Direct Optical Patterning of Poly(dimethylsiloxane) Microstructures for Microfluidic Chips

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ABSTRACT

In this paper, we present an optical maskless exposure approach for direct patterning of large-area high-resolution microfluidic chips using photosensitive poly(dimethylsiloxane) (PDMS) materials. Both positive- and negative-tone photosensitive PDMS (photoPDMS) were successfully patterned into various microfluidic devices with complex geometries by using an optical maskless lithography process. The positive-tone PDMS is used for patterning of large-area chips, while the negative-tone PDMS is demonstrated to fabricate high-resolution microstructures and on-chip devices. With the seamless pattern-stitching technique, a large-area microfluidic chip with size of 5.5 × 2.8 cm^2 with complex three-dimensional (3D) staggered herringbone mixers (SHMs) for micro-flow gradient generation has been directly fabricated within 125 minutes by using the positive-tone PDMS. A small microfluidic chip with feature size as small as 5 μm is demonstrated by using the negative-tone PDMS. The experimental results reveal that the optical maskless lithography technology enables to rapidly pattern high-resolution microstructures and is very promising for development of lab-on-a-chip devices.

Keywords: optical maskless lithography, direct patterning, photosensitive poly(dimethylsiloxane), microfluidics

1. INTRODUCTION

Microfluidics is one of the essential technologies driving the innovation and development of lab-on-a-chip (LOC) devices. It enables integration of complex microfluidics manipulation and analysis components on a single small chip. In recent years, the growing demand of microfluidic chips with lower cost and shorter cycle of fabrication has posed a significant challenge to the conventional manufacturing technologies. Therefore, it is appealing to develop a flexible high-resolution approach for rapidly fabricating microfluidic devices. To this end, various methods, e.g., laser direct machining, inkjet 3D printing, have been proposed.[1] On the other hand, poly(dimethylsiloxane) (PDMS) has recognized as an ideal material for microfluidic chips due to its nontoxic, electrically insulating, optically transparent and chemical inertness.[2] High-resolution PDMS microfluidic chips are usually fabricated by using soft lithography technology. However, such a technology needs preparation of physical mask and replication master, which are time-consuming and not flexible for device development.

Recently, we demonstrated an optical maskless lithography technology to rapidly pattern 2D/3D microstructures of hydrogels for tissue engineering[3] and ultrasensitive pH sensing.[4] In this paper, we propose a one-step approach for direct patterning of photosensitive PDMS (photoPDMS) for development of microfluidic devices and chips. It is demonstrated that two kind of photosensitive PDMS materials, positive- and negative-tone photoPDMS, allowed for fabrication of various high-resolution microstructures and microfluidic chips by using the developed technology. A large-area microfluidic chip with complex 3D staggered herringbone mixers (SHMs) for micro-flow gradient generation is directly fabricated by using the positive-tone photoPDMS.

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2. EXPERIMENTAL FABRICATION

2.1 Optical maskless lithography setup

By using a digital micromirror device (DMD) (DLi4120 0.7″ XGA, DLP Texas Instruments), an optical maskless lithography (OML) system, as depicted in Fig. 1a, is developed after integration with a high-power UV source (OmniCure 2000 System, Lumen Dynamic Group Inc.), a set of self-designed projection optics and high-precision motorized stages. The high-speed spatial-light modulator, i.e. DMD chip, acts a role of a dynamic virtual mask generating the optical patterns from a homogeneous UV light beam according to the images synchronized by a computer in real-time. A CCD camera is also integrated into the system to monitor the substrate under exposure. Moreover, seamless stitching between adjacent sub-patterns is developed to enable the fabrication of large-area microfluidic chips.

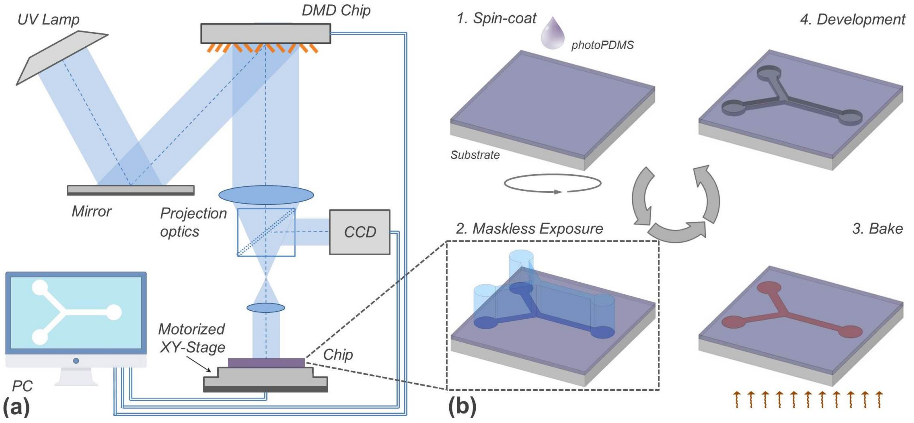

Figure 1. (a) Schematic diagram of the optical maskless lithography setup for fabricating microfluidic chip using photosensitive PDMS, (b) typical fabrication processes for fabrication of microfluidic chips.

