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Fabrication of PDMS Micro Through-holes Using Micromolding in Open Capillaries

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A modified micromolding process in open capillaries (MIMIOC) is put forward to pattern PDMS through-hole layers. In addition, a transfer technique, which includes changing bonding strengths between each layer by oxygen plasma treatment and surface silanization, is introduced to facilitate the release and bonding of through-holes layers. Its performance is verified by fabricating PDMS through-holes on SU-8 molds with 50-200 μm microstructures of cube, cylinder and rounded rectangle arrays. The feasibility of the micromolding process and its ability to achieve planar PDMS layer with protruding angle less than 2° is proved by changes of interfacial free energies and wetting morphology of liquid in micro grooves. As a method that with simple structure and low requirements for the equipment, the MIMIOC would contribute to the development of MEMS devices by patterning PDMS micro through-holes in a simple and low-cost way.

Introduction

Polydimethylsiloxane (PDMS) has been used pervasively in microfluidic systems due to its ease to micromold, low price, chemical inertness, biocompatibility and optical transparency [1]. As the rapid development of microfluidic devices, multi-layered devices come into being, which have more complicated structures and richer functions such as combinatorial mixing of fluids [2], integrated pneumatic valve devices [3], and passive auto-regulating components [4], highly broadening the application range of microfluidic devices.

One of the simplest fabrication approaches of PDMS through-holes is to manually punch out though-holes using a small gauge needle or biopsy punch as done for access holes for most microfluidic devices, which is time-consuming and limited by the needle size [5]. In the last decade, notable progress has been made in fabrication of PDMS through-holes. On one hand, etching, which based on the traditional lithography process[6-8], is hard to obtain satisfactory side walls[9], and the high price offsets the advantage of low cost of PDMS. On the other hand, there are several fabrication approaches derived from soft lithography, such as the micro transfer molding (μTM) [10-12] and the micromolding in capillaries (MIMIC) [13, 14]. In the μTM method, pressure is exerted on a mold and a substrate to pattern through-holes on PDMS gel. Differently, in the MIMIC method, a mold and a substrate are compressed together in advance, then PDMS gel is pulled by capillary force into the space between them. Through-holes fabricated by μTM is likely to leave undesired thin PDMS membranes on the opening of through-holes [15,16]. Moreover, in both μTM and MIMIC, either the mold or the substrate must be made of PDMS, and the surface of one of them must be treated to facilitate the latter demolding process[10,12], which increases the operating difficulty and cost of these techniques. Compared to μTM, a simpler approach is to leave the membranes in micromolding, and stick them away in the follow-up process [5,16], which will lead to irregular crack edges. Another low-cost method suiting for laboratory study is spin-coating the PDMS gel on the mold [17,18], utilizing air-blowing [11,15] to remove the undesired PDMS membranes on the top of mold. However, PDMS surface will form meniscus near the ends of through holes owing to surface tension. In summary, most of the methods above mentioned need additional labor or expensive experimental devices.

Compared to the MIMIC [13] which patterns PDMS in close capillaries, some types of microstrutures can also generate capillary force as open capillaries without extra covers or substrates. Hence, in this research, micromolding in open capillaries (MIMIOC) is proposed as a simpler method for PDMS through-holes fabrication, whose procedures are easy to observe and handle. In this paper, we utilize the MIMIOC to fabricate PDMS through-holes in different shapes and dimensions, confirming its ability to obtain planar PDMS through-hole layers by experiments. Theoretical analysis is also adopted to demonstrated the processing capacity, and its scope of application is also discussed.

Methods and materials

Micromolding in open capillaries

The specific process of MIMIOC is illustrated in Fig.1. The mold with microstructure arrays on its top and one or several reservoirs in the corner is made of SU-8 , which is compatible with photolithography and has good wettability with PDMS gel. In this research, microstructures on the SU-8 molds includes cylinder columns, square columns and rounded rectangular columns, which were made by conventional photolithography. SU-8 2150 was spin-coated on a Si(100) wafer at 3000 rpm for 40s, followed by soft baking at 65 ℃ for 5 min, and at 95℃ for 30 min. After UV exposure for 15 s (365 nm, 15 mW cm^{-2}), hard baking was performed at 65 ℃ for 5 min, and at 95 ℃ for 15 min. After development in an SU-8 developer, the SU-8 molds was throughly washed in isopropyl alchhol and dried. A 10:1 (w/w) mixture of the PDMS prepolymer and the curing agent was degassed for 15 min to prepare PDMS gel. Drop a little PDMS gel by a needle into the reservoir on the mold which was connected to the microstructure. Then the gel spreads in the entrenches of microstructure under capillary force. In the spreading, gel should be added continuously and carefully, as in Fig.1(b), avoiding overflowing the top of microstructures. After the gel fills the mold, add or remove a certain amount of PDMS gel from the reservoir to get a planar gel surface, as in Fig.1(c). Bake the mold with the PDMS gel in vacuum oven (60 ℃, 2 h) , then the through-hole layer (Fig.1(d)) was obtained after carefully released by a scalpel.

