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Wettability control and patterning of PDMS using UV–ozone and water immersion

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ABSTRACT

We demonstrate a simple method to tune and pattern the wettability of polydimethylsiloxane (PDMS) to generate microfluidic mimics of heterogeneous porous media. This technique allows one to tailor the capillary forces at different regions within the PDMS channel to mimic multi-phase flow in oil reservoirs. In this method, UV–ozone treatment is utilized to oxidize and hydrophilize the surface of PDMS. To maintain a stable surface wettability, the oxidized surfaces are immersed in water. Additionally, the use of a photomask makes it convenient to pattern the wettability in the porous media. A one-dimensional diffusive reaction model is established to understand the UV–ozone oxidation as well as hydrophobic recovery of oxidized PDMS surfaces. The modeling results show that during UV–ozone, surface oxidation dominates over diffusion of low-molecular-weight (LMW) species. However, the diffusivity of LMW species plays an important role in wettability control of PDMS surfaces.

1. Introduction

PDMS (polydimethylsiloxane) is commonly employed to fabricate microfluidic devices because it can be molded quickly, easily, and cost-effectively using soft lithography [1]. Moreover, various surface modification methods for PDMS are currently available, which have been summarized in the literature [2,3]. Of these techniques, oxygen plasma treatment is a convenient way to quickly render the naturally hydrophobic PDMS surface to be hydrophilic, as well as to provide irreversible seals for the microfluidic devices [4]. This process is achieved by converting the PDMS surface into an oxidized surface layer, where the non-polar groups (mainly $-CH_3$) are substituted with the polar groups (mainly –OH) in the presence of oxygen plasma [5,6]. Alternatively, a combination of UV light and ozone, have also shown to be effective to alter the wettability of PDMS [7], similar to those treated with oxygen plasma but at a much slower rate [8] which allows for wettability control. Typically a 10 mTorr pressure, 400 W oxygen plasma process for 1 min results in an advancing water contact angle of less than 10° [9], while UV–ozone with a 28 mW/cm^2 low-pressure mercury vapor lamp at a distance of 6 mm requires about 1 h to achieve the same water contact angle [8]. A challenge arising from these techniques is the rapid hydrophobic recovery (typically within a couple hours) that occurs on the PDMS surface after oxygen plasma or UV–ozone treatment, which is dominated by the migration of uncured and in situ produced low-molecular-weight (LMW) species toward PDMS surface [10,11]. To overcome this issue, efforts have been made to reduce the amount of uncured PDMS oligomers, either with additional curing time [12], or through a series of solvent extraction [13]. Moreover, by keeping the oxidized PDMS surface in contact with water, the hydrophilicity can also be maintained for over 14 days [14,15].

In addition to direct exposure to energy, grafting a hydrophilic polymer onto the surface was also used to alter the wettability of PDMS channels [16,17]. A sol–gel layer, which had been functionalized with photoreactive silanes, was used to alter and pattern the wettability of PDMS surface [18]. A hydrophilic polymer polyacrylic acid (PAA) was grafted on the sol–gel-coated PDMS, through polymerization process in the presence of photoinitiator-silanes and UV light. Portions of the channels which were desired to be hydrophilic were exposed to UV light, resulting in patterned wettability with a water contact angle difference of 83°. Wettability has also been spatially patterned in sol–gel-coated PDMS microchannels through flow confinement of a reactive surface treatment solution, where the reaction of wettability patterning can be initiated by either UV or thermal energy [19].

Despite the success of these surface modification techniques, they require additional chemical modifications to be made to the surface. UV–ozone is a facile technique to alter the wettability of PDMS and to bond the PDMS pieces to form microfluidic devices. UV–ozone uses less energy than oxygen plasma during the surface modification process of PDMS [11], resulting in a slower change in the water contact angle of the surface [8]. This feature can be beneficial to precisely tailor the wettability of PDMS, in combination with the approaches to minimize the rate of hydrophobic recovery discussed above.

In this study, we first demonstrate a simple method to tune and pattern wettability in a PDMS-based microfluidic porous medium. It is well known that for small pore diameters where low Reynolds

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number and low capillary numbers dominate, the wettability of the pore walls plays an important role in multi-phase flows [20,21]. For example, in the case of enhanced oil recovery processes in petroleum reservoirs, the different wettability of various mineral surfaces results in varying oil saturation, capillary pressures and relative permeability curves [22]. In our method, the desired water contact angles of the surface are attained with UV–ozone oxidation and subsequent water immersion. Previous studies showed that additional curing time can hinder hydrophobic recovery by reducing LMW species in PDMS matrix [12], and we utilize this property to control the rate of surface hydrophilization through UV–ozone in this study. Additionally, various contact angles are tuned with the proposed approach, allowing one to mimic various conditions of wettability to study fluid flow in porous media.

To better understand and control this process, a theoretical model is proposed to describe the change of wettability during the UV–ozone-induced hydrophilization process as well as the hydrophobic recovery of PDMS. The proposed model is based on the previous diffusion models involved in the process of hydrophobic recovery of electrically discharged PDMS [23]. We expand the previous models to describe and predict the changes of water contact angle within the diffusive reaction process of UV–ozone oxidation. In order to precisely tune the wettability of PDMS surface, a systematic understanding of the mechanism of this technique is still necessary. Specifically, the effect of curing time on surface hydrophilization of PDMS with UV–ozone method, as well as the stability of this wettability control approach will be investigated in the following study.

