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Flow-Restricted Etching Method on Isotropic Substrates and Its Mechanism

XIE Haibo, ZHENG Yi*, FAN Yurun, FU Xin, and YANG Huayong

The State Key Lab of Fluid Power Transmission and Control, Zhejiang University, Hangzhou 310027, China

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Abstract: With the development of analytical instrumentation to minimization, integration and automation, the microfluidic chips, which are more integrated, complex and diversified, have been applied widely on the manufacturing of analytical instrumentation. However, the present photolithography-based microfabrication technology, which is only able to pattern microchannels with simple inside structures, can not follow the rapid development of requirements. For solving the problem, a fabrication method based on the restricting effect of laminar flow is proposed for the micro etching on isotropic substrates. Experiments were conducted inside glass-based microchannels, in which certain etchant was used to form complicated microstructures. The flow parameters' effects on the aspect ratio, side wall profile and etching rate were revealed by the experiments. The experimental results reveal that the topography of micro structures patterned with the restricted flow etching method is mainly determined by the flowrates of separator and etchant. The computational fluid dynamics(CFD) model on the interface between multiple streams was established for the etching process, and analysis on the causes of various micro topographies was conducted based on the CFD simulation results. The experimental data consisted with the simulation results very well. The investigation depicted in this paper indicate that the flow restricted etching method provides sufficient references for the research and understanding on the mass transport at the liquid-liquid surface in the microchannel and can be used to pattern complex micro structures with high aspect ratios, meantime, it greatly enriches the microfabrication technology for microfluidic chips.

Key words: microfluidics, etching, computational fluid dynamics(CFD), laminar

1 Introduction

The microfluidic chip can be defined as a system which handles liquids of volumes of micro-liters or pico-liters. Microfluidic systems could benefit the areas of biology, biotechnology, and chemistry. Systems for these applications should integrate the elements of acquisition, pre-treatment, mixing-reaction, separation, post-treatment and detection. Compared to an ordinary automatic chemical analyzer, microfluidic system has the advantages of superior portability, high accuracy, low consumption of reagents, and ability to handle small amounts of sample with very homogeneous temperature distribution[1–2].

At present stage, the materials that can be used for microfluidic chip fabrication include silicon, glass and some kinds of organic materials[3–5]. Because of its excellent light transmittance, high strength and favorable insulation property, glass has been most widely used as the substrate material[6–7]. Typically, glass is processed with the wet etching method and the microchannels thus processed usually have low aspect ratios. As the demand for the micromation and complication gets higher, new micro fabrication techniques were proposed recently, such as LIGA (which is a German acronym for Lithographie, Galvanoformung, Abformung) and soft lithography[8–11], but the low-aspect-ratio problem still has not been overcome quite well.

Microscale flow is usually laminar since the invention of the first microfluidic chip, research on the laminar feature of microscale flow has been a scientific focus. The effective mixing is very important for many microfluidic chip applications, such as drug solution dilution and reagent introduction for chemical analysis; and most of the researches address to how to disturb the laminar situation and achieve efficient mixing[12–13].

In recent years, the studies on utilizing the laminar characteristics in microscale etching techniques are at exploring stage. KENIS, et al[14–15], put forth the flow etching/deposit concept first and conducted some exploring experiments on the microfluidic chips patterned on glass. Their emphasis is on depositing some organic fiber that possesses biological compatibility and reactive etching at the interface between streams at nanoscale. ISMAGLIOV, et al[16] and KAMHOLZ, et al[17], did some research on the molecule diffusion between multiple laminar streams, taking the Navier-Stokes equation into account, and predicted that the molecule diffusion and interface would present so called "butterfly effect". However, for the application of restricted flow etching, there remains lack of

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* Corresponding author. E-mail: yizheng@zju.edu.cn

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quantitative relationship between the etching quality, topography and flow parameters.

Our restricted etching method based on laminar feature is described in Fig. 1. We fabricated a microchannel which had three inlets and one outlet, and injected an etchant into the middle inlet and a separator into the other two inlets. Since the characteristic dimensions of the micro channel are very small, each stream will keep steady laminar condition. The etchant will produce soluble matter through the reaction with the substrate while the separator will constrain the effective reaction region. Through a period of time of reaction, a secondary micro structure will be patterned inside the original microchannel. We can obtain secondary micro structures with high aspect ratios by changing the flow parameters of the etchant and separator.

