DEVELOPMENT OF SURFACE MODIFICATION AND PATTERNING METHOD USING TiO_2 INTEGRATED EXTENDED NANOCHANNELS

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ABSTRACT

Development of surface modification method of extended nanospaces (10 - 1,000 nm) expands the possibilities of various fluidic applications. Although surface modification for microchannels is essential for controlling the behavior of fluid, they are difficult to apply to nanometer-sized channels. Here, we developed a novel surface patterning method for extended nanochannels using fluorinated-phosphonic acid (FPS) and titanium oxide (TiO_2). Performances of the modification method could be confirmed by measurements of Laplace pressure.

KEYWORDS: Surface modification, Extended-nanochannel, Laplace valve, Titanium oxide, Fluorinated-phosphonic acid,

INTRODUCTION

Integrated fluidic devices are downsizing from microspace to extended nanospace. Popular agents for surface modification such as silane coupling and polymer coating have been generally utilized for hydrophobic/hydrophilic patterning in microchannels fabricated into glass substrate (SiO_2). However, these reagents are not adequate for extended nanospaces, because they can cause the clogging of nanochannels. In addition, surface modification based on a photo-patterning method is difficult to apply to extended nanospaces due to the diffraction limit of light.

To overcome these problems, we focused on utilization of FPS immobilized onto a TiO_2 matrix. FPS is well-known reagents for surface treatment, and make it possible to fabricate self-assembled monolayer on metallic oxides. Furthermore, the stability of FPS depends on the quality of metal substrates, *e.g.*, FPS can be formed high density monolayer onto TiO_2 surface [1], but easily eliminated by water onto SiO_2 surface [2]. Such unique properties of FPS are expected to be useful for modification of extended nanospaces. In this study, we developed a novel surface patterning method using FPS and TiO_2 into extended nanochannels, and examined not only advanced contact angles of FPS-TiO_2 modified surfaces but also Laplace pressure at the modified nanochannels.

EXPERIMENTAL

Fabrication of extended nanochannels [3] and hydrophobic/hydrophilic patterning were carried out. Extended nanochannels were fabricated on a silica substrate (KEN-W 30.0×70.0×0.70 mm, Shin-Etsu Chemical Co., Ltd.) by electron beam lithography and plasma etching. TiO_2 was deposited onto an arbitrary position in extended nanochannels and annealed. A glass substrate with channels and a cover one were washed by piranha solution (30 % H_2O_2 : 96% H_2SO_4 = 1:3), and the substrates were bonded at 300 °C under vacuum conditions. Dehydrated tetrahydrofuran (THF) solution containing 0.1 wt% *1H,1H,2H,2H*-perfluoro-n-decylphosphonic acid (FPS) (F330, Dojindo molecular technologies, Inc.) was introduced into extended nanochannels at 40 °C for 24 hours. The channels were washed with THF for 1 hours, and dried in oven (SDN/W-27, Sanyo Electric Co., Ltd.) at 140 °C for 2 hours. Ultrapure water (18 MΩ, MilliQ) was introduced for 3 hours to remove FPS layer immobilized onto SiO_2 area. Finally residual solution was dried at 200 °C. Sample solutions were introduced into the nanochannels by pressure controller (PC20, Nagano Keiki). Laplace pressure was determined from the observation of fluid behavior by using optical setup consisting of microscope (IX 71, Olympus) and CCD camera (ImagEM C9100-13, Hamamatsu Photonics K.K.).

Surface modification of FPS onto TiO_2-coated plates and glass plates was performed in a similar manner to the nanochannels as mentioned above. Contact angles onto each plate were measured by the contact angle meter (S Image 02, Excimer Inc.) in order to confirm hydrophobic/hydrophilic and/or lipophilic/lipophobic properties. Deionized water and 1-octanol were dropped onto TiO_2-coated plates and bare glass plates. Contact angles of their solutions onto each plate were measured 4 times. Advanced contact angles were also measured by extending the droplet.

RESULTS AND DISCUSSION

Figure 1 shows the results of water introduction into nanochannels having SiO_2-TiO_2 surface patterning. We found that the front of water in the nanochannels could be stopped under pressures less than 200 kPa, because the interface region between SiO_2 and TiO_2 surfaces could act as pressure valve. When the pressures exceeded over 200 kPa, the valve function against water disappeared and the water filled in whole nanochannels.

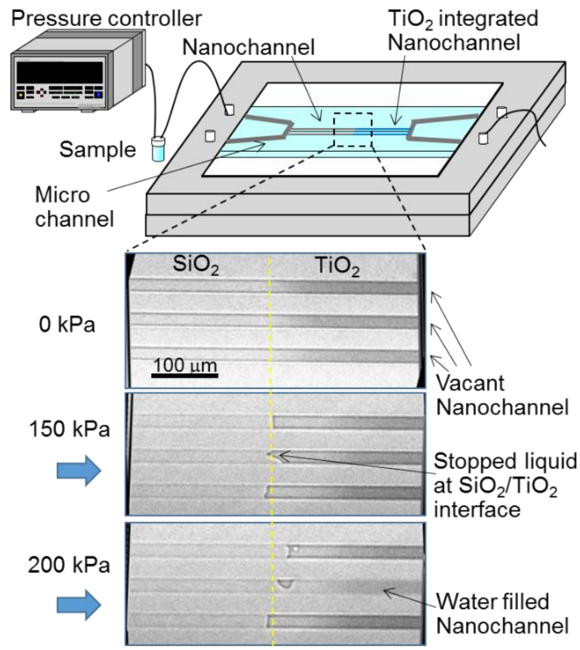

Figure 1. Experimental setup of measurements of Laplace pressure at SiO_2/TiO_2 interface, and results by water introduction.

