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This study reports the penetration properties of various Parylenes (i.e., C, N and HT) inside long microchannels. The work broadly covers the effects of the dimer type, loaded dimer mass, substrate temperature and channel size on the penetration length, i.e., the length that Parylene can be deposited into the microchannel from the inlet. Understanding the mechanism of Parylene penetration into microchannel helps to develop mass-producible inner surface protection design and process for microfluidic devices.

Parylene, penetration, microchannel

Parylene, a family of poly(p-xylylene), has been widely studied [1-2] and used in various industries because of their many excellent properties, such as superior barrier property used to protect the electronic devices against damages from moisture and corrosive etchants [3-4]. PDMS is anthor very popular material in microdevices [5]. Coating/caulking PDMS with Parylene has been considered as an effective way to decrease the permeability required by various applications [6-8]. For PDMS microfluidics, the surface treatment can be fulfilled before or after the bonding operation. For the pre-bonding treatment, a further surface treatment was usually required to remove Parylene on top of PDMS to recover the oxygen plasma bonding. [9] While, thanks to the good conformal deposition capability, Parylene C [7, 8, 10] and N [8] have been used to seal the inner surfaces of PDMS microfluidic devices as a post-bonding surface treatment. M. Akhtar et. al. recently reported that coating Parylene AF4 (Parylene HT) into PDMS channels will improve its on-chip droplet storage life. [11] However, a comprehensive understanding of the Parylene penetration inside the microchannel is still lacking and the important factors of this penetration process are largely unknown.

This work established a theoretical modeling of parylene deposition into the microfluidic channel based on with the time-independent free molecular flow. The effects of the dimer type, loaded dimer mass, substrate temperature and channel size on the penetration process were experimentally studied. A penetration length, i.e., the length that Parylene can be deposited into the microchannel from the inlet, was used to evaluate the Parylene penetration performance.

The deposition pressure for Parylene usually ranges from 10 mTorr to 100 mTorr, under which the mean free math of the Parylene monomer is of the order of 0.5 mm. Since the typical characteristic size of a microfluidic channel is expected to be of the order of tens of micrometers, the mean free path λ of the Parylene monomer in the vacuum deposition chamber is far larger than the characteristic size (i.e. the hydraulic diameter D_h) of the microfluidic channel. In another word, the Knudsen number λ is much larger than 1, hence the free molecular flow condition is satisfied, for which intermolecular collisions rarely happen. The Knudsen diffusion coefficient for the free molecular flow is only dependent on the molecular weight, the deposition temperature and the channel characteristic size. The deposition rate as a function of deposition pressure for Parylene N was measured at room temperature, and then became the reaction term in the mass balance equation. The deposition thickness was small compared with the channel height h and width w therefore the channel cross-sectional shape was assumed invariant with time during the deposition. Finally, a theoretical model was proposed, in which the rectangular micro-channel was confined at one side as in Figure 1.

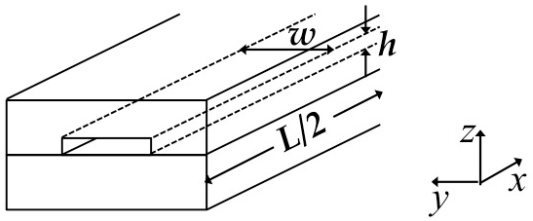

Figure 1: The illustration of the microfluidic channel. The channel width w, height h and half-length L/2 are indicated.

The Parylene N deposition rate $R_d(x)$ at room temperature only depends on the molar concentration $c(x)$ of the Parylene N monomer,

$$R_d(x) = k \cdot [c(x)RT / p_0]^n, \quad (1)$$

where R is the gas constant, T is the room temperature, p_0 is the deposition pressure in the vacuum deposition chamber, equal to 45 mTorr in our experiment, and the rate constant k and the reaction order n were fitted based on our own measurement data, equal to 0.675 μm/hour and 0.8225, respectively.

As discussed above, the Parylene N monomer gas flow inside the channel is a Knudsen diffusion process, hence the molar flux $j(x)$ of the Parylene N monomer is given by,

$$j(x) = -\frac{D_h}{3}\sqrt{\frac{8RT}{\pi M}}\frac{dc(x)}{dx}, \qquad (2)$$

where the hydraulic diameter D_h is given by $2wh/(w+h)$, and M is the molar mass of the Parylene N monomer.

The mass balance equation for this one-dimensional flow model is given by,

$$\frac{d\left[wh \cdot j(x)\right]}{dx} = -2(w+h)R_d(x)\frac{\rho}{M}, \qquad (3)$$

where ρ is the Parylene N film density.

The boundary conditions are,

$$c(0) = \frac{p_0}{RT}, \quad \left.\frac{\partial c}{\partial x}\right|_{x=L/2} = 0, \qquad (4)$$

where L is the total channel length, equal to 10.5 cm according to the following experiment.

The model equations were solved numerically using the finite element analysis (COMSOL™).