2.2 Positive and negative photosensitive PDMS

The positive photosensitive PDMS (P-photoPDMS) contains PDMS base, curing agent and benzophenone.[5] Firstly, the PDMS base and the curing agent (Sylgard® 184 Silicone Elastomer kit, Dow Corning) was fully mixed in a 10 : 1 (m/m) ratio. Benzophenone (Sigma-Aldrich) was fully dissolved in xylene and then was mixed with the PDMS mixture for 30 min. Different benzophenone to PDMS mixture ratios (0.25 wt %, 0.5 wt %, and 0.75 wt %, respectively) were used in the experiments, while the ratio between xylene and PDMS mixture kept constant, 15 wt%. The mixture was then degassed for 30 min to completely remove air bubbles caused during mixing.

The PDMS base monomer is usually vinyl terminated, while the crosslinking monomer is methyl terminated due to its silicon hydride groups. During curing process, reaction between the monomer vinyl groups and the crosslinker silicon hydride groups makes PDMS monomers crosslinked. The presence of benzophenone in the PDMS mixture, producing benzophenone radicals upon UV exposure (365 nm), which reacts with the silicon hydride groups contained in the crosslinker and thus inhabits the crosslinking reaction between the PDMS monomer and crosslinker. After post-exposure bake, the unexposed PDMS becomes crosslinked and cured, while the exposed PDMS region remains uncrosslinked and can be washed away in xylene.

The negative photosensitive PDMS (N-photoPDMS) contains PDMS copolymer VDT 954 (Gelest Inc.) and 2,2-dimethoxy-2-phenyl acetophenone. VDT 954 was firstly dissolved in methyl isobutyl ketone (MIBK, Sigma-Aldrich) in a 6 : 4 (m/m) ratio, and then 2,2-dimethoxy-2-phenyl acetophenone (Igracure 651, Ciba Specialty Chemicals Inc.) was added into the solution as photoinitiator.[6] Different Igracure 651 to VDT 954 ratios (1 wt %, 3 wt %, and 5 wt %, respectively) were used in the experiments. The mixture was fully mixed for 1 hour and degassed for 30 min. Upon UV exposure (at the wavelength of 365 nm), the Igracure 651 photoinitiator generates free radicals, which induce the crosslinking of VDT 954. The unexposed PDMS region remains uncrosslinked and can be washed away using a mixture of MIBK and isopropanol (1:1, v/v).

2.3 Fabrication process of microfluidic chips

As shown in Fig. 1b, the patterning of PDMS in our experiments involves four critical steps: spin coating, optical exposure, bake and development. For P-photoPDMS, the prepared P-photoPDMS mixture is spin-coated on a clean 1-mm-thick glass substrate (1″ × 1″) at the spin rate ranging from 700 rpm to 3000 rpm (depending on the desired thickness) for 30 seconds. The P-photoPDMS coated substrate is then placed under the OML setup for optical exposure. 3D models of the microfluidic chips or microstructures are designed by using a commercial CAD software, an own-developed add-on program is used to slice the 3D models into a seriers of images with 200 layers. Each image is then sequentially uploaded to the DMD chip to dynamically generate predefined light patterns. optical exposureOwing to the additive penetration depth of UV light, microstructures can then be fabricated on the P-photoPDMS. Both the projection optics and the substrate keep motionless during the exposure of individual sub-pattern. The exposed time of each microstructure is calibrated according to the model feature and thickness of the P-photoPDMS layer, ranging from several seconds to tens of seconds. Following the optical exposure process, a post-exposure bake is conducted on a hotplate at 85 °C for 3 ~ 5 minutes depending on the thickness of the P-photoPDMS layer. Finally, the sample is immersed into the MIBK and isopropanol (1:1, v/v) solution for 1 hour for complete development, and is rinsed with isopropanol and dried with nitrogen gas.

For N-photoPDMS, the fabrication process is very similar to that of the P-photoPDMS, except the post-exposure bake step, which can be skipped as the N-photoPDMS gets cured during the optical exposure step.