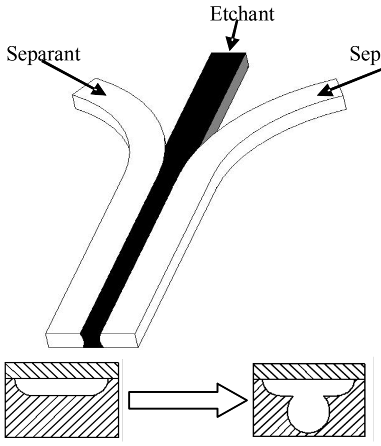


Fig. 1. Theory of restricted flowing secondary etching

In the first part of the paper, the microfabrication method and experiment procedure are illustrated. The quantitative analyses on experimental results and computational fluid dynamics(CFD) simulation are conducted. Finally, it is the conclusion.

2 Fabrication and Experimental Setup

2.1 Fabrication of a glass-PDMS microfluidic chip

For convenience of comparing the etching topographical features, we observe the cross-sections of micro structures processed by the flow etching method. The common method of high temperature bonding used for bonding microfluidic glass chips is irreversible, that is, it is difficult to open the channel after etching. So we bonded the glass substrate by using a Polydimethylsiloxane(PDMS) membrane to form an impermanent package, it can be separated conveniently after experiments. The fabrication process of the Glass-PDMS chip is described as follows (Fig. 2).

(1) A vectorgraph photofilm generated from a high-resolution laser plotter (10 000 dot/in.) was chosen as the first photomask to transfer microchannel patterns onto photoresist(PR) layer by using standard photolithography process.

(2) The developed PR was used as the etch mask for subsequent Cr etching to transfer patterns onto Cr layer.

(3) Etch Cr lay, and the patterned Cr layer was used as the etch mask for glass etching.

(4) Etch the glass substrate at the constant temperature of 50 °C in water area; the etchant is a mixture of HF, HNO_3 and NH_4Cl ($HF:HNO_3:NH_4Cl$=0.75 mol/L:0.5 mol/L: 0.5 mol/L).

(5) Strip the residual PR and Cr layer.

(6) Fabricate a PDMS membrane and drill holes at certain places, rinsed with ethanol and treated with ultraviolet for 25 min (light intensity is about 10 mW/cm^2), then bring the glass and PDMS membrane into conformal contact and achieve this seal for 24 h.

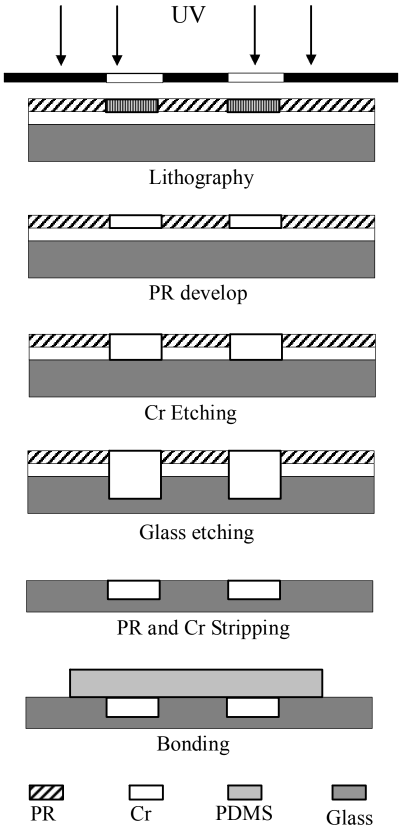
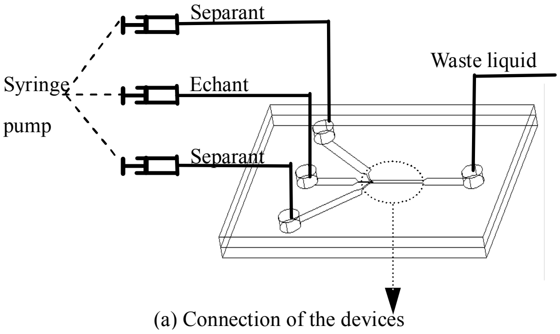


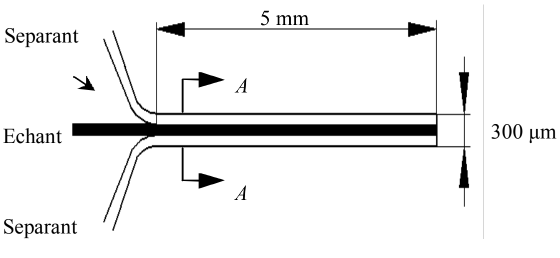
Fig. 2. Simplified fabrication process of microchannels

2.2 Etching experiment setup

The microchannel used in the experiment is about 300 μm in width and 50 μm in depth and has three inlets and one outlet. The etchant and inert solvent were introduced into the microchannel from a syringe pump, which can adjust the flow rates injected into the inlets, and the waste liquid was elicited from the outlet, see Fig. 3(a). The etchant used is the same as that for chemical wet etching; the inert solvent is deionized water. For smoothing the flow path, we adopted arc connection at the inlets. The configuration of microchannel is shown in Fig. 3(b). After finishing the etching process, we cut the microchannel at the *A*-*A* section which located at 5 mm from the inlet. In the experiment, we tested the cases of, respectively, the constant inlet flow rates of 1 mL/h and 3 mL/h with the etching time changing from 1 h to 5 h.