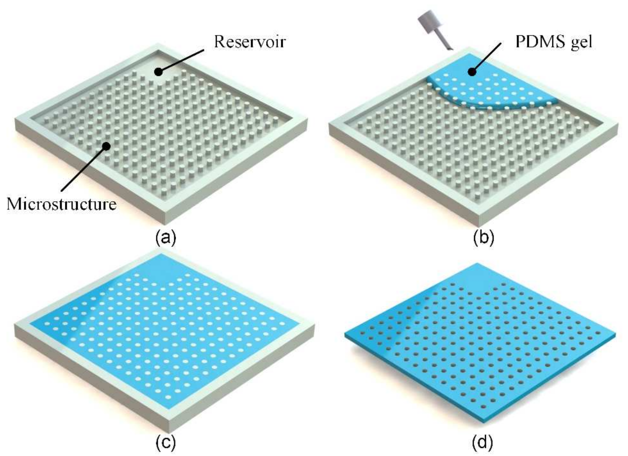

Figure 1. Process for the fabrication of a PDMS through-holes layer by MIMIOC

The MIMIOC is a simple and effective approach to fabricate PDMS through-holes, eliminating the likelihood of leaving undesired PDMS membranes and meniscus near the ends of through holes. Furthermore, the PDMS through-holes obtained by the above process is geometrically related to the mold, so hole array with complicate structure can be achieved by utilizing complicate mold structure. Therefore, the above process can be used for not only fabrication of quasi three-dimensional structures like the column through-holes, but also some true three-dimensional structures. The SU-8 mold used in this method can get 3D structures by multiple photolithography, also, epoxy molds fabricated by stereolithography and nickel molds fabricated by LIGA may be utilized in this method.

Transfer and bonding of through-hole layers

Fabricated PDMS through-hole layers should be bonded to other microstructures to fulfill their functions, so a corresponding transfer and bonding method is necessary. In this study, the fabrication process was implemented as follows. At first, the SU-8 mold with micro column array fabricated by photolithography(Fig. 2(a)) was ultrasonic cleaned and blow dried. Use the MIMIOC method shown in Fig.1 to pattern a PDMS through-hole layer without releasing.

Next, a PDMS transfer layer of about 1 mm was coated and cured (60 ℃, 2 h) on the top of unreleased PDMS through-hole layer, then these two layers were released from the mold by a scalpel, as shown in Fig. 2(c)~(d). The transfer layer was applied as a temporary carrier for through-holes to avoid substantial deformation of microstructures of the through-hole layer, whose thickness usually ranges from tens of to a hundred microns.

The magnitude of releasing resistance of above two layers is related to the shape of the microstructures on the SU-8 molds and SU-8 binding force with PDMS. It is a practical way to reduce this binding force by sputtering a layer of aluminum on the surface of molds. However, for those microstructures with high aspect ratio, it needs a considerable thickness of metal to cover the sidewall, which distorts the dimensions of patterns. In this research, the surfaces of SU-8 molds were silanized by Trichloro(octadecy)silane, which formed self-assembled monolayers (SAM) to reduce the releasing resistance.

After release the thin through-holes by introducing a transfer layer, a PDMS substrate may with microstructure was aligned and bonded with the PDMS through-holes(Fig.2(e)). For the convenience of operation, the PDMS substrate was adhered to a rigid silicon wafer. Oxygen plasma can treat PDMS in a considerable area without affecting microstructure on PDMS, and form a chemical bond [19]. In this study, plasma cleaner (PDC-MG, Mingheng Science &Technology Co. Ltd.) was utilized to treat PDMS through-hole layer and the PDMS substrate (25W, 40 Pa, 40s), then they were pressed together immediately for 60 min, at 60℃。

When the bonding was completed, the PDMS transfer layer was peeled off the through-holes, as in Fig. 2(f). Furthermore, a multi-layer structure could be easily fabricated by repeating this process to stack more patterned PDMS layers on the top of obtained structure. At last, release the PDMS substrate with all structure above from the rigid silicon wafer.

