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# Anti-stiction coating of PDMS moulds for rapid microchannel fabrication by double replica moulding

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**Abstract**

In this paper, we report a simple and precise method to rapidly replicate master structures for fast microchannel fabrication by double replica moulding of polydimethylsiloxane (PDMS). A PDMS mould was surface-treated by vapour phase deposition of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS), which resulted in an anti-stiction layer for the improved release after PDMS casting. The deposition of FDTS on an $O_2$ plasma-activated surface of PDMS produced a reproducible and well-performing anti-stiction monolayer of fluorocarbon, and we used the FDTS-coated moulds as micro-masters for rapid replication of micro-structures, avoiding the necessity to have to use other, more costly and fragile master materials. Our protocol has been shown to reliably fabricate PDMS-based microfluidic devices in a low-cost and efficient manner. The replicas were further employed as micro-contract stamps to fabricate polymer-based waveguides.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Polydimethylsiloxane (PDMS) is a widely used material for the fabrication of microfluidic devices to achieve the goal of lab-on-a-chip systems [1–3]. It is most often used as the device material itself, especially for biological or micro-optical applications [3–8]. Fabrication of PDMS-based devices usually employs very economic and straightforward soft lithographic methods based on rapid prototyping and replica moulding [9, 10], which are more easily accessible to chemists and biologist working under benchtop conditions without requiring cleanroom facilities.

However, the achievable quality when using soft lithography is still dependent on the availability and performance of appropriate masters. Until recently, primary masters for rapid prototyping of PDMS have commonly been fabricated in silicon, glass or SU-8. Generally, master structures made from silicon or glass have a high quality, but are rather expensive and fragile, and the fabrication procedures are time-consuming. These disadvantages have somewhat restrained the use of these materials. Compared to silicon or glass, an SU-8 master is a less costly alternative. Many features of SU-8 make it attractive for rapid prototyping [11]. However, SU-8 masters are fragile as well, and show signs of micro-structure delamination after approximately five replication cycles due to adhesion problems, at least according to our experiences.

Because of the limited lifetime and the relatively high cost of masters made from the materials mentioned above, it is attractive to find a more straightforward approach to reduce costs and improve the lifetime of masters while still yielding precise structure copies. PDMS is potentially a very interesting master material due to its excellent properties for rapid prototyping. It has been reported that rapidly prototyped PDMS moulds were conveniently used for the production of non-PDMS polymeric devices, e.g. when moulding thermoset polyester resins against a PDMS master [12, 13]. We believe that double replica moulding by moulding PDMS over a PDMS master is a feasible method to make microfluidic structures. However, significant adhesion of the PDMS layers to each other is a big challenge for this approach. Due to strong adhesion, it is difficult to achieve a smooth

 

peel-off procedure without surface treatment of the PDMS master. One possibility is to derivatize the surface of the PDMS master with silanes. However, this is often rather elaborate and time-consuming (requiring, for instance, at least a 1 h treatment with 3% tetraethylorthosilicate (TEOS) in an ethanol solution) [14]. Double replica moulding has been demonstrated by silanizing the PDMS master with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-trichlorosilane vapour overnight under vacuum to aid the subsequent release of PDMS [15, 16]. However, an anti-stiction coating deposited using vapour is not very stable and has a rather limited lifetime. A possible reason is that surface silanization by vapour deposition depends strongly on physical absorption, which is not the case for a covalent chemical reaction. According to our experience, after three or four copies, the anti-stiction layer no longer works. The master needs to be silanized again by vapour deposition to enhance the anti-stiction properties. Additionally, surface silanization by vapour deposition also takes quite a long time (typically overnight, i.e. more than 8 h). Recently, a straightforward process has been reported to cast PDMS over a PDMS master by wetting the surface of the mould with a phosphate buffer solution containing the hydrophilic polymer hydroxypolymethylcellulose (HPMC) [17]. However, in these similar methods surface treatment is performed in solution, especially in organic solution, which bears the strong risk of swelling the PDMS [18] and thus impairing a precise replication of structures.

