Photodefinable polydimethylsiloxane (PDMS) for rapid lab-on-a-chip prototyping†

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In this paper, we introduce a new and simple method of patterning polydimethylsiloxane (PDMS) directly using benzophenone as a photoinitiator. The photodefinable PDMS mixture (*photoPDMS*) is positive-acting and only sensitive to light below 365 nm, permitting processing under normal ambient light. Features of the order of 100 μm, which are sufficiently small for most microfluidic applications, were successfully fabricated using this novel process. A parametric study of process parameters was performed to optimize the fabrication. As a demonstration, microfluidic channels of varying dimensions were successfully fabricated using this process and experimentally characterized using fluorescence microscopy. To further demonstrate *photoPDMS* potential, thin (<30 μm) free-standing films with through patterns were fabricated and successfully used as shadow masks. The *photoPDMS* process completely eliminates the need for a master, permits processing under normal ambient light conditions, and makes fabrication fast and simple. This process for rapid prototyping of low-cost, disposable LOCs can be accomplished without cleanroom facilities and thus can be employed for a wide range of applications.

1. Introduction

Lab-on-a-chip (LOC) systems have numerous applications in chemistry and life sciences. Today, the LOC field is driven by the need for low-cost disposable devices with relatively large areas but micrometre-size features. Many LOCs are fabricated in polydimethylsiloxane (PDMS) elastomer, which has numerous advantages over silicon and glass. Perhaps the most critical advantage of PDMS is the simple and inexpensive fabrication process, which permits rapid prototyping. PDMS is optically transparent above ~230 nm, making it compatible with a variety of optical detection and microscopy techniques. It has become a popular choice for biological studies because it is nontoxic to cells and permeable to gases. PDMS remains flexible and stable over a wide range of temperatures from −50 °C to +200 °C; a property not available in most materials. Furthermore, PDMS surfaces can be modified through adsorption of proteins or *via* plasma processing to obtain specific surface characteristics. Cured PDMS substrates can then easily be bonded to another PDMS slab or glass wafer using a brief O_2 plasma treatment.

Procedures for the fabrication of PDMS-based microfluidic devices have been described in detail in a recent review by Sia and Whitesides.[1] Typically, a master for casting PDMS is first fabricated with conventional microfabrication techniques. The master represents the negative (inverse) structure of the desired PDMS structure. To create PDMS structures, liquid PDMS prepolymer is mixed at a 10 : 1 (m/m) ratio with curing agent and poured onto the master. The PDMS is cured at 80 °C for approximately 2 h and peeled off the master, producing the final replica containing the microstructures.

The microfabrication process is only necessary one time for the fabrication of the master structure that is then replicated many times in PDMS. However, master fabrication is also a critical limitation of the PDMS microfabrication process. Master fabrication using traditional microelectromechanical system (MEMS) methods typically requires cleanroom facilities and equipment, which increase process time and costs, and may not be readily available or accessible. Cost and simplicity are important for developing LOCs for medicine. Thus there is a continued interest in alternative, low-cost, rapid, microfabrication methods.

One solution is to make the PDMS polymer photosensitive, and thus directly patternable. This can be accomplished by addition of a photoinitiator 2,2-dimethoxy-2-phenyl acetophenone (DMAP) and making PDMS perform as a negative photoresist.[2–4] Exposure to UV light results in PDMS cross-linking and curing the exposed regions. The DMAP photoinitiator is difficult to dissolve at room temperature and in the process described by Lotters *et al.*[3] the mixture had to be prepared and stored overnight before use (the reason for this was not given by the authors). Extensive care must be taken to minimize presence of oxygen during the UV exposure as it prevents PDMS from curing by inhibiting photocrosslinking.[5] Addition of DMAP photoinitiator also made PDMS sensitive to ambient light, and now required processing inside a ''gold room'' (a room with 480–900 nm filtered light for processing light-sensitive materials such as a photoresist). Thus, this process has not gained popularity for fabricating LOC devices.

Another recent example is the photodefinable silicone introduced by Dow Corning[6–8] to the semiconductor packaging market. Thin films of thicknesses ranging from 6 μm to

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† The HTML version of this article has been enhanced with colour images.

50 μm can be obtained using this product. This material is patterned as any traditional photoresist with processing steps such as spin coating, soft bake, UV exposure, post exposure bake, solvent development, and hard bake. However, this product is very similar to negative photoresist in terms of high cost and the need for cleanroom photolithography facilities.

