquare$), which exceeds the volume found in the mold trench ($\blacklozenge$).