THIN FILM DIFFUSION BARRIER FORMATION IN PDMS MICROCAVITIES

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ABSTRACT

We describe a method to form glass like thin film barrier in polydimethylsiloxane (PDMS) microcavities. The reactive fragments for the surface reaction were created from O_2 and hexamethyldisiloxane (HMDS) in RF plasma environment. The reaction is based on migration of the reactive fragments into the microcavities by diffusion, to form a glass like thin film barrier to conceal the naked surface of PDMS. The barrier successfully blocked penetration of a fluorescent dye rhodamine B (RhB) into PDMS. The thickness of the barrier could be controlled by the time of reaction and the pressure inside the reaction chamber. There is a wide range of applications of such a technique in various fields, e.g. for coating the covered surfaces of microfluidic channels, tubes, capillaries, medical devices, catheters, as well as chip-integrated capillary electrophoresis and advanced electronic and opto-fluidic packaging.

KEYWORDS

Polydimethylsiloxane, diffusion barrier, microfluidics, plasma enhanced vapor deposition, hexamethyldisiloxane

INTRODUCTION

Materials like glass, silicon, and plastics have been used for the fabrication of microfluidic devices. In particular, the elastomeric material PDMS has been a popular for the fabrication of microfluidic devices [1, 2] because of its numerous advantages such as, its amenability for rapid prototyping, its inertness, biocompatibility, optical transparency, and (gas) permeability. However, PDMS provides a hydrophobic surface which promotes nonspecific adsorption or even absorption of small molecules into the bulk mass. Thus, the surface chemistry of the microfluidic channels in PDMS remains a major issue, and it is desirable to create hydrophilic surface of the channels to conceal hydrophobic nature of the surface for a range of applications in chemical and biological analyses [3, 4].

Usually, PDMS channels are made hydrophilic by exposing them to UV ozone or oxygen plasma for a short time before assembling the devices. But such a treatment is temporary and the hydrophobic character returns in less than an hour [5, 6]. For this purpose, various wet chemical strategies have been reported such as graft polymerization,

silanization, adsorption of detergents, proteins, poly-electrolytes [3, 7-9], and sol-gel based coating [10, 11]. However, these techniques are tedious, require skilful handling and, moreover, multiplexing of such methods on a large scale may perhaps induce complications in the process parameters.

Gas phase chemical reactions to modify the surfaces in microfluidic devices are relatively unexplored. Chemical vapor deposition is a useful technique which provides reactive chemicals in the gas phase for surface reaction. Various strategies have been reported for functionalized and non-functionalized surface polymerization in microfluidic devices [12-14].

In this paper, we describe a novel method of creating a glass-like thin film barrier in deep PDMS microcavities/channels. The method is based on gas phase fragmentation of O_2 and HMDS in RF plasma environment. The reactive fragments created in the plasma migrate into the cavities and react to form a glassy thin-film barrier, presumably composed of oxides of silicon. This barrier created in this way shows excellent blocking to the penetration of small molecules like rhodamine B.

RESULTS AND DISCUSSION

Soft photolithography was used to create microfluidic features in PDMS substrate which was bonded to glass surfaces to form the microcavities. The SiO_x barrier formation reaction was performed in a plasma chamber. The microcavities bearing devices were placed in the plasma environment of a computer controlled PECVD reactor Europlasma, model CD300. Then O_2 and HMDS gases were released into the plasma in a desired volume ratio. The impact of energetic electrons and ions on O_2 and HMDS molecules in the plasma resulted into fragmentation and a stable source of the reactants such as ions, radicals and elemental species. Reactive species produced in the gas phase diffuse into the channels and react with the walls, resulting in the formation of a thin film that acts as a barrier between the wall that forms the fluidic channels and the contents flowing through them. The formation of thin-film SiO_x on the channel wall reduced the contact angle from 120º to 60º.