In this paper, a novel low-cost, rapid, and simple process for patterning PDMS directly is introduced. Benzophenone is added to PDMS, which is then patterned with UV light exposure, cured and developed. Benzophenone is a photosensitizer often used to initiate free-radical polymerization by UV light of acrylates and monomers with other functional groups. A number of investigators have already reported its use with siloxanes.[9–11] The process offers the advantages of PDMS elastomer, yet simplifies fabrication by eliminating the need for a master. The new fabrication process is not sensitive to ambient light. By using transparency masks and a portable UV light source, LOCs can be prototyped ultra rapidly in any lab, eliminating the need for a cleanroom.

2. Experimental

2.1. Materials

All chemicals were analytical reagent grade and were used as received. Toluene and xylene solvents, sulfuric acid and hydrogen peroxide were purchased from Fisher Scientific. White crystalline benzophenone powder was purchased from Sigma-Aldrich. PDMS was purchased as a two-component kit containing the vinyl-terminated base and curing agent from two manufacturers: Sylgard 184 from Dow Corning and RTV 615 from GE Silicones. Sulfuric peroxide solution was prepared by mixing H_2SO_4 and H_2O_2 in a 7 : 3 (v/v) ratio.

2.2. Fabrication

The PDMS mixture was first prepared by mixing the PDMS base and the curing agent in a 10 : 1 (m/m) ratio. Benzophenone was dissolved in xylene and was mixed with the PDMS mixture for 15 min. This mixture was degassed for 15–20 minutes to remove air bubbles formed during mixing. The effect of the various benzophenone ratios (0.1%–5%) is discussed in the results section. Fig. 1(a) illustrates the fabrication sequence.

A 300 μm glass wafer (3″ × 3″) was initially cleaned using acetone, methanol and DI water for 3 min followed by 12 min in sulfuric peroxide solution. The prepared *photoPDMS* mixture is then spin coated on the wafer for 30 sec at spin rates ranging from 500 rpm to 5000 rpm depending on the desired thickness. These thickness measurements were made using a surface profilometer (P11, KLA Tencor). Other substrate materials such as silicon, cyclic olefin copolymer (COC) or polymethylmethacrylate (PMMA) could also be used. The spin-coated wafer was then placed under a UV lamp for exposure. In this work, a hand-held UV lamp of 12 mW cm^{-2} intensity was used. A high resolution chrome mask containing the desired patterns was then positioned above the spin-coated wafer by placing it on 400 μm thick glass slides on either side of the wafer. Thus the mask was not in direct contact with the spin-coated wafer, as illustrated in Fig. 1(b). The gap between the mask and the wafer was maintained as low as possible

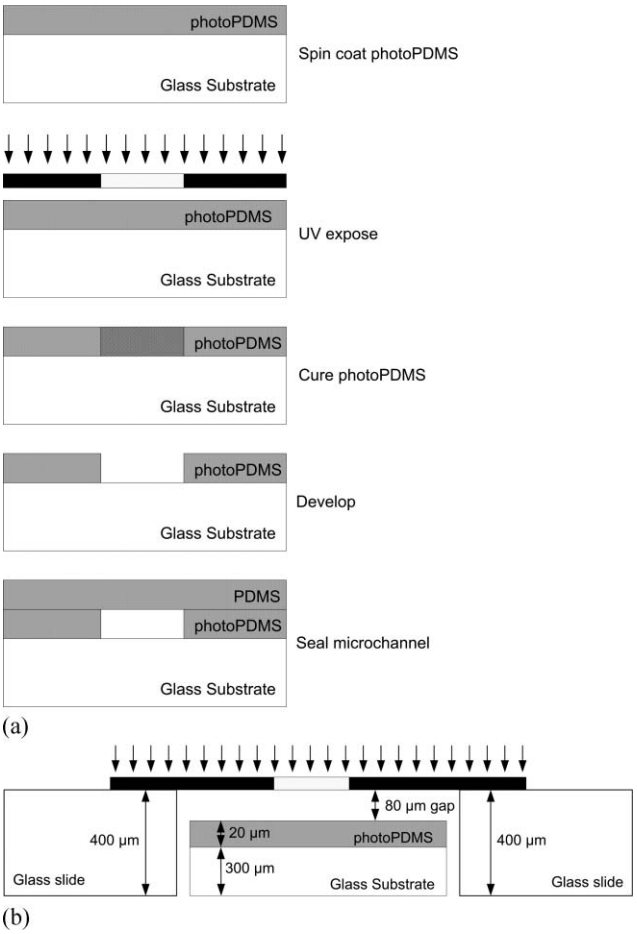


Fig. 1 Schematics illustrating (a) the *photoPDMS* process sequence and (b) positioning of the mask above the *photoPDMS* wafer during exposure.