In this paper, we present a simple surface treatment process to allow moulding of PDMS against a PDMS master involving vapour phase deposition of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) onto the PDMS surface to reduce adhesive interaction. A similar approach for silicon substrates or SU-8 moulds has previously been reported to provide excellent anti-stiction surfaces to improve the release of structures [19–21]. But, to our knowledge, there have been no previous reports on vapour deposition of FDTS on PDMS to promote anti-stiction. The obtained PDMS masters with anti-stiction layers were applied directly for soft lithography and micro-contract stamps to make polymer-based waveguides and microfluidic structures. Figure 1 shows a schematic illustration of the presented double replica moulding method for rapid microchannel fabrication.

## 2. Experimental details

### 2.1. PDMS master fabrication

To facilitate the moulding of PDMS replicas from PDMS masters, the PDMS masters themselves were first fabricated by casting over two more conventional masters: one made from SU-8 and the other from PMMA.

The design of the SU-8 master is a microchip flow cytometer with integrated polymer-based optical elements, including waveguides, a focusing lens and fibre-to-waveguide couplers. A similar design has been described previously by our group [22]. The incident SU-8 waveguide here is 30 $\mu$m wide and 75 $\mu$m high. The rectangular shaped main fluidic channels are approximately 100 $\mu$m wide and 75 $\mu$m deep.

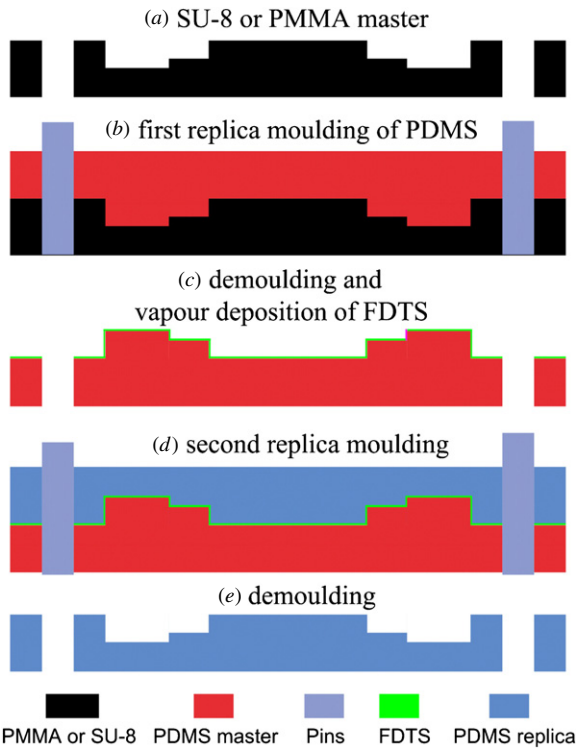


**Figure 1.** Schematic illustration of the double replica moulding. (*a*) SU-8 or PMMA master fabricated by standard photolithography and micomilling, respectively. (*b*) The first PDMS moulding of the design of the microchip. (*c*) The first demoulding from the SU-8 or PMMA master and vapour phase deposition of anti-stiction coating on PDMS moulds. (*d*) The second PDMS moulding over the treated PDMS master. (*e*) PDMS replica peeled off the treated PDMS master.

The main fluidic channels as well as the micro-optical elements were fabricated in a single SU-8 layer on silicon substrates by standard photolithography. In brief, a 75 $\mu$m layer of SU-8 2075 (Micro Resist Technology, Germany) was spun onto a silicon wafer, soft-baked at 60 °C for 15 min and 90 °C for 20 min, ramping at 7 °C min$^{-1}$. After exposure by UV lithography, the wafer was treated by a crosslink bake at 60 °C for 10 min and at 90 °C for 15 min, ramping at 7 °C min$^{-1}$ as well. The final SU-8 master was obtained after development.