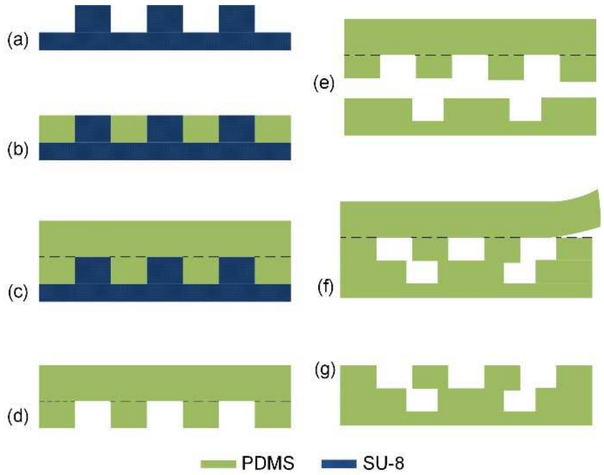

Figure 2. Process of fabrication of a PDMS flexible device.

Materials

SU-8 2150 and SU-8 developer were purchased from Microchem (Newton, MA, USA). PDMS prepolymer (Sylgard 184) and the curing agent were purchased from Dow Corning (Midland, MI, USA). Trichloro(octadecy)silane was purchased from Sigma-Aldrich (St. Louis, MD, USA).

Results and discussion

Through-hole layers

By using the MIMIOC method on SU-8 molds, PDMS through-holes with different shape and size are achieved, and the SEM images are shown in Fig. 3. For microstructures of cylinder, square and rounded rectangular column arrays, a certain area of plane through-holes with the corresponding well-defined shape have been obtained. We gained through-holes of 100 µm thick with a diameter of 50 µm and an interval of 40 µm (Fig.3(a)). Furthermore, the diameters of through-holes obtained were ranging from 50 to 200 µm, and for the sake of strength, their intervals should not be considerably less than the thicknesses.

Furthermore, to exhibit that PDMS gel did not overflow the top of columns on the mold, PDMS was patterned by a SU-8 mold sputtered a 200 nm thick of aluminum. Because aluminum also has good wettability to PDMS gel, the thin aluminum layer cannot influence the wetting morphology of MIMIOC significantly. As shown in Fig. 4(a), the aluminum on top of columns showed darker color than the cured PDMS around, which could deny the overflow of PDMS.

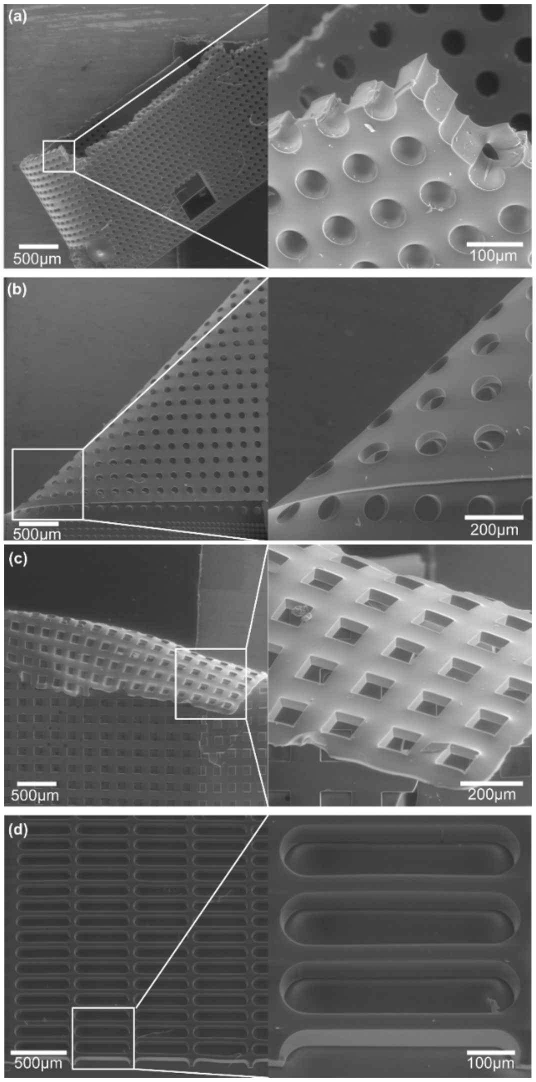

Figure 3. PDMS through-hole layers with circle patterns (a) and (b), square patterns (c) and rounded rectangular patterns (d), and their partial enlarged images

Transfer and bonding technique

The transfer of through-holes was accomplished as shown in Fig. 4(b). Fig.4(c) shows the down side of the transfer layer after being peeled off the through-hole layer on the left. We can see that the transfer layer replicate the surface morphology of through-holes.