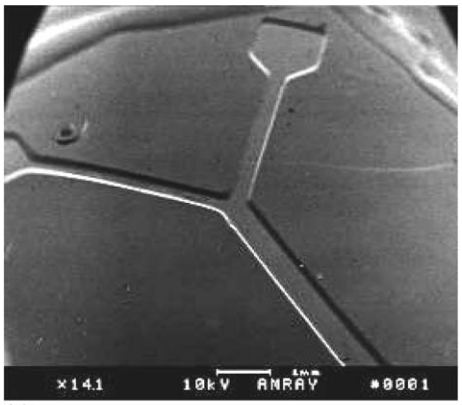
(<80 μm) to minimize effects on feature dimensions and sidewall definition. Other investigators[3,5] reported that additional protection was needed for the spin coated wafer from air, as the presence of oxygen prevented PDMS from curing by inhibiting photocrosslinking. In this process, however, oxygen sensitivity was not a concern and thus no additional steps were necessary.

Next, the *photoPDMS* coated wafer was exposed to UV light <365 nm for about 10 min at 12 mW cm^{-2}. Following the exposure, a post-exposure bake was carried out in a conventional oven at 120 °C. Initially, a hotplate was used, but since the heat distribution was not uniform, some of the features were lost due to under-curing. During post-exposure bake, the unexposed regions get cured while the exposed regions remain uncured. The curing time ranged from 40–120 sec depending on the thickness of the PDMS film. The uncured PDMS was developed by dipping the wafer in toluene for 3–5 sec. The wafer was then rinsed with isopropanol and blow dried with N_2 gas.

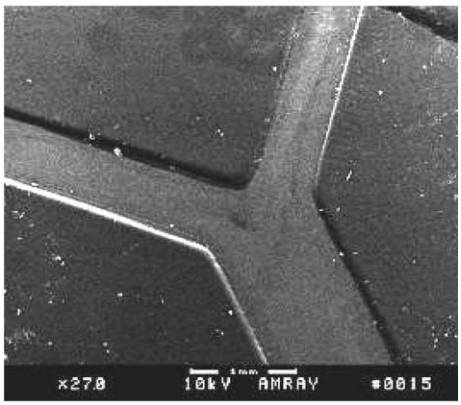
3. Results and discussion

3.1. PhotoPDMS

Conventional PDMS consists of repeating $–OSi(CH_3)_2–$ units. The PDMS base monomer is vinyl terminated, while the



(a)



(b)

Fig. 2 (a) SEM of a 400 μm wide channel with 200 μm wide inlets. (b) SEM image illustrating the entrance region of a 1 mm wide channel. The image shows vertical channel walls similar to those achieved using conventional photoresists.

crosslinking monomers are methyl terminated and contain silicon hydride –$OSiHCH_3$– units. During curing, PDMS monomers cross-link *via* a reaction between the monomer vinyl groups and the crosslinker silicon hydride groups to form Si–CH_2–CH_2–Si linkages.

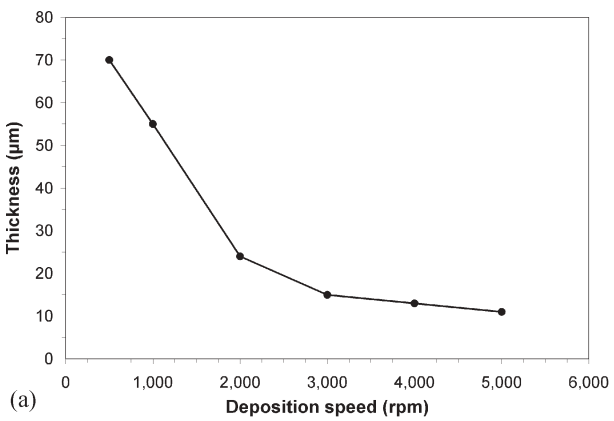
When benzophenone (also known as diphenyl ketone) is mixed with PDMS and irradiated using UV <365 nm, a benzophenone radical is formed, which will abstract a hydrogen atom from a suitable hydrogen donor.[12–14] These radicals react with the silicon hydride groups present in the PDMS crosslinkers and prevent them from undergoing the traditional crosslinking reactions with the PDMS monomer. During the post-exposure bake, the unexposed PDMS gets cured and cross-linked, while the exposed PDMS remains uncrosslinked and can be washed away in toluene. Thus, benzophenone, which is commonly used as a photoinitiator in free radical polymerization, acts as a photoinhibitor in this case.