For the second test purpose, namely to carry out a rapid test of fabrication of polymer-based waveguides with a PDMS replica employed as a micro-contract stamp, a PMMA master was fabricated by a CNC controlled micromilling machine generating 100 $\mu$m wide and 100 $\mu$m deep microchannels on a 50 × 50 mm PMMA substrate.

A mixture of PDMS prepolymer and curing agent at a weight ratio of 10:1 (Sylgard 184, Dow-Corning, USA) was stirred and degassed in a vacuum chamber and then poured onto either the SU-8 or the PMMA masters mentioned above and cured in an oven at 80 °C for 1 h. The fully cured PDMS was then gently peeled off the masters.

### 2.2. Anti-stiction coating onto PDMS master

One of the micro-structured PDMS slabs of 3 mm thickness (figure 1(*c*)) obtained in section 2.1 was then used as a master

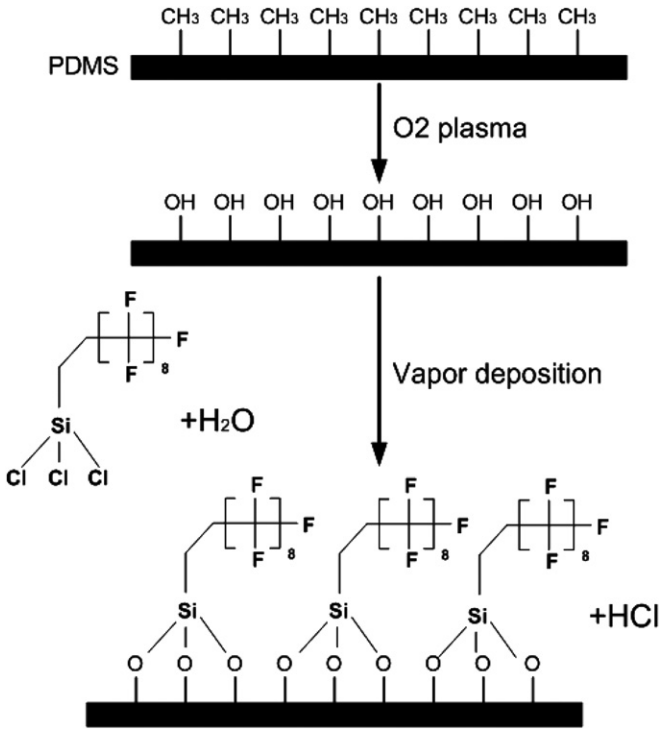


**Figure 2.** The methyl groups of a PDMS surface are activated by $O_2$ plasma to create hydroxyl groups, which can further react with FDTS yielding a monolayer of the fluorocarbon. FDTS may also crosslink with neighbouring molecules.

for the second PDMS moulding. To improve the release process, the PDMS master was first coated with an anti-stiction layer using deposition of FDTS over 15 min in a molecular vapour deposition system (Applied MST, MVD100). The treated PDMS master was washed with deionized water and isopropanol to remove any loosely bound FDTS. The MVD process sequence consists of the following four steps: (1) cleaning and conditioning step for surface activation by the $O_2$ plasma process, which breaks the methyl groups on the PDMS surface to form free hydroxyl groups; (2) purge step for chamber pressure preparation; (3) injection step: a number of chemicals are pumped into the chamber according to their vapour pressure; (4) reaction step for the chemical reaction for FDTS deposition. Figure 2 schematically illustrates the procedure and idealized mechanism of surface activation and vapour phase deposition of FDTS.

### *2.3. Contact angle measurements*

Contact angles of PDMS surfaces under different treatment conditions were obtained using a drop shape analyser (DSA100, Krüss, Germany) by oscillating 2 $\mu$l water droplets. Average and standard deviations were collected from at least three measurements on three different positions of tested samples.

