CHARACTERIZATION AND APPLICATIONS
OF GLASSY BARRIER ON POLYMERIC MICROCAVITIES
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ABSTRACT
This paper describes formation of a glassy barrier in long microcavities through gas phase reaction. The barrier is characterized as composed of oxides of silicon (SiOx). The SiOx barrier was grown in assembled elastomeric microfluidic devices and tested successfully for various applications.

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

INTRODUCTION
Previously, we demonstrated that the reactive species created from the fragmentation of O2 and hexamethyldisiloxane (HMDSO) in an RF plasma environment diffused into microcavities of polydimethylsiloxane (PDMS) to form a thin film barrier [1]. Polydimethylsiloxane (PDMS) has been the most popular material for microfluidic devices, which offers a range of advantages such as, rapid prototyping, inertness, biocompatibility, optical transparency, and gas permeability [2]. However, surface chemistry of PDMS remained a major issue because of its hydrophobic surface, which promotes nonspecific adsorption/absorption of certain organic and biomolecules. To deal with this problem various wet chemical strategies have been reported [3, 4]. However, our method is based on gas phase reaction to create a SiOx barrier in the microchannels. The process is shown schematically in Fig. 1.

Figure 1. Schematic illustration of formation of SiOx barrier in PDMS microcavities.

Figure 2. Energy Dispersive X-ray characterization of SiOx in microcavity.
EXPERIMENTAL

Microcavities in PDMS were fabricated using standard photolithography techniques [2]. For all experiments the SiO$_x$ barrier forming reaction conditions were as: RF power: 300 W; O$_2$ flow: 500 sccm; HMDSO flow: 16 sccm; pressure: 300 mTorr; substrate temperature: 50 °C; deposition time: 1 hr. The EDX measurements were taken in an extended pressure mode at 273 Pa in the back scattered mode where the beam current was 40 µA, probe current was 4.6 nA, EHT at 20 kV, and filament at current 1.943 A. Probing area (~10 mm$^2$).

RESULTS AND DISCUSSION

A schematic illustration of the barrier formation process is shown in Fig. 1. Formation of reactants Si and O occurs in the plasma environment, which migrate into the cavities through molecular diffusion and react on the surface to create a thin film of the barrier. The barrier could be characterized by using energy dispersive X-ray as composed of Si and O (Fig. 2). Since PDMS contains inherent Si and O the EDX studies were done by acquiring the barrier on a plastic Zeonor devoid of Si and O. The glass-like barrier in PDMS cavities could be used for various microfluidic application such as, blocking of penetration/absorption of small molecules, resistance to organic solvents and, stable electroosmotic flow (EOF) and reproducible electrophoresis.

PDMS is widely used in microfluidic devices and in the majority of its applications a glassy-surface of the channels is desired. Our SiO$_x$ barrier in PDMS microchannels successfully blocked the absorption/adsorption of small molecules such as biotin-TRITC (biotin-tetramethyl rhodamine isothiocyanate) into PDMS (Fig. 3). The barrier also showed strong resistance to organic solvent like toluene and prevented PDMS from swelling and deformation (Fig. 4). Moreover, the formation of SiO$_x$ barrier on PDMS microfluidic channels solved the stability problem of EOF in native PDMS microfluidic devices (Fig. 5), with reproducible electrophoretic separations comparable to that in conventional fused silica capillaries.

Figure 3. Absorption of small molecules in PDMS. Fluorescent images (I & IV) of TRITC labelled biotin solution (50 µM) stored in the channels for 1 hr. Washing of the native/bare (II)&(III) and SiO$_x$ barrier (V)&(VI) channels with 0.1 M and 1.0 M (III) NaOH solutions. (VII) The relative intensities after washings. Channel: 100 µm x 30 µm x 1 cm. Scale bare 50 µm.

Figure 4. Resistance to deformation with toluene. Differential contrast images of native/bare (I) and SiO$_x$ barrier (II) PDMS channels. Toluene was allowed to flow into the channels under gravity. Scale bar 100 µm.
CONCLUSIONS
We demonstrated a gas phase chemical reaction that can be used for modification of covered surfaces in microcavities and channels. SiOx thin film barrier was grown in PDMS microcavities. The formation of glassy surface in the assembled plastic and elastomeric microfluidic devices is very important to induce hydrophilic nature and further chemical and biological modification of the surfaces. We showed that our SiOx barrier in PDMS microfluidic devices could be used to block the small nonpolar molecules from entering into PDMS. The SiOx barrier showed excellent resistance to swelling and deformation of the PDMS channels when organic solvent like toluene was stored in the channels. Stable electroosmotic flow was realized in SiOx coated channels resulting into reproducible electrophoretic separations.

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REFERENCES

Figure 5. Stable Electroosmotic Flow and Reproducible Electrophoresis. Electrophoresis experiments were performed in a standard cross channel network of 50 μm x 50 μm x 2 cm. Separation buffer: 100 mM N-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid, 82 mM triethylamine (pH 9.0). Sample: a mixture containing 10 μM of each, fluorescein and 2,7-dichlorofluorescein in the buffer solution. Injection: 100 V for 10 s, and separation: 1000 V with anode at injection end. EOF measurements (n = 3) (left). Electropherograms (right) showing base line (res: 1.4, migration time RSD 3%) separation of the sample. Peak numbering: 2, 7-dichlorofluorescein (1); fluorescein (2). Detection at 1.5 cm; \( \lambda_{\text{excitation}} \) 490, \( \lambda_{\text{emission}} \) 520 nm (helogen-xenon lamp).