Photosensitive PDMS is positive-acting, which simplifies LOC design and fabrication. Fig. 2 illustrates entrance regions of two Y-junction micromixers fabricated in *photoPDMS*. Patterns with features ranging from 100 μm to several millimetres can be easily replicated in *photoPDMS* layers 10 μm to 60 μm thick. Unlike the traditional fabrication method in which PDMS channels are negative replicas of a master, the PDMS channels shown in Fig. 2 were patterned directly.

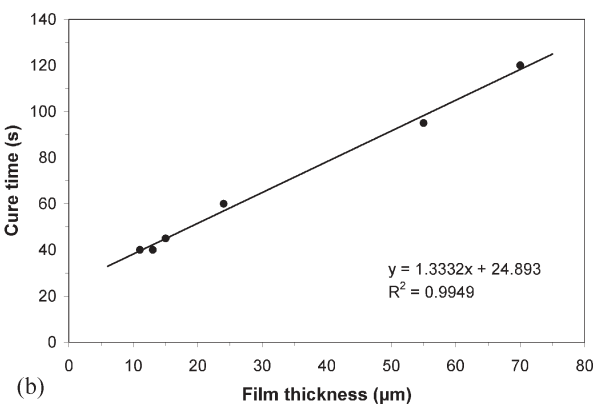
PhotoPDMS is only sensitive to light below 365 nm due to the absorption spectrum of benzophenone that peaks at 260 nm, with a tail at 365 nm.[15] Thus, the *photoPDMS* is processed under the normal ambient light conditions in a conventional laboratory, eliminating the need of a "gold room." Indeed, dust particles seen on the surface of the device in Fig. 2(b) are due to processing outside the cleanroom. Either a conventional aligner (without an I-line filter) or a hand-held UV lamp capable of at least 12 mW cm^{-2} can be used for exposures. Transparency masks can also be easily used with this process to further reduce costs and increase speed of prototyping.

Fig. 3 illustrates the dependence of the *photoPDMS* film thickness on spin-coating deposition speed. These results are in agreement with those reported in literature for conventional PDMS formulations.[16] Thus, addition of benzophenone and xylene to the PDMS mixture does not appear to have a significant effect on deposition.

Contact angle measurements were performed to assess the influence of benzophenone content in *photoPDMS* on surface properties. The contact angle of unmodified PDMS was measured to be 109.3 ± 1.6° which agrees with values reported in the literature.[17] The measured contact angles of the PDMS surface containing 2%, 3% and 4% benzophenone (by weight) were 113.4°, 113.0° and 114.7° with a standard deviation of



(a)



(b)

Fig. 3 (a) Spin speed *vs.* thickness plot for the *photoPDMS* mixture. (b) Dependence of cure time of *photoPDMS* at 120 °C on film thickness.

Table 1 Summary of the parameters used to optimize the process

Parameter				
Benzophenone–PDMS monomer ratio (m/m)	1 : 1000	1 : 100	1 : 50	1 : 33
Curing agent–PDMS monomer ratio (m/m)	1 : 20	1 : 10	1 : 5	
Exposure time/min	8	10	12	
Curing temperature/°C	90	120	150	

1.95°. Thus, addition of benzophenone does not have a substantial change on the PDMS surface contact angle.

3.2. Process optimization

The *photoPDMS* process was optimized by examining the effects of benzophenone concentration, PDMS monomer to curing agent ratio, exposure time, bake time and temperature. Levels of these parameters used in a factorial experimental design are summarized in Table 1.

A benzophenone concentration of 3% (w) with respect to the *photoPDMS* mixture was found to be the optimum. Concentrations below 3% yielded patterns with poor side wall definitions, and features with dimensions smaller than those on the chrome mask. No patterns could be replicated at 0.1% (w) benzophenone as the generated benzophenone radicals were not sufficient to prevent PDMS from curing. Increasing benzophenone concentration to 4% or 5% yielded good quality patterns, but excess benzophenone caused the mixture to crystallize shortly following preparation. This instability could be avoided by increasing the amount of xylene (from 1 g to 1.5 g) for dissolving benzophenone.