### *2.4. Performance evaluations of PDMS masters*

In order to evaluate the lifetime of the PDMS master and the reproducibility of the double replica moulding method, more than ten PDMS replicas were created from a single FDTS-deposited PDMS master over the course of two months. Micro-contact printing was also carried out with a PDMS mould peeled from a PMMA master, where the PDMS part acted as a micro-contact stamp for fabricating polymer waveguides. The principal approach to using micro-contact printing for waveguide fabrication has been described previously by our group [23]. Briefly, the doped PMMA solution (80% PMMA and 20% styreneacrylonitrile copolymer dissolved in anisole), with a higher refractive index (1.50) than undoped PMMA, was poured onto the PDMS stamp treated by vapour deposition of FDTS and covered with a PMMA plate ($n = 1.49$). The PMMA plate was pressed against the PDMS stamp with a weight, holding this pressure overnight at room temperature. Any excess of the doped PMMA was allowed to flow to the sides. The multimode polymeric waveguides were completed by drying in an oven, thus evaporating the solvent. Figure 3 shows the SEM image of the PDMS stamp, which has been used for waveguide fabrication with the micro-contact printing process.

## 3. Results and discussion

The methyl groups of a PDMS surface are not directly accessible to the chlorosilane chemistry provided by FDTS, which is why the surface needs to be activated first, via the generation of hydroxyl groups. As shown in figure 2, the $O_2$ plasma facilitates this process. During the vapour phase deposition step, water hydrolyzes the FDTS, which in turn reacts with the hydroxyl groups on the surface releasing HCl. In this way, a monolayer of fluorocarbon is formed, which serves as a release layer for improved demoulding. In initial experiments, $O_2$ plasma treatment of the pristine PDMS master was carried out in a plasma processor (Model 300, PVA Tepla, Germany) at 300 W for 30 s. Results indicated, however, that there is no effect on the ease with which release is performed from a PDMS master whether this step was done or not, since the MVD process sequence already includes a 5 min $O_2$ plasma treatment, which is good enough to form the surface hydroxyl groups.

Wetting experiments to measure contact angles were carried out in a drop shape analyser, which was used to compare the contact angle change of PDMS surfaces treated with $O_2$ plasma and FDTS, and also to verify the successful deposition of FDTS. For this, an unstructured PDMS substrate was cut into two pieces. Both of them were treated by $O_2$ plasma oxidation (plasma power 300 W, and treatment times 30 s). After that, one PDMS piece was placed into the MVD100 chamber for deposition of FDTS. The second PDMS piece was stored in air until the FDTS-treated PDMS was ready for contact angle comparison. Figure 4 shows the comparison of different contact angles resulting from different treatment conditions for PDMS substrates. The contact angle on untreated PDMS surface remained fairly constant, between 110° and 112°, regardless of the storage time, while the water drop on the treated PDMS surface spread completely immediately after $O_2$ plasma oxidation, which was considered to correspond to a contact angle of less than 5°.