3. RESULTS AND DISCUSSION

3.1 P-photoPDMS microfluidic chips

Microfluidic chips of P-photoPDMS can be directly patterned by the OML technology , as shown in Fig. 2a. As the P-photoPDMS is positive-tone, the exposed region will produce notched channels. To quantify the characteristics of the P-photoPDMS for fabrication of microfluidic devices, the generation of straight channels under different experimental conditions is initially investigated. Fig. 2b illustrates the depth variation of the patterned channel with respect to the exposure energies for different benzophenone concentrations, 0.25%, 0.5% and 0.75%, respectively. The width of the designed channel is 100 μm, and the UV intensity is 330 mW/cm^2, while the exposure time ranges from 2 to 16 seconds with an interval of 2 seconds. One can see that deeper microfluidic channel can be obtained with more photoinhibitor as more radicals are released to react with the curing agent. Channel depth up to 40 μm can be patterned when the concentration of benzophenone is 0.75% and the exposure energy is ~ 5300 mJ/cm^2. Although higher concentration of benzophenone can produce deeper channel, excess benzophenone will cause crystallization of the mixture shortly after the spin-coating, which will cause of degradation of the surface quality of the sample.[5] In our experiment, crystallization was observed in the 0.75% mixture but not in the 0.25% mixture. Furthermore, UV intensity of our OML setup is adequately strong to pattern the P-photoPDMS channel within a few tens of seconds, which greatly shorter than that in the previous works.[5, 7] Therefore, photoinhibitor concentration of 0.25% is chosen in the following experiments. It is noteworthy that the increment of the channel depth trends to get saturated due to the Beer-Lambert law because UV light gets weaker with the penetration in P-photoPDMS. The inset in Fig. 2b shows the profile of the patterned channel with applied exposure energy of ~ 5300 mJ/cm^2. One can see that the surface profile of this patterned channel is very smooth. Fig. 2c shows a directly printed 5-loop double spiral microfluidic device. The whole size, channel width and height of the device are 7.2 × 5.0 mm^2, 250 μm and 28 μm, respectively. Such a spiral microfluidic device can be used in various microfluidic applications, e.g., filtration,[8] and mixing.[9]

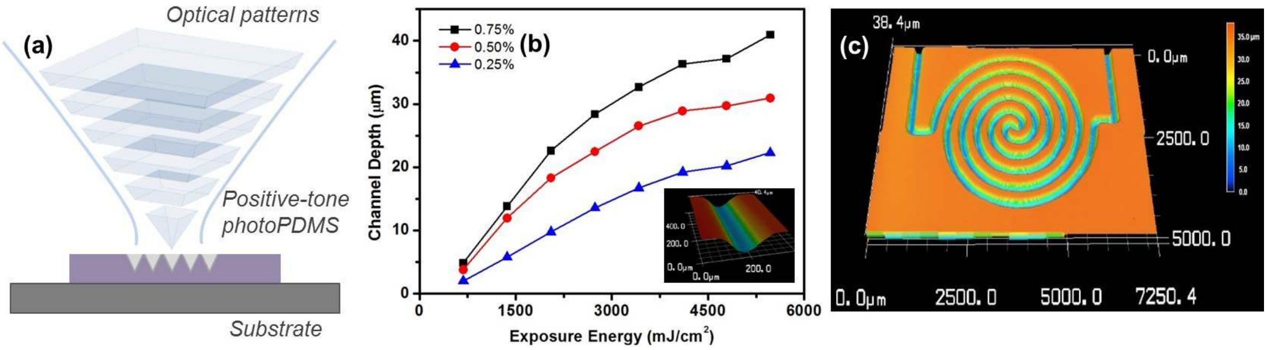

Figure 2. (a) schematic of the layer-by-layer exposure process. (b) the depth variation of the patterned channels with respect to exposure energies. The inset is the profile of a patterned straight channel, and (c) the laser scanning confocal image of a 5-loop double spiral microfluidic device.