The commonly used 10 : 1 (m/m) ratio of PDMS monomer base to curing agent was found to yield the best results. It was observed that the 20 : 1 ratio took longer to cure since the amount of curing agent was not sufficient. Higher amounts of curing agent (*i.e.*, a 5 : 1 ratio) caused very fast curing, making the *photoPDMS* process difficult to control. In terms of feature definitions, there was no significant difference between the 5 : 1 and the 10 : 1 ratios. The 10 : 1 ratio takes approximately 55 sec to cure for a 20 μm thick *photoPDMS* film.

When the UV exposure time was varied, the 10 min exposure at a UV intensity of 12 mW cm^{-2} resulted in patterns with the best side wall definitions. Shorter exposures (*e.g.*, 8 min) proved insufficient to create enough benzophenone radicals and thus the patterns were not well defined. Longer exposures (*e.g.*, 12 min) resulted in overexposure, with feature enlargement similar to conventional photoresists. Exposure times of the most conventional photoresists range from 10 to 200 sec. However, the exposure time required for the *photoPDMS* is longer since it needs a longer time for the benzophenone radicals to be generated, which then react with the PDMS crosslinker and prevent it from crosslinking.

The curing time during post-exposure bake was found to be critical for pattern development, and varied linearly with the film thickness (Fig. 3(b)). Several challenges were encountered while optimizing the curing time during these experiments. When the curing time was too low, all the *photoPDMS* was washed away in toluene during development. Low curing times resulted in underbaking, leading to a widening of features. However, overbaking the *photoPDMS* films caused some of the exposed *photoPDMS* to cure, leading to the formation of thin PDMS residue films at the bottom of the glass substrate. Fig. 4(a) illustrates a SEM image of a typical overbaked pattern. Excessive post-exposure bake resulted in the entire film being cured with no pattern, just as a conventional PDMS film. Thus, it is of primary importance to optimize the baking time while using the *photoPDMS* mixture. A baking time of 60 sec at 120 °C was used for a 24 μm thick film. An intermediate PDMS layer between the glass substrate and the *photoPDMS* layer can be used to take advantage of PDMS low thermal conductivity to increase flexibility in bake time. This intermediate layer was spun at 4000 rpm and cured completely before spin-coating the *photoPDMS*.

Effects of curing temperature were also investigated (Table 1). At 90 °C, *photoPDMS* took a longer time to cure when compared to 120 °C, causing the PDMS at the bottom of the pattern to cure and resulting in a residue. At 150 °C curing

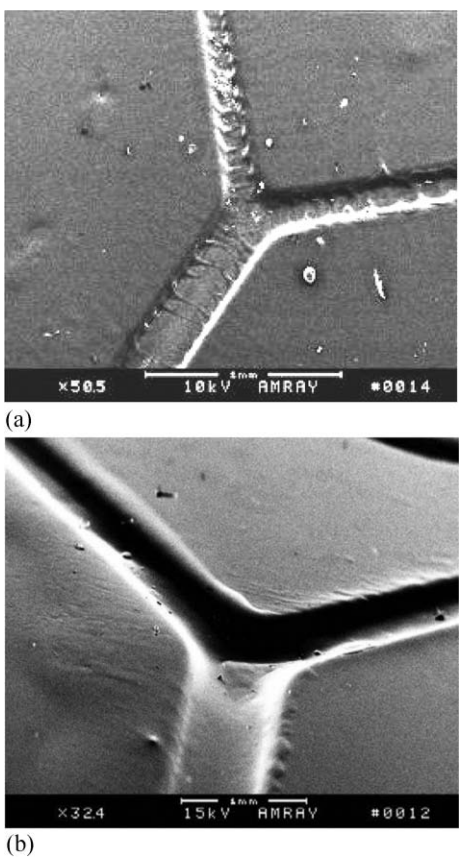


Fig. 4 (a) SEM image of an over-cured *photoPDMS* film, illustrating PDMS residue at the bottom of the channel that remains following development. (b) SEM image of a poorly defined 20 μm deep microchannel due to PDMS spreading and relaxing similar to reflow observed in conventional photoresists.

temperature, the cure time was relatively short, and made the process extremely difficult to control. At this high temperature, over-curing by even a few seconds resulted in the entire film being cured, while under-curing by a few seconds yielded very poor pattern definition. Curing for almost 12 h at room temperature (25 °C) for a 20 μm thick film also yielded poor patterns due to PDMS spreading and relaxing similar to reflow observed in conventional photoresists (Fig. 4(b)). From these results, curing at 120 °C was selected as the optimum in terms of process control; for a 70 μm thick film the cure time at 120 °C was found to be 120 sec (Fig. 3(b)).