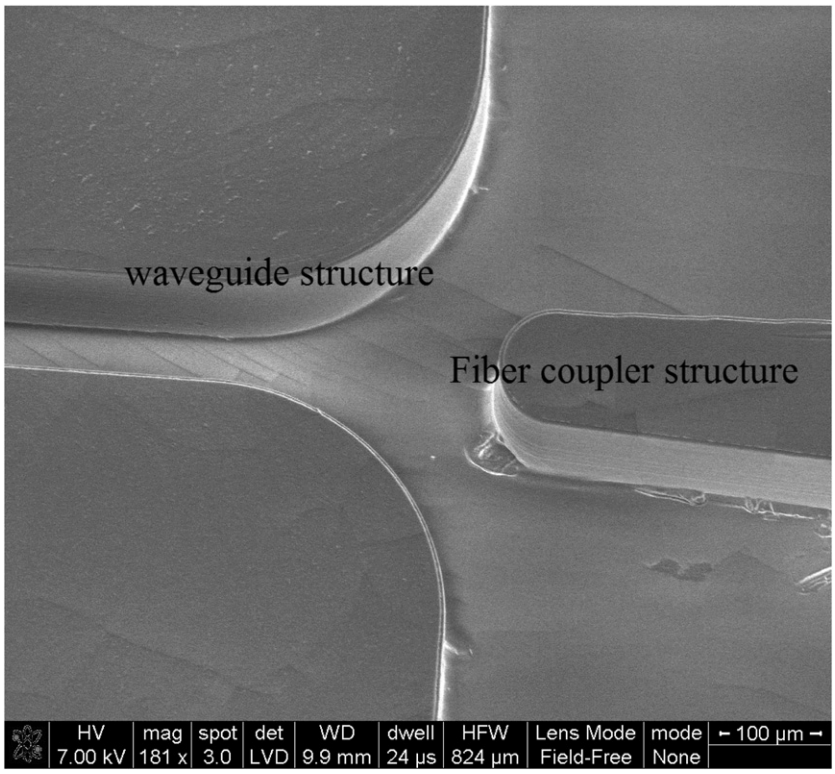


**Figure 3.** A SEM image of a PDMS stamp for waveguide fabrication by micro-contact printing.

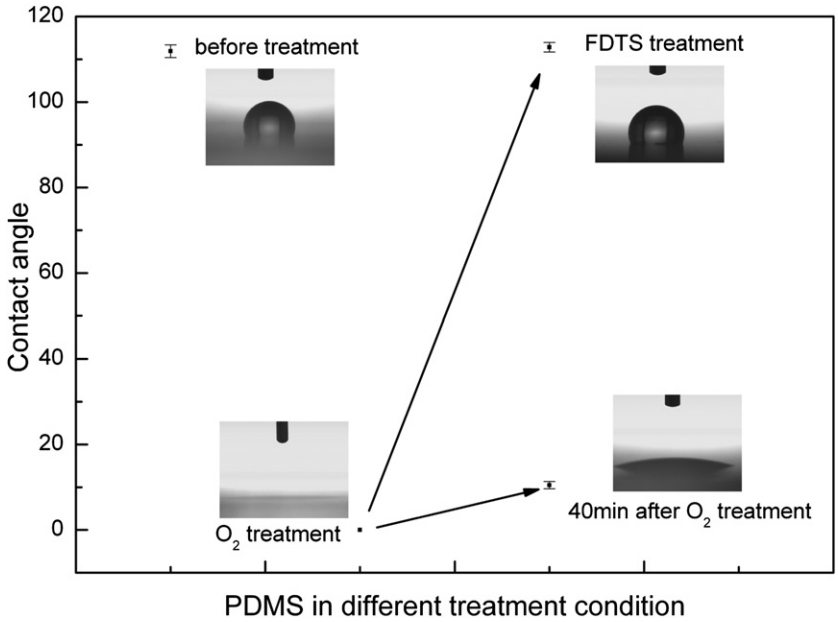


**Figure 4.** Contact angle versus treatment conditions for PDMS substrates.

The FDTS-deposited PDMS had a contact angle of 112 ± 1°, thus retaining a similar hydrophobicity as the untreated PDMS surface, as shown in figure 4. At the same time, the second $O_2$ plasma-treated PDMS piece stored in air for 40 min still had a very hydrophilic surface with a contact angle of 10°, although some slight hydrophobic recovery had begun [24–27]. It is apparent that the deposition of FDTS on the $O_2$ plasma-treated PDMS master was successful, causing a surface wetting property change from hydrophilic to hydrophobic after deposition of FDTS. Even after thorough washing with isopropanol and multiple castings, very little or no effect on the contact angle is observed, which verifies that the deposition of FDTS results in covalent bonds, and not simply adsorption to the surface (figure 2).