In the bonding of PDMS through-hole layer and substrate, due to the flexibility of PDMS, the deformation of these two layers must be precisely controlled to align microstructures on both sides. The substrate was stick onto a rigid silicon wafer, which decreased its tendency to distort. In the transfer technique shown in Fig. 5, it is critical to guarantee that binding force between the transfer layer and through-holes must be greater than demolding resistance. On the other hand, it should be less than the bonding force between through-holes and substrate for the integrity of through-holes after the transfer layer is peeled.

Hence, to lower the operative difficulty of the transfer and bonding process, bonding force between the through-holes and the substrate must be enhanced while demolding resistance reduced.

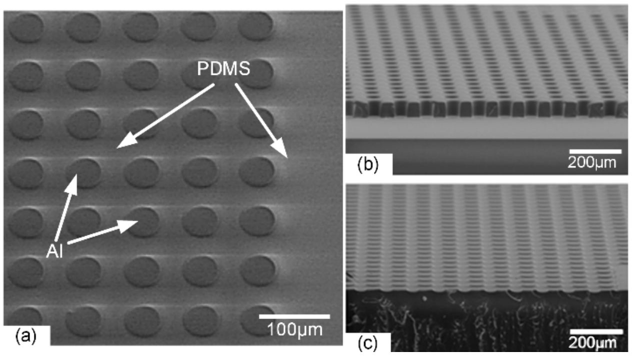

Figure 4. (a) Cured PDMS through-holes layer on a SU-8 mold with aluminum sputtered on the mold surface (b) Through-holes layer bonded on a PDMS slab (c) The down side of transfer layer after being peeled off

Mechanism of the MIMIOC

Feasibility To demonstrate the feasibility of the MIMIC, the changes in interfacial free energies for capillary micromolding process was discussed by Kim[7]. In this paper, a similar model is applied to investigate the changes in interfacial free energies in the MIMIOC, which is regard as a process that gel is pulled by capillary force from a reservoir to open channels or grooves on a mold (Fig. 5). If the capillarity fill the grooves which are oriented perpendicular to the force of gravity, the changes in interfacial free energies ΔG should be negative, meeting the eq. 1:

$$\Delta G = \gamma_{LV}\Delta A_r - [(2y+x)\Delta z(\gamma_{SV} - \gamma_{SL}) - x\Delta z r_{LV}] \quad (1)$$

$$\approx -[(2y+x)\Delta z(\gamma_{SV} - \gamma_{SL}) - x\Delta z \gamma_{LV}] \quad (2)$$

$$= -[(2y+x)\Delta z \gamma_{SV}\cos\theta - x\Delta z \gamma_{LV}] \quad (3)$$

$$= (x - x\cos\theta - 2y\cos\theta)\Delta z \gamma_{LV} \quad (4)$$

Where ΔA_r is the change of gel surface area in the reservoir; $\gamma_{LV}, \gamma_{SV}, \gamma_{SL}$ are liquid-vapor, solid-vapor and solid-liquid interfacial free energies, respectively; and θ is the gel contact angle of the mold; x, y, z are there dimensions of the gel in the groove shown in Fig. 5. For a reservoir whose volume is much larger than grooves, ΔA_r can be neglected, and eq.1 becomes eq.2, from which eq.4 is deduced.

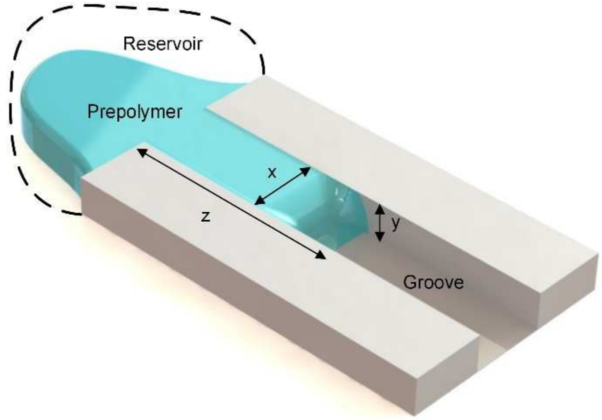

Figure 5. A model of capillary process in open groove

As we can see in Eq.4, only when ΔG is negative will the groove fill. Therefore $(x - x\cos\theta - 2y\cos\theta)$ should be negative. For a groove with aspect ratio of 1, the contact angle $\theta < 70.5^\circ$. In this study, the weighing method was used to measure the contact angle of PDMS gel (10:1) to SU-8, which is about 10°. Consequently, SU-8 microstructures with a aspect ratio larger than 0.0076 are suitable for MIMIOC of PDMS.