(a) Connection of the devices



(b) Partial enlarged view of the microchannel

Fig. 3. Schematic drawing of experiment set

3 CFD Simulation

From the principle of restricted flow etching shown in Fig. 1, we can expect that the main factors which can affect the topography are the interface shape and molecule diffusion. The topography of the microchannel will change during the etching process; moreover, the shape of the microchannel will affect the concentration distribution of the etchant and then affect the etching process. Flow field simulation is an effective method to explore the mechanism of microscale flow, especially for the study on the change of interfaces between streams. Because the interfaces between the streams usually are three-dimensional, it is rather difficult to do experimental observations, such as micro-PIV(particle image velocity), We used a CFD model to calculate the topography of the cross sections according to the experiment conditions.

The model for describing the microscale flow adopts the Navier-Stokes equation for incompressible flow:

$$\rho\left[\frac{\partial \boldsymbol{v}}{\partial t}+(\boldsymbol{v}\bullet\nabla\boldsymbol{v})\right]=-\nabla p+\mu\nabla^2\boldsymbol{v},$$

where ρ is the fluid density, $\boldsymbol{v}$ the velocity, p the pressure and μ is the dynamic viscosity. The convection and diffusion equation for the concentration of etchant C is

$$\frac{\partial C}{\partial t}+\boldsymbol{v}\bullet\nabla C=D\nabla^2 C,$$

where D is the diffusion coefficient of the etchant in water.

Three-dimensional calculations were carried out by using FLUENT, a commercial software based on finite volume scheme. The simulation conditions were as follows: The species mixing model was adopted; no wall slip was assumed; in the species model, we selected water as the separant with ρ=998.2 kg/m^3, μ=0.001 003 kg/ms, and the etchant as a hypothetical liquid A with the same density and viscosity; the diffusion coefficient of the etchant in water is D=0.005 mm^2/s.

The chemical reaction of the etchant with glass substrate can be expressed by

$$SiO_2+6HF\rightarrow H_2SiF_6+2H_2O.$$

H_2SiF_6 is a complex compound which may adhere to the wall and prevent further reaction. Though we added a certain amount of HNO_3 to weaken this effect, most of the complex compounds still need to be swept out of the micro channels by the flow. Due to lack of appropriate reaction constants, we did not simulate the chemical reaction process. In stead, we used the experimental channel profiles and calculated the flow field and the ethant concentration distribution only due to the convection and molecular diffusion.

4 Results and Discussions

4.1 Cases with constant etchant flowrates

The micrographs of the cross section and the CFD results are shown in Fig. 4 and Fig. 5, where the echant concentration isoplethic curves of 20%, 40%, 60%, 80% are labeled. These results were obtained by different etching time with the time step of 1 h, and they reflect the detailed pattern process of the secondary structures,

The substrate etching rate is determined by the etchant concentration. We assume that the area where the concentration is higher than 80% as the effective etching area, and the area where the concentration is between 20% and 80% as the transitional area. The development of the maximum depth and maximum of the patterned structure versus the etching time is presented in Figs. 6(a) and 6(b). From Fig. 6, one can see that for both the inlet flow rates of 1 mL/h and 3 mL/h, the maximum width and maximum depth grow linearly with the etching time. That is to say, though the topography and concentration distribution changed with the etching process, in different time intervals, the growth rate of maximum width and maximum depth was almost constant. As shown in Fig. 6, for the inlet flow rates of 1 mL/h and 3 mL/h, there is no large difference of the depth etching rates (28 μm/h and 32 μm/h, respectively), but the side etching rate varies dramatically (11 μm/h and 27 μm/h, respectively).