We characterized this coating layer by studying the penetration of RhB into PDMS, as shown in Figure 1. An aqueous solution of RhB was stored in a bare and a SiOx

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barriered channel. Fluorescent images showed that RhB molecules penetrated into the bare PDMS (Fig.1a), resulting into a successive increment in the fluorescent region with time. However, in the treated channels, the fluorescence of RhB molecules remained confined to the channel region due to SiO$_x$ barrier (Fig. 1b).

Fragmentation of O$_2$ and HMDS in plasma provides various ionic, neutral radicals, and elemental species. We could observe the presence of Si radicals and elemental oxygen through their characteristic emission lines near 519 nm, 777 nm, and 884 nm, respectively, as also reported by others [15]. Since the microcavities are in a strong dielectric medium, we suggest that the radicals or elemental species of Si and O are more likely to migrate by diffusion into the cavities rather than the ionic species.
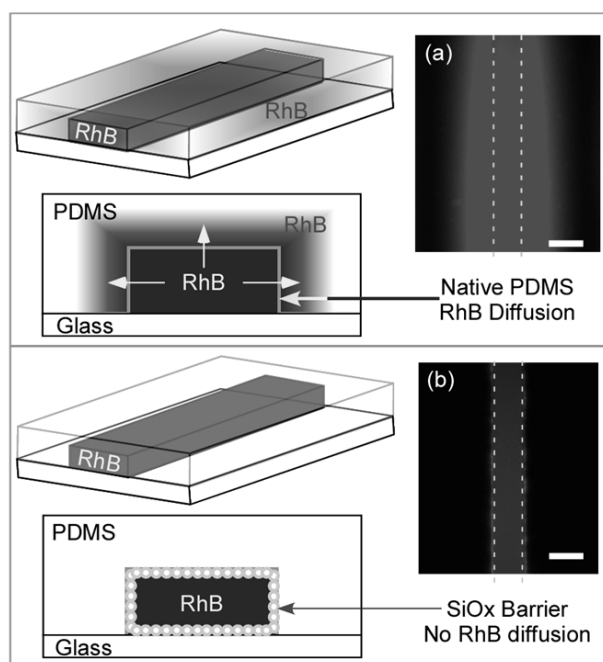

Figure 1. Formation of thin-film SiO$_x$ barrier on the walls of PDMS channel and characterization by Rhodamine B diffusion. (a) Native PDMS, (b) PDMS channel with SiOx barrier. Scale bar: 50 μm. The channel was filled and stored with RhB solution (10 μM) and after 3 hours it was microscopically examined. Conditions: RF 300 W, O$_2$: HMDS 500 : 16 sccm, 270 mTorr, 40 min, 50 °C.

For fixed conditions as given in Fig. 1, the efficiency of the barrier to block RhB penetration into PDMS drastically improved with increasing cross sectional area of the inlet of the cavity (Fig. 2). Efficient barriers in wider microcavities could be attributed to the fact that the net flux 'J_{net}' of the particles diffusing into the cavities increases with increasing the cross section 'A' as given in relation (1) [16],

$$J_{net} \approx -DA\frac{dn}{dx} \qquad (1)$$

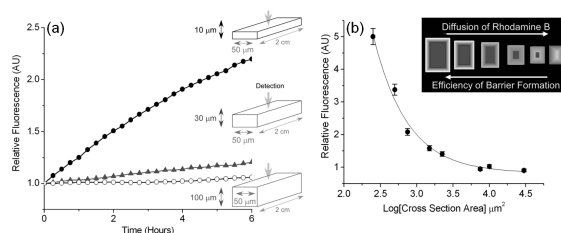where 'D' is the diffusion coefficient, and 'n' the density of the particles.

Figure 2. Fluorescence of RhB vs. time, in SiOx-coated channels of various dimensions (a). Effect of cross-sectional area of channels on efficiency of the thin film formation (b). Solid line shows the exponential fitting of the data points (y = y$_o$ + A$_1$e$^{(-x/t1)}$), y$_o$ = 0.8186, A$_1$ = 702.5, and t$_1$= 0.4694, R^2= 0.987). Schematic illustration of thin film formation with cross section of the channels. Reaction conditions as in Figure 1.