Compared to MIMIC, it is more complicated to predict the gel surface in the mold used in MIMIOC theoretically, because the mold is open in MIMIOC. In 2005, Seemann[20] investigated the wetting morphologies of liquid in capillary grooves with rectangular cross-section. According to his study, for grooves with different aspect ratio and different contact angle, the liquid could form overspilling droplets (D region) or extended filaments (F^+ and F^- regions), as shown in Fig. 6[20]. In the morphology of extended filaments, the liquid shape in different cross-sections is essentially constant while extending. So increasing the volume of liquid could only cause the grow of filaments in length. Furthermore, in the region of filaments, the liquid surface was convex (F^+ region) when the substrate had a greater contact angle and concave (F^- region) when the substrate had a smaller contact angle. The principle of the MIMIOC rightly bases on the above phenomena, and the morphology of the PDMS gel that suits for the MIMOC must belong to the region of F-. In F-, insufficient liquid will lead to concave in the extending length. Therefore, the volume of newly added liquid after its fully extended on the mold could be used to control the liquid shape from concave to plane or convex.

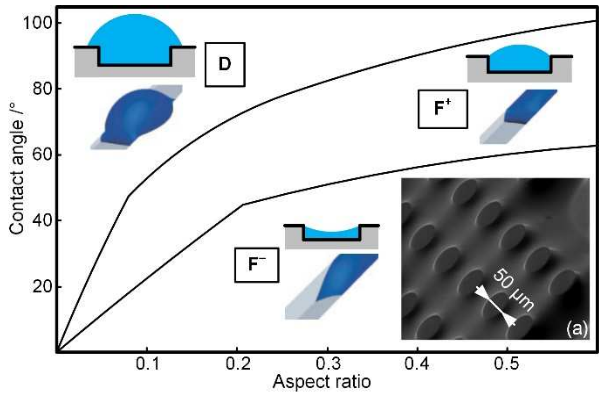

Figure 6. Morphology diagram of liquid in micro grooves, which is determined by aspect ratio of grooves and contact angle.(a) A SEM image shows that PDMS is cured in spreading on a SU-8 mold with cylinder array (Because the samples were observed on a stage with a tile angle of 45 degrees, there are elongations in one direction of each sample).

Relationship mentioned above is suitable for straight capillary grooves, however, a portion of patterns used for through holes molding is column arrays, such as the cylinder array in Fig. 1. Grooves formed by column arrays are crossed, which have a more complicated structure. Therefore, the corresponding morphology diagram will be different. Nevertheless, in a local scale, crossed grooves conform with the characteristic of straight grooves, the discipline that liquid surface changes with the contact angle and the aspect ratio are similar.

We used SU-8 molds with typical cylinder array microstructure to pattern PDMS. Before PDMS gel fully spread on the molds, they were baked at 80℃ for 2 hours. The leading edges of cured PDMS on the molds were observed by SEM, as in Fig. 6(a). In the main extending direction, PDMS concaves as liquid in the F- region could be observed.

Planarity The aspect ratio of capillary grooves on the mold must be in the F- region (Fig.6). PDMS has considerable wettability to common materials. As the contact angle of PDMS to SU-8 is about 10°, according to Fig.3, when the aspect ratio of the mold is greater than 0.04, wetting morphology of PDMS gel will be in the F- region. Take mold structure height of 50 μm as an example, the maximum width is 1.25 mm, which already meets the requirements of common structures of microfluidic.

Within F- region, the concave liquid surface can be adjusted by properly adding the gel, but the liquid surface is not restrained in the open mold. We consider the groove with rectangular cross-section as an example to analyze the surface of spread PDMS gel. When the liquid is insufficient, the gel spreads in the groove and comes to be stable. According to Seemann[20], the surface shape can be determined, which is related to the contact angle and the groove aspect ratio. When the liquid fills the mold, the surface shape can be controlled by properly adding the liquid if the wetting morphology is in the F- region. On the contrary, in the F+ region, the increasing of liquid amount will lead to the rise of liquid level, which is impossible to obtain a planar through-hole layer.