2. Materials and methods

2.1. Fabrication of microfluidic devices

The channel pattern is designed using AutoCAD. The porous medium consists of a 4000 μm (length) × 3520 μm (width) rectangular reservoir with a quadrilateral network of cylindrical pillars with a radius of 150 μm aligned at a distance of 60 μm. For wettability patterning purpose, this porous medium is divided into the upper half and the bottom half, and the fluid inlet is designed in the middle of the two halves with a channel width of 200 μm. Two 200 μm wide fluid outlets are designed at the upper and lower right corners of the porous medium. Based on the designed geometry, the overall porosity of this porous medium is 45.0%.

The microfluidic devices are fabricated with standard soft lithography techniques [24,25] as described below. A 4-in. silicon wafer (University Wafer) is used as a substrate and cleaned with IPA (Sigma Aldrich), followed by a DI water rinse. To dehydrate the surface, the substrate is baked at 200 °C for 5 min on a hotplate. The SU-8 50 photoresist (Microchem Corporation) is spin coated onto a 4 in. silicon wafer (University Wafer) with a spin coater (Headway Research, Inc.) at 2000 rpm for 30 s. The substrate is pre-baked on a hot plate at 95 °C for 20 min before exposure. An SF-100 maskless lithography tool (Intelligent Micro Patterning, LLC) is used to expose the photoresist with the desired pattern. After exposure, a post-exposure bake is performed at 95 °C for 5 min. The substrate is subsequently developed in SU-8 developer (Microchem Corporation) for 6 min at room temperature, which results in a positive microfluidic pattern relief on the substrate. A pattern thickness of 75 μm is determined by a Dektak 6M profilometer (Veeco Instruments), which is the resulting height of the PDMS porous medium.

To fabricate the microfluidic device, a poly(dimethylsiloxane) (PDMS) elastomer kit (Sylgard 184; Dow Corning Corp.) is used. The kit consists of a liquid silicon elastomer base (vinyl-terminated PDMS) and a curing agent (mixture of a platinum complex and copolymers of methylhydrosiloxane and dimethylsiloxane) that are combined in a 10:1 ratio and poured onto the silicon master in a Petri dish. The wafer and PDMS are degassed under vacuum for 20 min and cured at 80 °C in a convective oven. The curing time varies from 0.5 h to 24 h. After curing, the patterned PDMS is removed from the silicon master and inlet and outlet holes are punched into the PDMS using a cork borer. To pattern the wettability of the surface, the patterned PDMS is treated with UV–ozone (Novascan Technologies, Inc.) prior to bonding. As reported by the manufacturer, a low-pressure mercury vapor lamp with an output of 20 mW/cm^2 at a distance of 25 mm is used in the UV–ozone instrument. A photomask is used to shield part of the microfluidic pattern from UV light (Fig. 1). Our alignment tool (ATS115 motion controller, Aerotech, Inc.) is able to achieve a resolution of 5 μm in the patterning process. The area masked by the black regions is shielded from the UV–ozone and remains hydrophobic after UV–ozone exposure, while the unmasked region alters its wettability depending on the time of UV–ozone exposure. Finally, the patterned PDMS piece is placed in an UV–ozone chamber for an additional 5 min and then immediately brought into contact with a blank (featureless) PDMS that has been processed with the same conditions. Note that the 5 min UV–ozone treatment used for bonding is not long enough to significantly alter the wettability of the PDMS. After sealing, the microfluidic device is immediately saturated with DI water prior to experiments.

2.2. Apparatus for evaluating wettability patterning

The effect of surface wettability is tested by observing how well gas displaces a dye solution from the porous medium. The microfluidic device is placed on the stage of an inverted microscope (Olympus IX 71). To saturate the porous medium with water, a syringe pump (Harvard Apparatus PHD 2000) is used at the outflow end to pull out the fluid. After a 48-h water immersion, a 3.0 wt.% aqueous dye solution (ESCO Foods, Inc.) is injected into the microfluidic device until the color of aqueous phase in the porous medium is homogeneous. Then air is injected at a volumetric flow rate of 1.0 ml/h into the system. A CCD camera (Phantom V4.3, Vision Research, Inc.) is used to record the flow patterns that emerge once the gas thread enters the porous medium.

2.3. Monitoring surface wettability

To determine the surface wettability inside the microfluidic device, an unpatterned PDMS is treated with the same conditions, including UV–ozone oxidation (with or without the photomask) and water immersion, as the patterned PDMS. The thickness of all PDMS pieces in this study is controlled uniformly at 2.8 ± 0.2 mm. The water static contact angle of the unpatterned piece of PDMS is measured by the sessile drop method with a KSV CAM 200 contact angle and surface tension meter (KSV Instruments, Ltd.). All the experimental data of contact angles are acquired by three repeated measurements. There is no significant difference of static contact angle on PDMS between DI water and the diluted dye solution used in our experiments.

3. Results and discussions

3.1. Wettability patterning

Table 1 shows the wettability of two microfluidic devices used in this study. In both devices, the PDMS is subject to 1-h curing and 4-h UV–ozone treatment. In Device A, the upper half is exposed to UV–ozone and made hydrophilic with a water contact