Diffusive migration of reactive molecules during the PECVD process was evident from the fact that the long and meandering channels could be coated with SiO$_x$. In Figure 3, an image taken at ~ 2.3 cm beyond a 357º (180º + 177º) turn shows blocking of RhB diffusion (Figure 3d). A qualitative 2D simulation of concentration profiles along the cavity wall is also shown in Fig. 3f, which shows a similar trend as for the experimentally determined thickness profiles of the barrier along the length of the cavity (Fig. 4).
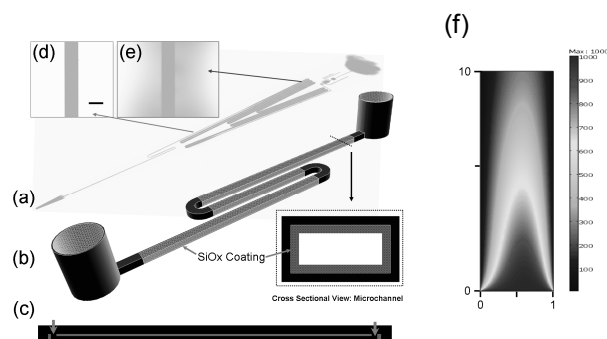

Figure 3. (a) A long meandering microfluidic channel (50 μm x 30 μm x 20 cm), exposed to reaction conditions as given in Figure 1, for 120 min. (b & c) Schematic representation of thin-film deposition. (d) Region of channel showing a good barrier to RhB penetration. (e) Region of channel showing poor barrier to RhB penetration. (f) Qualitative gas diffusion concentration profile (COMSOL simulation) through microfluidic channel when both sides are reactive.

The thickness of the barrier was physically measured by using a surface profilometer. A piece of PDMS bearing micro-grooves was reversibly bonded on a Si wafer to form the microcavities and the reaction was performed. After formation of the barrier the PDMS was removed and

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Si wafer was used for measuring the thickness of the barrier. Experimental results in Figure 4 show a trend towards increasing film thickness with increasing time of the reaction and pressure. The pressure was varied in the reaction while the flow ratio of O_2 and HMDS gases was fixed (31.3 : 1). These results reveal that increasing the time of the reaction and pressure provides more reactant species to be deposited, hence forming a thicker barrier.
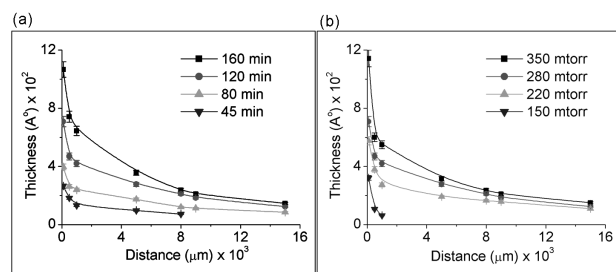

Figure 4. Effect of reaction time (a), and the concentration of HMDS (b), on the thickness and coating distance of SiO_x thin film. In this experiment, PDMS-coated channels (50 μm x 100 μm x 10 cm) were bonded to a Si wafer instead of a glass substrate, and after thin film deposition the device was disassembled. The Si wafer was used to measure the thickness of SiO_x film mechanically using a profilometer.