Figure 2 shows a bar graph of advanced contact angles of water on FPS-modified TiO_2 and SiO_2 surfaces after immersion into water and NaOH solution. FPS-modified TiO_2 substrates were found to be kept hydrophobic surfaces (almost 120°) regardless of water immersion. The contact angle is comparable with nanopillar-based surface [4]. On the other hands, contact angles of FPS-modified SiO_2 substrates were much smaller than those of FPS-modified TiO_2. Furthermore, we examined each advanced contact angle of FPS-modified TiO_2 and SiO_2 substrates against 1-octanol droplets. The results showed that FPS-modified TiO_2 surfaces have also high lipophobic properties compared with those of SiO_2. Contact angles of both TiO_2 and SiO_2 surfaces were slightly changed by immersing in base solution for 3 hours. These results indicate that a FPS monolayer on TiO_2 was quite stable, rather than silane coupling agents on glass surfaces which are generally broken by base solution.

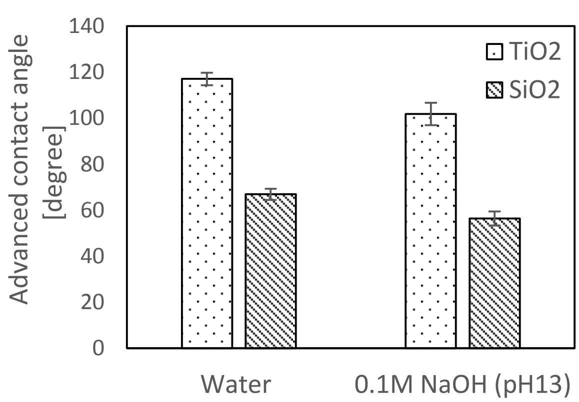

Figure 2. Contact angles of water on modified surfaces of both TiO_2 and SiO_2 plates after washed by deionized water for 3 hours (left), and by base solution (right).

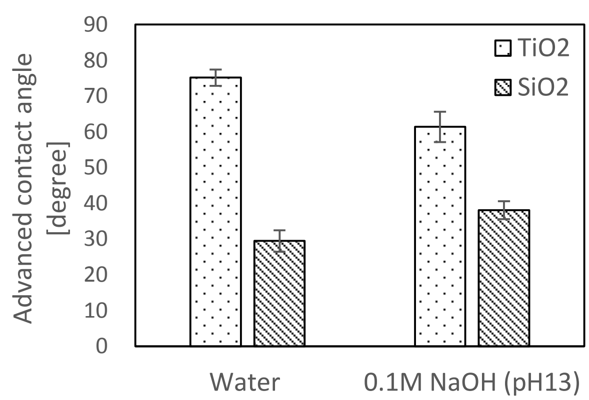

Figure 3. Contact angle of 1-ocatanol on modified surfaces of both TiO_2 and SiO_2 plates after washed by deionized water for 3 hours (left), and by base solution (right).

From the pressure at SiO_2/TiO_2 interfaces in nanochannels, Laplace pressure (P_{LP}) can be calculated by following equation [5];

$$P_{LP} = \sigma \left\{ \frac{\cos\theta_1 + \cos\theta_3}{H} + \frac{\cos\theta_2 + \cos\theta_4}{W} \right\}$$

where, σ is the surface tension of water in air, and H and W means the height and the width of a channel, respectively. θ_1 and θ_3 correspond to contact angles of a bottom and top of surface, and θ_2 and θ_4 are those of walls of rectangular extended nanochannels, respectively. Experimental P_{LP} value was compared to calculated ones, which were estimated by advanced contact angle measurements, as shown in Table 1. Calculation 1 was performed using following condition; θ_1, θ_2, and θ_4 are the average advanced contact angles of TiO_2 surfaces after modification and water immersion, and θ_3 was that of SiO_2. On the other hands, in calculation 2, θ_1 ~ θ_4 were equal to advanced contact angles of TiO_2 substrates. It is noteworthy that P_{LP} value expected from the surface condition of the fabricated nanochannels should be consistent to calculation 1, but was similar to calculation 2. This fact suggests that the hydrophobic properties of FPS-modified TiO_2 surfaces dominate the meniscus structure of water confined in extended nanochannels. We needs further discussion about this result.

Table 1. Measured Laplace pressure in extended nanochannels and calculated one. Calculation 1 was obtained using contact angle of side and bottom TiO_2 surfaces and upper SiO_2 surfaces. Calculation 2 was obtained using only contact angle of side and bottom TiO_2 surfaces.

	Measured in nanochannel	Calculation 1	Calculation 2
Laplace pressure [kPa]	240±50	20	250

CONCLUSION

The surface modification into extended nanochannels was achieved by the new patterning method based on fluorinated-phosphonic acid (FPS) and titanium oxide. Laplace valve function was confirmed in the FPS-modified TiO_2 nanochannels, and the measured value was well accorded with the calculated value. This surface modification method could have important advantages for nanofluidic control.

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