3.2 N-photoPDMS microfluidic chips

For N-photoPDMS, the spin-coated substrate was inversely placed with a spacer for exposure process, as shown in Fig. 3a. UV-transparent substrates, e.g., cover glasses, is used in the experiments. Similar with that of P-phtoPDMS, direct patterning of straight channels of N-photoPDMS is investigated under different exposure conditions by using the OML process. To produce a microfluidic channel, the region outside the channel need fully exposed, while the channel region keeps unexposed. As the thickness (T_l) of the spin-coated layer is usually fixed, the channel depth (D_c) of the partially cured N-photoPDMS with the thickness (T_p) is then $D_c = T_l - T_p$. In experiment, the width of the designed channel is 100 µm, the initial thickness (T_l) of the spin-coated layer is 40 µm, UV intensity is 125 mW/cm^2, and the exposure time is between 4 to 30 seconds. Fig. 3b illustrates the variation of the thickness (T_p) of the cured N-photoPDMS with respect to the exposure energies for the photoinitiator concentrations of 1%, 3% and 5%, respectively. One can see that thickness of the cured N-photoPDMS increases with exposure energy. Fig. 3c shows a small microfluidic chip of the size of 450 × 450 µm^2.. One can see that two main channels with width of 20 µm were fabricated and another three connecting channels with width of 5 µm were also successfully produced.

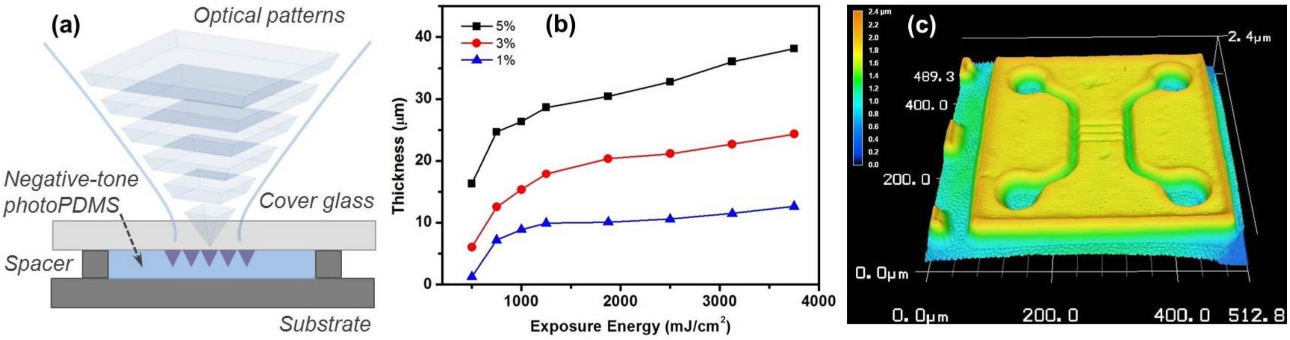

Figure 3. (a) schematic of the layer-by-layer photopolymerization process exposing from bottom, (b) the variation of the thickness of the cured N-photoPDMS with respect to exposure energies, (c) the laser scanning confocal image of a small microfluidic chip with 5-µm-wide channels.

3.3 Direct µ-printing of a microfluidic chip with herringbone mixers

A large-area microfluidic chip with complex 3D staggered herringbone mixers (SHMs) for gradient generation is demonstrated in the experiment. Such a device allows much shorter mixing section, which could improve the integration of the microfluidic chip for chemical biological analysis.[10, 11] In experiments, 3D model of a 5-level gradient generator was designed by using a CAD software, as shown in Fig. 4a, the size of this device is 5.5 × 2.8 cm^2, the channel width is 400 µm while the height is 30 µm, the width of the outlet channel was 2800 µm, combining 7 branching channels. The 3D model is then sliced into 50 layers by using the own-developed add-on program. The generated image has a size of 15500 × 7392 pixels, and each pixel represents 2.7 µm in the system. The OML system can convert this image into 20 × 13 sub-images and automatically process one by one. The exposure time for each sub-image was set to 60 seconds and the UV intensity was 330 mW/cm^2. A pre-cured conventional PDMS film with the thickness of 1 mm was used as a substrate instead of a glass wafer in the fabrication. The whole patterning process was completed within 125 minutes.