The SiO_x could be created quite reproducibly. Reproducibility of the barrier formation was studied in a multiplex of a longer ($\sim$ 20 cm) meandering cavities of 40 individual units (Figure 5). This multiplex platform was subjected to the barrier formation and efficiency of the barrier was studied using RhB penetration into PDMS. The distances coated with the barrier in the cavities could
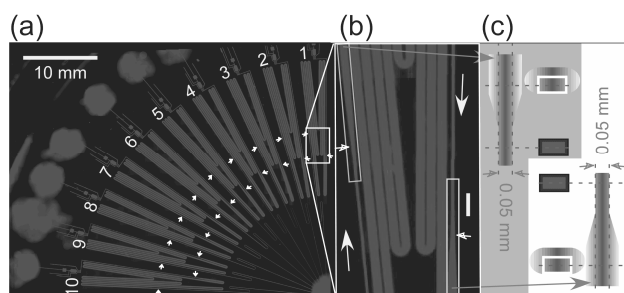

Figure 5. Thin film formation in a multiplexed platform of 40 individual channels (1/4 shown). White arrows show the SiO_x coated distance of the thin film barrier. (b) Close view of approaching penetration of the thin film barrier. (c) Schematic illustration of transition to RhB diffusion zones in the channels from both sides of the channel. Reaction time 120 min, other conditions as in Figure 1.

be clearly discerned from the fluorescence of RhB, which is indicated by arrows. The SiO_x coated distances in the multiplex channels were highly reproducible (60 mm $\pm$ 5, n = 10).

The significance of HMDS in the formation of the SiO_x barrier could be established as shown in Fig. 6, when the reactions were performed in the absence and presence

of HMDS supply to the reaction chamber. The efficiency of the barrier was examined by storing a solution of RhB in the channels. The channels which were treated in the absence of HMDS showed penetration of RhB into PDMS. However, the channels treated in the presence of HMDS showed an efficient protection to RhB molecules from penetrating into the PDMS.
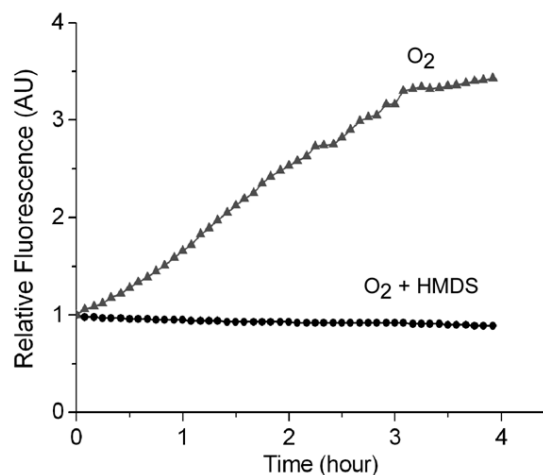

Figure 6. (a) Penetration of RhB through O_2 plasma and O_2 plasma + HMDS-treated PDMS channels. Other conditions as in Figure 1.

CONCLUSIONS

We report a novel method of thin film formation in deep microcavities/channels using a plasma-enhanced chemical vapor deposition (PECVD) technique. The field of gas-phase reaction is relatively unexplored for surface modification within assembled microfluidic devices. We have demonstrated for the first time a gas-phase chemical process for creating a glass-like surface in assembled PDMS microfluidic channels. Our aim is to further investigate such thin-films in assembled microfluidic devices for surface bio-functionalization and capillary electrophoresis applications.

Reactive species produced in the gas phase diffuse into the channels and react with the walls, resulting in the formation of a thin film that can act as a barrier between the materials that form the walls of the fluidic channels in touch with the liquids. Successful deposition of thin-film oxides of silicon (SiO_x) deep into microchannels is attributed to the diffusion of reactant molecules into the channels. Since thin film formation is attributed to molecular diffusion, this method allows coating of long, meandering channels as well as straight channels. The extent of thin film formation along the channels and its thickness are controlled by the time of reaction and concentration of the reactant precursor hexamethyl-disiloxane (HMDS). We show that thin-film SiO_x formation in microfluidic channels cast in polydimethyl-siloxane (PDMS) effectively blocks the penetration of

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rhodamine B (RhB) from aqueous solution within the channels into the PDMS that comprises the channel walls. This method of formation of thin film SiO$_x$ in micro-cavities is simple and robust, and up-scaling may be more straightforward than for conventional wet chemical methods.

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