Ignoring gravity, liquid surfaces shape after spreading over the mold is shown in Fig. 7. Owing to surface tension of the liquid, the relationship between the pressure difference inside and outside and the radius of curvature meets Laplace's equation:

$$p_{\text{in}} - p_{\text{out}} = \gamma_{\text{LV}}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{5}$$

In which, pin and pout are the pressure inside and outside the liquid respectively , R1 and R2 are two main curvature radii for the gas-liquid interface at any point.

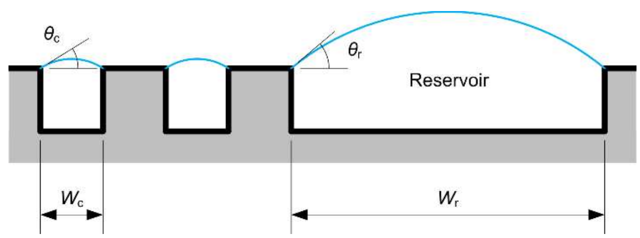

Figure 7. Cross section of a typical mold for the MIMIOC method.

In Fig. 7, because the cross-section shapes of liquid in the capillary groove are almost identical, there is a large difference between two principal curvature radii. Therefore, compared to the curvature radius in the direction parallel to the paper in Fig. 7, the other curvature radius along the groove can be considered infinite large; On the other hand, to the liquid surface in the reservoir , which can be approximated to a spherical cap , the two main radii of curvature are equal. Considering the liquid is stable, the internal pressure is equal everywhere, so the liquid shapes in the capillary groove and the reservoir should have the following approximate relationship:

$$\frac{1}{R_c} = \frac{2}{R_r} \tag{6}$$

where R_c is the significantly smaller curvature radius of the liquid surface in the groove, and R_r is the curvature radius of the liquid surface in the reservoir.

Thus, the liquid curvature in the capillary groove and the reservoir can be summarized in a simple proportional relationship. Liquid reservoir size can be designed to be larger, so that to slow the surface change caused by injection of the liquid, making it easier to control the curvature of liquid in the capillary grooves by changing that in the reservoir. Furthermore, as the liquid reservoir has much larger size compared to the size of capillary grooves, the shape change of liquid in the capillary grooves induced by that in the reservoir can be further reduced, which can be observed by comparing the protruding angles of liquid surface in the capillary grooves and the reservoir in Fig. 6. According to the geometric relationship between the radius of curvature, the groove width and the protruding angle, combined with Eq. 6, it is easy to get:

$$\frac{\sin\theta_c}{\sin\theta_r} = 2\cdot\frac{W_c}{W_r} \tag{7}$$

where W_c is the characteristic width of grooves and W_r is the characteristic width of the reservoir. θ_r is the protruding angle of PDMS gel in the reservoir and θ_c is that in the grooves.

When $W_c << W_r$, the liquid surface in the capillary grooves is nearly planar. For instance, the capillary groove width is 100 μm and liquid reservoir size is 1mm, when the liquid surface in the reservoir has a 10° protruding angle, the angle in the capillary groove is only 2°. In fact, 10° has reached the contact angle of PDMS gel to SU-8 mold, which can be considered as the upper limit of the protruding angle of the liquid in the reservoir.

Conclusions

In this study, we proposed a MIMIOC method to realize the fabrication of PDMS through-holes in open capillaries without any cover for molding, whose procedures could be easy to observe and handle. The performance of this method was confirmed by patterning PDMS through-holes on SU-8 molds with cylinder/square/rounded rectangle column arrays, whose diameters were between 50 μm and 200 μm, and thicknesses were less than 200 μm. At the same time, a PDMS supporting transfer layer was introduced to facilitate the transfer of through-hole layers and the alignment and bonding between through-hole layers and substrates. In this process, oxygen plasma treatment and surface silanization were utilized to change the bonding strengths between each layer. Furthermore, the feasibility of this method was discussed by investigate the changes in interfacial free energies in the molding process and the wetting morphology of PDMS in SU-8 quasi grooves, and its ability to achieve planar PDMS layer with protruding angles less than 2° was proved theoretically. Therefore, it could be concluded that MIMIOC is an effective, low-cost and simple approach to pattern PDMS through-hole layers, which has great potential for developing MEMS devices, especially for multi-layer devices where PDMS through-hole array is employed.

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Notes and references

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