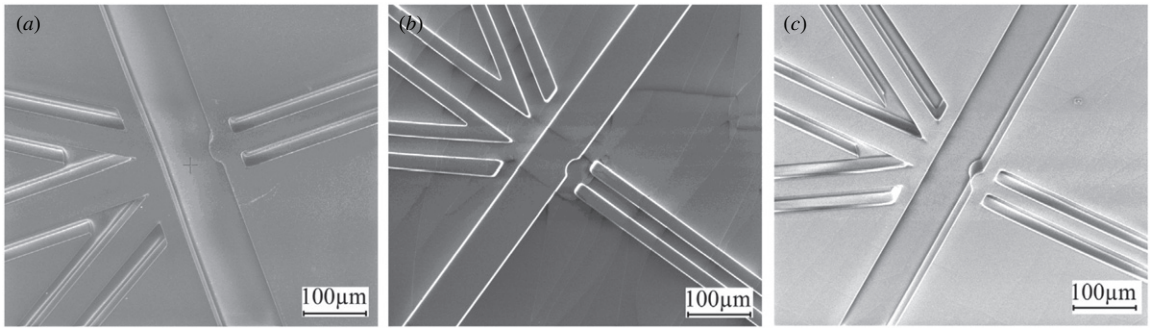


**Figure 5.** (*a*) A SEM image of the primary SU-8 master. (*b*) The PDMS master. (*c*) The tenth PDMS replicate.

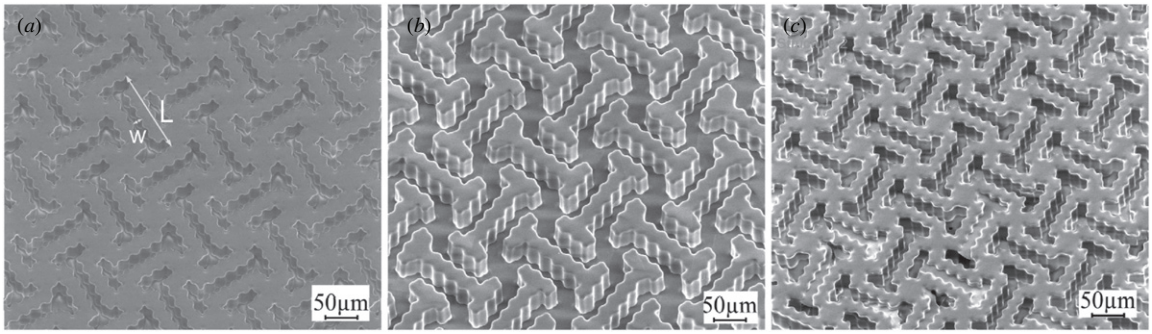


**Figure 6.** (*a*) A SEM image of scattering structures in SU-8. (*b*) The FDTS-deposited PDMS master. (*c*) The tenth copy from the PDMS master.

**Table 1.** Averaged dimensions of the scattering structures and standard deviations for length and width.

| | SU-8 master | PDMS master from SU-8 | PC1 | PC 2 | PC 3 | PC 4 | PC 5 | PC 6 | PC 7 | PC 8 | PC 9 | PC 10 | SD |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $L$ ($\mu$m) | 136 | 139 | 137.8 | 138.2 | 138.1 | 137.8 | 136.9 | 137.2 | 137.8 | 136.8 | 138.3 | 136.8 | 0.6 |
| $W$ ($\mu$m) | 20.6 | 20.8 | 19.6 | 20.4 | 20.5 | 19.8 | 19.6 | 19.8 | 20.2 | 19.6 | 20.8 | 19.6 | 0.4 |

PDMS copy: PC
Standard deviation: SD.

Casting a second-generation PDMS chip from the FDTS-treated PDMS master produced structures identical to those of the original SU-8 master. Scanning electron microscopy (SEM) was employed to verify the fidelity of reproduction by double replica moulding. The quality of structures as monitored by SEM revealed excellent fidelity in reproducing PDMS moulds against a FDTS-deposited PDMS master. Figure 5(*a*) shows the smooth structures of the SU-8 master (including microlens and waveguide structures), which were replicated with high fidelity in the PDMS moulds (figures 5(*b*) and (*c*)).

