SUPERHYDROPHOBIC, PASSIVE MICROVALVES WITH CONTROLLABLE OPENING PRESSURE, AND APPLICATIONS IN FLOW CONTROL

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ABSTRACT

Plasma processing is used to create passive superhydrophobic on-off valves with tailored opening pressure inside microfluidic devices. First, anisotropic O$_2$ plasma etching on polymeric microchannels is utilized to controllably roughen (nanotexture) the bottom of the microchannel. Second, the nanotextured surfaces are hydrophobized by means of a C$_6$F$_8$ plasma deposition step. The superhydrophobic valves exhibit predesigned opening pressure threshold (in the range 40-110 mbar), determined by the microchannel dimensions and the size of the nanotexture on the patch. The proposed valves present an example of how effectively plasma nanoscience and nanotechnology can be applied to microfluidics/nanofluidics and analytical chemistry.

KEYWORDS: Autonomous Microfluidics, Superhydrophobic, Plasma Nanotexturing

INTRODUCTION

Microfluidic systems are powerful tools for handling biomolecules, such as DNA, RNA and proteins or cells, as well as for chemical analysis. They have been applied to polymerase chain reaction (PCR), DNA analysis and sequencing [1], protein separation [2], immunoassays [3], as disposable or multiple-use lab-on-chip systems with promising commercial potential.

However, the main obstacle for successful miniaturization and commercialization of fully integrated microfluidic systems is the development of reliable components, such as micropumps and microvalves. In particular, “passive” components are even more important for “autonomous” microfluidic systems. Recently, there is a growing interest in micro-components such as microvalves [4] and world-to-chip microfluidic interfaces towards the fabrication of a completely autonomous diagnostic system [3, 5].

In this work, we present a series of different nanotextured superhydrophobic valves of predesigned threshold pressure and their integration in a programmable passive switchboard device that can deliver fluids according to a preferred sequence. For the fabrication of the valves, we simply use a plasma nanotexturing step, followed by a plasma polymer deposition step. The duration of each plasma process step is approximately a few min, and no complex microfabrication designs are needed, such as flow constrictions etc. To our knowledge, this is one of the first efforts to fabricate superhydrophobic valves on polymers with predesigned pressure threshold using a simple and fast, mass-production amenable technology. We therefore think that these components represent a promising tool for microfluidic-based autonomous systems.

THEORY

Let us assume a superhydrophobic surface in which $\theta_0$ is the Cassie-state static contact angle on a rough surface wetted by a fraction $\phi$, from water, and, $\theta_b$ is the initial static contact angle for water on a flat, smooth surface. For a microchannel with rectangular cross section we can prove that the threshold pressure value of a valve as a function of ($\phi$, $\theta_b$, and geometrical features (width-$W$, and height $h$) is:

$$P_{th} = \gamma_0 \left[ \frac{2 c_s t h + \frac{\phi}{h} (c_s t h - 1) + \frac{\phi}{h} (c_s t h + 1)}{w_0} \right]$$

Equation (1) shows that the threshold pressure depends mainly on channel depth and width and can be fine-tuned by changing the plasma processing conditions so that $\phi$ and $\theta_0$ are changed.

EXPERIMENTAL

The microchannels were fabricated by a hot embossing procedure using 175 $\mu$m wide and 20 or 40 $\mu$m deep silicon masters. Hot embossing was selected to ensure that all channels were smooth prior to plasma etching. Plasma processing follows the hot embossing and contains two steps:
1) Plasma Nanotexturing

First, we perform an O$_2$ plasma deep reactive ion etching with simultaneous nanotexturing of the polymer for 1, 2 and 4 min in a high-density plasma reactor (Helicon plasma reactor, Micromachining Etching Tool, MET, from Adixen-Alcatel). The conditions used are: 1900 W, 100 sccm O$_2$, 0.75 Pa, 15 $^\circ$C and bias voltage -100V. These highly anisotropic conditions produce nanotexture on a PMMA plate, while simultaneously etching down the microchannel with a rate of 1 $\mu$m/min. We did not change the height of the microchannel since both the bottom and the top walls were simultaneously etched. This nanotexture has been already used to produce robust superhydrophobic surfaces on PMMA [6]. We note that this nanotexture is dual scale comprising approximately 200 nm wide and 50 nm wide columnar structures for the first minutes of treatment and grows into the microscale after several minutes of treatment.
2) Plasma fluorocarbon deposition
Second, we perform a thin fluorocarbon film deposition through a stencil mask that allows the selective and conformal deposition of the film only on the preferred part of the channel using $C_4F_8$ gas at conditions (900 W, 0 V, 5.33 Pa $C_4F_8$, deposition rate 30 nm min$^{-1}$).

RESULTS AND DISCUSSION

The valve working principle is illustrated in Fig. 1. Fig. 1a depicts the stopped microfluidic flow inside the microchannel when the liquid front reaches the superhydrophobic patch, while Fig. 1b shows the filled microchannel after the valve is opened.

![Figure 1. Operation of a passive superhydrophobic microvalve. Photograph of the microchannel inside the chip holder. The hydrophobic patch is placed in the middle of the microchannel and its SEM image is shown as inset. (a) Stopped fluid flow (red dye) at the nanotextured hydrophobic patch (b) filled microchannel after the valve opens. For more details, see related video in supporting information.](image)

The valve operation is explained below and can be clearly understood by looking at the pressure versus time curves before and after valve opening, shown in Fig. 2. A syringe pump imposes a certain flow rate inside a microchannel. With that flow rate, the advancing liquid front reaches the superhydrophobic patch, where it is stopped due to the threshold pressure of the valve. The pump increases the pressure trying to maintain the liquid flow rate and overcome the superhydrophobic patch threshold pressure. When this is done, the fluid shoots out at a fairly high velocity, and a sudden pressure decrease is observed, see Fig. 2. This is expected because once the pressure barrier is “broken,” very little pressure is required to maintain flow through the narrow channel. The time axis is dependent on the liquid volume in the tubing (1100 μl) and pressure sensor (4490μl). In our set-up, this time is relatively long due to the large total volume (5590μl).

![Graph showing pressure versus time curves before and after valve opening.](image)

<table>
<thead>
<tr>
<th>20 μm</th>
<th>Pressure threshold</th>
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<tr>
<td>60 s</td>
<td>73 mbar</td>
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<td>120 s</td>
<td>86 mbar</td>
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<tr>
<td>240 s</td>
<td>109 mbar</td>
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Figure 2. Pressure rise curves versus time in microchannels containing superhydrophobic patches a) 20μm deep microchannel, b) 40μm deep microchannel, both for three different etching times 1 min, 2 min, 4 min. Pressure threshold values are given for each case. Standard deviation between successive measurements in the same device ±5 mbar. Standard deviation in pressure threshold between measurements in different devices ±8 mbar.

CONCLUSION

We have presented an easy-to-implement technique for rapid fabrication of nanotextured superhydrophobic valves. We fabricated valves of different pressure threshold that can be customized according to the application, by changing either the geometrical dimension (rough control) or the etching time (fine-tuning). For easier fabrication, valves of the same geometrical dimensions are created, differentiated only by means of their plasma-induced nanotexture. The presented technology is flexible and rapid, and can easily be adapted to control the flow inside polymeric microchannels for analytical applications.

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