PDMS microchannels with different sizes (120 µm, 240 µm, and 480 µm wide; 18 µm, 30 µm, 60 µm, 120 µm deep)were prepared following the standard soft lithography process. Briefly, prepolymer was prepared by mixing the base and the curing agent (Sylgard® 184, Dow Corning Comp.) with mass ratio of 10:1. After degassing in vacuum for 15 min, the prepolymer was poured onto the silicon master and cured at 100°C for 1h. Inlet and outlet were obtained by punching through holes. The so-prepared PDMS microchannels were direct attached to A174-treated silicon wafers to form close microchannels. Parylene depositions were then performed in PDS 2035CR Parylene coater (SCS) with Parylene C/N/HT dimers. A home-made hot plate was used to control the substrate temperatures under deposition. After the deposition, the PDMS microchannel was peeled off and the Parylene film left on the silicon wafer was measured by the profilometer (P15, KLA-Tencor).

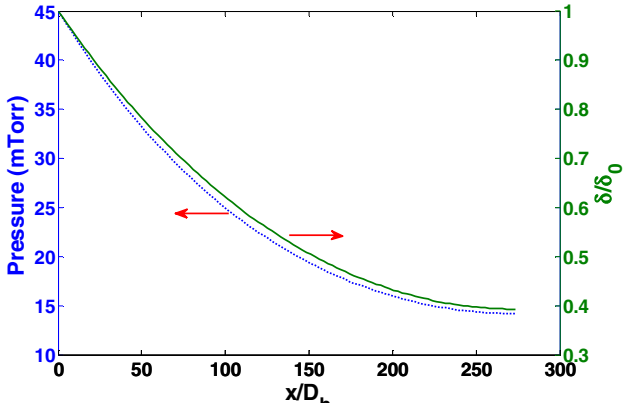

Figure 2: Variations of the pressure and film thickness along the microchannels calculated based on the time-independent free molecular flow model. Deposition is a Parylene N deposition at room temperature, and the channel is 120 µm deep and 480 µm wide.

A typical distribution of pressure and film thickness inside a microchannel calculated based on Eqns 1-4 is showed in Figure 2.

Figure 3 shows the Parylene thickness distribution along the microchannels with different dimers. The results show that the penetration length (characterized by the half thickness length) of Parylene HT is the longest likely because of the extreme low stiction coefficient. On the other hand, lighter molecules, e.g., the Parylene N monomer, have larger free molecular diffusivities and thereby are likely to penetrate deeper than the heavier ones e.g., the Parylene C monomer. The experimental measurement gave a shorter penetration compared to that obtained based on a theoretical model. This gave us a clue that deposition onto PDMS, a nanoporous material, will be different with that on silicon.

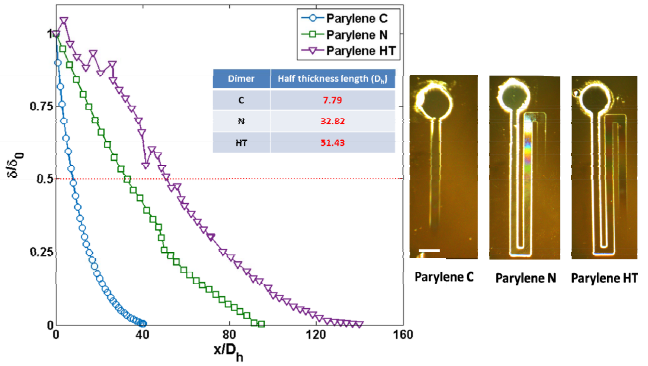

Figure 3: Variation of the film thickness along the microchannels with different dimers. The right three figures showed the deposited films on the silicon wafers. The scale bar is1mm. Deposition conditions: Parylene C, m=11.13 g, P=22(15) mTorr; Parylene N, m = 20.41g, P = 60(13) mTorr; Parylene HT, m = 30.73g, P = 65(15) mTorr. Substrates in all depositions are at RT.

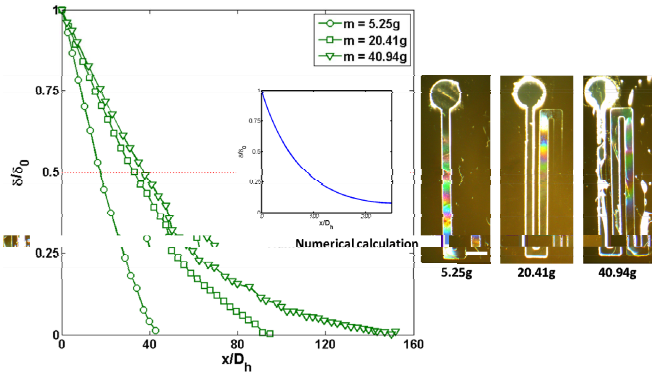

Figure 4: Variation of the film thickness along the microchannels with different loading Parylene N dimer masses. Insert figure is the numerical calculation based on

the present model. The right three figures showed the deposited films on the silicon wafers. The scale bar is1mm. Deposition conditions: P = 60(15) mtorr. Substrates in all depositions are at RT.