To evaluate the long-term performance and lifetime of the PDMS masters, a PDMS master was fabricated by replica moulding from an SU-8 master featuring light scattering structures, as shown in figure 6, which are intended to reduce stray light in a microchip flow cytometer. Each scatter structure is 20 $\mu$m wide and 75 $\mu$m deep, and designed as a repeating pattern with sharp-toothed sidewalls. The dimension of the sharp-toothed structure on the sidewalls is 5 $\mu$m wide. The complex structure was again transferred with high fidelity to PDMS by the presented double replica moulding method, which indicates that the anti-stiction coating layer by FDTS vapour deposition works as expected and effectively assists in the release of PDMS replicas from PDMS masters for at least ten copies (figure 6(*c*)). Our experiments showed no signs of sticking between PDMS pieces for at least 20 copies.

For each of the light scattering structures shown in figure 6, the main dimensions, length ($L$) and width ($W$), were measured for ten copies and averaged leading to a standard deviation (SD) of 0.6 and 0.4 $\mu$m for length and width, respectively (table 1). Except for a minimal tendency of channel broadening due to the elastic properties of PDMS, profile measurements and SEM images show that the dimensions of PDMS replicas obtained from PDMS masters match well with the original SU-8 master.

In a second test application, where the PDMS mould acted as a micro-contact stamp to fabricate polymeric waveguides, the FDTS coating also assisted in the release of the resulting waveguide structures from the PDMS mould. The rectangular shaped polymeric waveguides are approximately 80 $\mu$m wide and 100 $\mu$m deep. The structured tapered fibre grooves are designed to make the alignment of the fibre easy and precise.

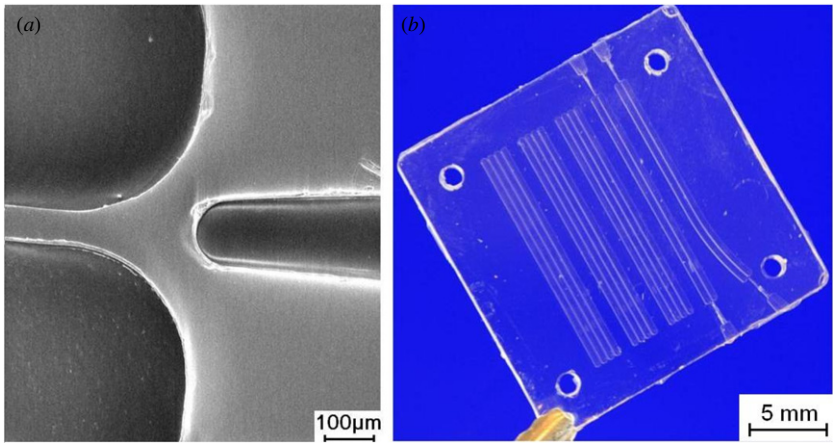


**Figure 7.** (*a*) A SEM image of the fabricated waveguide and fibre coupler and (*b*) the chip. They were fabricated by micro-contact printing process of the FDTS-deposited PDMS stamp.

Figure 7 shows the chip and an SEM image of one of the waveguides fabricated with the micro-contact printing process using the FDTS-deposited PDMS stamp mentioned in figure 3.

## 4. Conclusion and outlook

In this paper, we presented a simple method for fast and precise replication of microfluidic structures by double replica moulding of PDMS. An anti-stiction monolayer was formed on the surface of a PDMS master by vapour phase deposition of FDTS, which acts as a release layer to reduce the adhesive interactions and allows PDMS structures to be peeled from a PDMS master. $O_2$ plasma plays an important role in the process of vapour deposition of FDTS. It introduces hydroxyl groups on the PDMS surface, which can then be derivatized using chlorosilane chemistry resulting in covalent bonds, thus yielding a long-lasting anti-stiction layer.

The method presented here provides the option of a straightforward structure replication from PDMS masters to PDMS or other curable polymers. We believe that the double replica moulding of PDMS will be employed in many microfluidic applications as a valuable alternative, fast and inexpensive fabrication method.

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