3.3. Free-standing patterned films

PhotoPDMS experiments were performed with two formulations of PDMS, namely Sylgard 184 from Dow Corning and RTV615 from GE Polymers. Both yielded similar results. However, due to the weak bond (physical adsorption) between underlying glass and PDMS and the high elasticity of RTV 615 silicone, the patterned *photoPDMS* films can be completely peeled off from the substrate resulting in free-standing patterned PDMS films. Fig. 5(a) illustrates a 30 μm thick, patterned, free-standing *photoPDMS* film using RTV 615 silicone. The film has square through patterns ranging from 500 μm to 2 mm in size. This novel approach may be used to fabricate sensors on these flexible films and perhaps provide a viable alternative to Kapton® in medical applications. These flexible films can also be used as a stencil for microfabrication applications as shown in Fig. 5(b) where UV-cured adhesive was patterned using the free-standing *photoPDMS* film. Patterns are 500 μm to 2 mm on a side.

As a further demonstration of the *photoPDMS* process capabilities, dual layer *photoPDMS* films were fabricated using this novel process. First, *photoPDMS* was spin-coated, exposed, cured, and developed, thus forming the first patterned layer. A second *photoPDMS* layer was then spin-coated on top of the first layer and patterned, similar to the multi-layer fabrication process used with photoresists. Fig. 5(c) illustrates a 40 μm thick film with square features (each of the two layers is 20 μm thick) patterned using this dual layer technique. The through pattern is formed by aligning smaller 500 μm square patterns in the top layer with the larger 2 mm square patterns in the bottom layer.

3.4. Application to microfluidic channel fabrication

To test the feasibility of this novel process, microfluidic channels were fabricated and characterized with fluorescence microscopy. To complete the microchannels fabricated with *photoPDMS*, the patterned glass wafers were bonded to a 1 mm thick PDMS slab. The *photoPDMS* patterned wafers and PDMS slab were bonded by exposing both of them to O_2 plasma (20 sccm, 13.56 MHz) for 15 sec at 70 W.[18] Following plasma treatment, the surfaces were immediately brought into contact with each other and placed on a hotplate at 85 °C for 2 h to complete the bonding. Holes for the inlet and outlet were punched in the PDMS slab using 14 gauge needles. Although channels can also be enclosed using a glass slide, PDMS was preferred since it is easier to punch inlet and outlet holes. An important observation is that even though the PDMS contains benzophenone, it still bonded well with the PDMS slab, which was similar to the conventional PDMS bonding method. The benzophenone did not affect the quality of the bonding.

Fig. 6(a) shows the fabricated microchannels of Y-micromixers 24 μm in depth and 200 μm, 400 μm, or 1 mm in width, illustrating large area patterning on a 3″ × 3″ glass wafer. The insets show close-up images of the "Y" input regions. The microchannels were filled with red dye, demonstrating excellent channel definition and no leakage. This was further confirmed by fluorescence microscopy. During testing, two syringe pumps (NE-1000, New Era Syringe Pumps) were used to pump a 1 μM solution of fluorescein dye into one microchannel input and DI water into the other. The two fluids were observed with an inverted epi-fluorescence microscope (Olympus IX71) equipped with a 12-bit CCD camera. Fig. 6(b–c) shows representative fluorescence images taken at the entrance and 5 mm downstream of a Y-micromixer, illustrating mixing of 1 μM of fluorescein and water, and confirming excellent channel definition and no leakage.