Theoretically, Parylene N is a more applicable choice for microchannel inner surface coating so the deposition performance of Parylene N inside the microchannel with different dimer loading masses were studied in Figure 4. It shows that more dimers will result in a longer penetration length, which is mostly attributed to its longer deposition time.

To study deposition temperature effects, *in-situ* heating the substrate was applied during the deposition. As shown in Figure 5, the penetration lengths were nearly the same with substrate temperature of 20°C, 60°C, and 80°C, while the film thicknesses were dramatically decreased. This results supports the fact that the mass transport under the free-molecular flow deposition condition was the dominant factor, instead of the deposition temperature (which then has a bigger effect on surface mobility of the adopted monomers). Beside the diffusion inside the microchannel and the surface movement of Parylene monomers, Parylene monomers will also penetrate into the PDMS substrate, which requires further study in the future. Penetration into PDMS substrate may also affect the reaction boundary (Eq. 4) considerably and thereby lead to the present experimental observation.

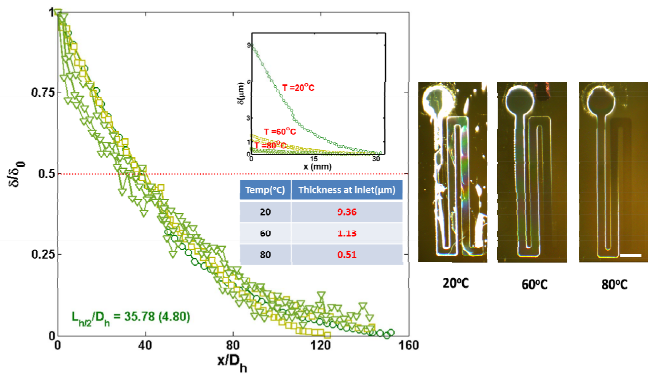

Figure 5: Variation of the film thickness along the microchannels with different substrate temperatures. The right three figures showed the deposited films on the silicon wafers. The scale bar is1mm. Deposition conditions: Parylene N, m = 41.18(0.98)g, P = 60(15) mTorr.

The results of size effects of Parylene N in microchannel were shown in Figure 6. It shows that channels with smaller characteristic heights have longer deposition depths, indicating a surface effect because of the porous PDMS surface.

Rhodamine (1mM in DI water) diffusion tests were carried out to examine the inner surface protection performances. As shown in Figure 7, Parylene N deposition at a higher temperature has the best inner surface sealing performance.

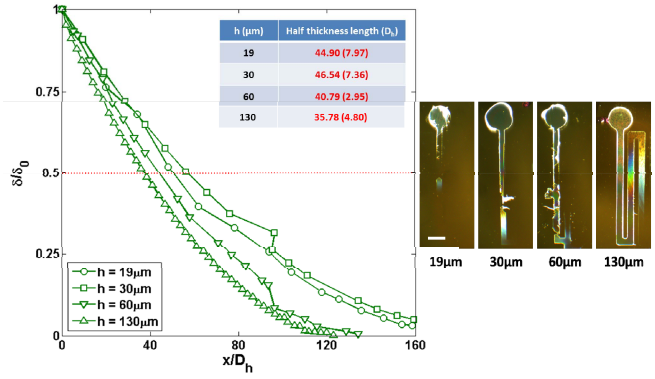

Figure 6: Variation of the film thickness along the microchannels with different geometric channel sizes. The right four figures showed the deposited films on the silicon wafers. The scale bar is1mm. Deposition conditions: Parylene N, m = 40.32g, P = 60(15) mTorr, T = 60°C.

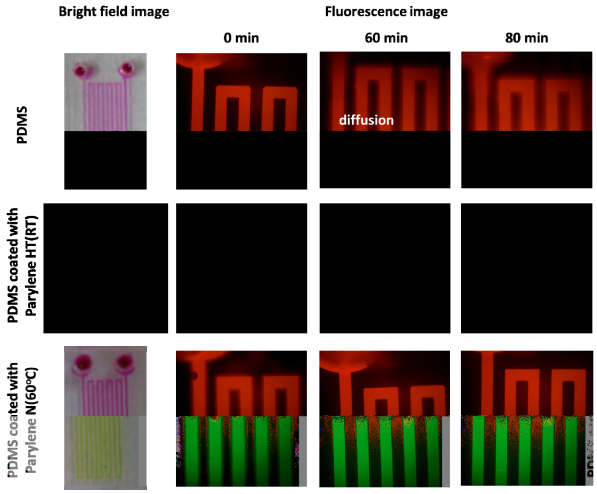

Figure 7: Rhodamine diffusion tests in pure PDMS, Parylene HT coated PDMS (RT) and Parylene N coated PDMS (60°C) microchannels.

Deposition of Parylene inside a microchannel holds promising applications in the surface treatment of PDMS microfluidic device. This work studied the effects of the dimer type, loaded dimer mass, substrate temperature and channel size on the penetration preformation. Based on the preliminary experimental and theoretical data, Parylene can penetrate into the microchannel to a certain distance. Further study on the Parylene deposition on PDMS is required to achieve a more accurate boundary condition for a comprehensive understanding on this diffusion-reaction system.

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