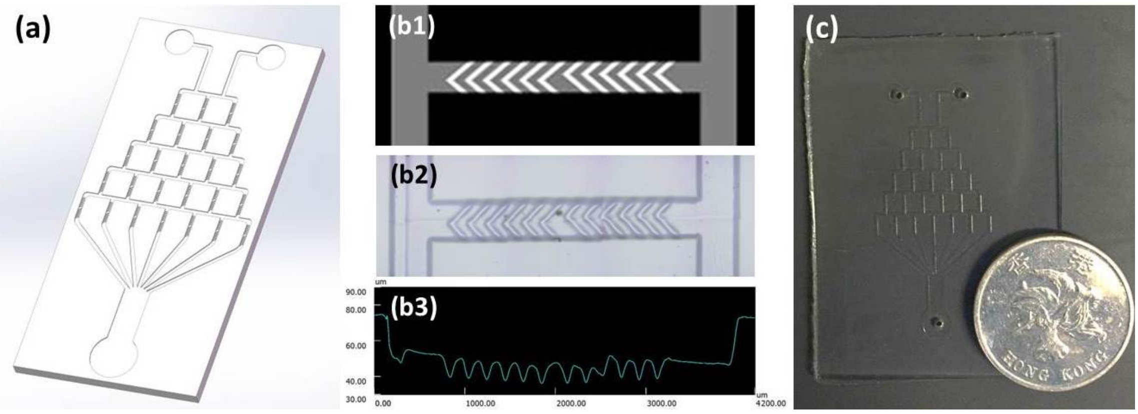

Figure 4. Direct patterning of a large-area microfluidic chip with complex 3D staggered herringbone mixers. (a) the 3D model of the chip, (b) the fabricated staggered herringbone mixer: b1, the grayscale image constructed by the 3D model for patterning process, b2, the microscope image of the fabricated SHM, b3, the cross section profile of the SHM, (c) a photograph of the fabricated device.

Fig. 4b shows the close-ups of the direct patterned staggered herringbone mixer (SHM). Part of the constructed grayscale image from the 3D model for patterning process is shown in Fig. 4-b1. It has three grayscale level, 0, 127 and 255 respectively, and is used to control exposure time during the patterning process. Fig. 4-b2 shows the microscope image of the fabricated SHM. indicating that clear staggered herringbones can be directly patterned. Cross section profile of the SHM is presented in Fig. 4-b3, which was measured by 3D laser scanning confocal microscope (VK-X200, KEYENCE, Japan). One can see that, below a plain microfluidic channel with depth of ~ 22 µm, the grooves with depth of 12 µm are successfully fabricated. The profile of the patterned SHM agrees well with the designed structural parameters. Fig. 4c shows the fabricated large-area microfluidic chip with complex 3D SHMs after development. The fabricated PDMS microfluidic device is highly transparent.

The microfluidic chip was then bonded with a clean glass wafer after O^2 plasma treatment. Thereafter, rhodamine 6B dye solution (dissolved in ethanol, 5 %wt) and pure ethanol were injected into the chip simultaneously at a rate of 0.5 µL/min by using two syringes mounted on a syringe pump. As solutions stably flowed through the chip, gradient generation was successfully observed in the outlet channel region, as shown in Fig. 5a. Fig. 5b shows the enlarged image of the outlet channel region. Fig. 5c shows the normalized concentration distribution of the solution across the outlet channel, which was calculated according to color intensity of the region marked with green dashed line in Fig. 5b. Two parallel dashed lines in Fig. 5c donate the outlet channel boundary. The quantitative analysis result is consistent well with that in the previously reported works.

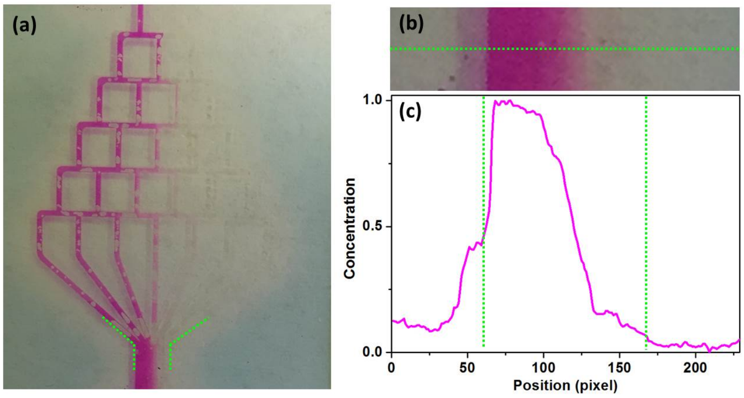

Figure 5. Gradient generation test of the patterned microfluidic chip. (a) photograph of the solution-injected chip, (b) enlarged image of the outlet channel region, (c) normalized concentration distribution of the solution across the outlet channel, calculated according to color intensity of the region marked with green dashed line in fig. 5b.

4. CONCLUSIONS

In conclusion, a new direct patterning technology has been demonstrated to fabricate microfluidic chips using both positive- and negative-tone photosensitive PDMS. Various microstructures and microfluidic devices with different geometries have been successfully demonstrated, which reveals the feasibility and the versatility of the proposed technology. In particular, a large-area microfluidic chip with complex 3D staggered herringbone mixers has been fabricated on positive-tone photosensitive PDMS by using the one-step process and demonstrated for microfluidic gradient generation. This technology will offer new opportunities for rapid fabrication of novel microfluidic devices for various applications.

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