4. Conclusions

A new simple method of patterning PDMS directly was successfully demonstrated in this work. This promising method will make fabrication simpler, easier, quicker and inexpensive and can be exploited for a wide range of

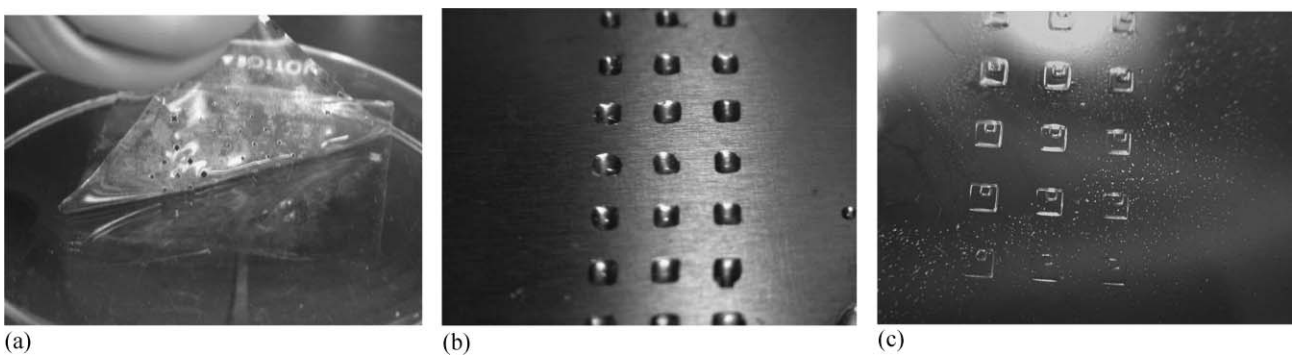


Fig. 5 (a) Photograph of a 30 μm thick patterned free-standing *photoPDMS* film illustrating square through patterns with feature size ranging from 500 μm to 2 mm. (b) UV-cured adhesive bumps patterned using a free-standing *photoPDMS* film as a shadow mask. (c) Photograph of a dual-layered *photoPDMS* structure fabricated using a two-step lithography process.

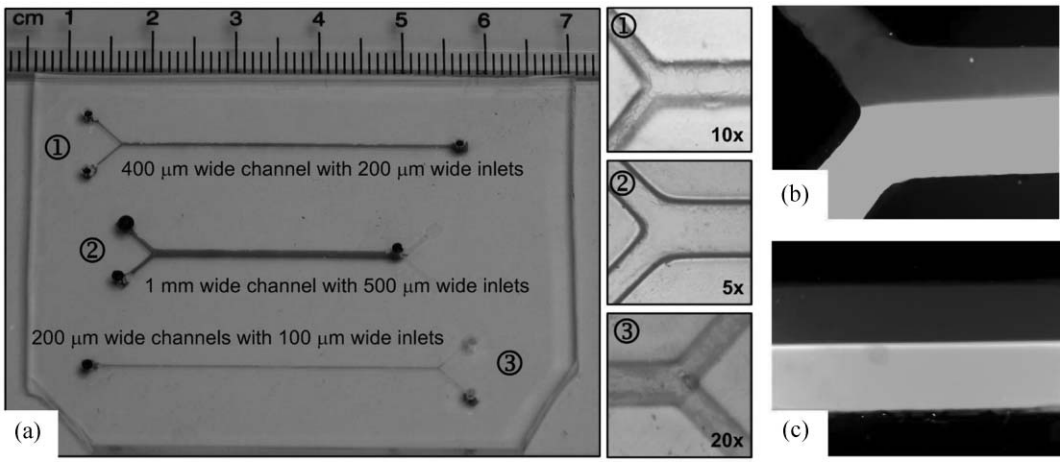


Fig. 6 (a) Microfluidic channels fabricated in *photoPDMS*. Close-up bright field images of the channel entrance regions are shown on the right. Representative fluorescence images of a microchannel at the entrance (b) and 5 mm downstream (c), illustrating mixing of a 1 μM solution of fluorescein (bottom half) and water (top half).

applications. The *photoPDMS* is robust and could be processed even under normal ambient light. The critical advantages of the new material are: directly photodefinable (*i.e.*, no master); processing in ambient light (*i.e.*, no gold room); positive-acting (*i.e.*, easier fabrication); precise thickness control *via* spin coating; simple preparation; and all the advantages of PDMS including low cost. Although PDMS is known to have good biocompatibility, further studies to identify effects of benzophenone in *photoPDMS* on biocompatibility for LOC applications involving cell culture are needed. Overall, the *photoPDMS* process will enable rapid prototyping of low-cost, disposable LOCs without cleanroom facilities, envisaging its numerous applications in the microfluidics and LOC fields.

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