The development of aspect ratios at different flowrate is shown in Fig. 7. Since the glass is isotropy, the etching rate in the depth and the side directions should be equal in a static etching process. However, in the flowing etching process, the molecular diffusion will cause etchant concentration reduction at the interface between etchant and seperant. In fact, when the flow rate is large (3 mL/h), the etching rates at different directions are nearly equal; while for the flow rate of 1 mL/h, the side etching rate becomes obviously smaller than the depth etching rate. This difference can be well explained by the corresponding

different diff t the same
cross section of 1 mL/h
obtained a p ct ratio of
approximatel ndard wet
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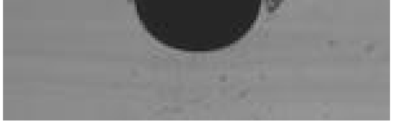
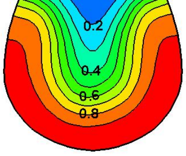


Etching time 4 h

Etching time 5 h

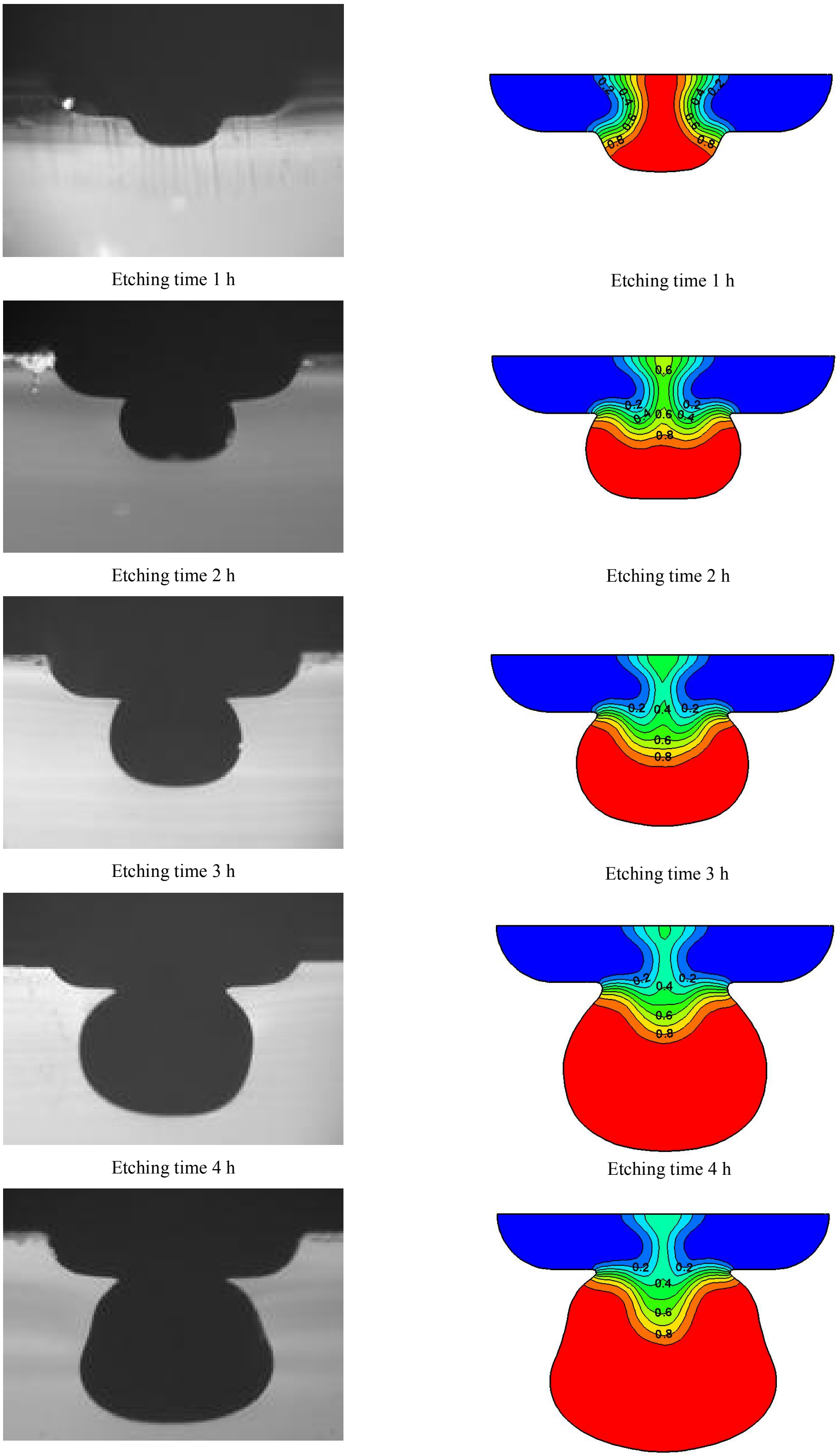
(a) Micrographs

Fig. 4. Profiles of secondary micro structures developed w



Etching time 5 h

(b) CFD results



Etching time 1 h

Etching time 1 h

Etching time 2 h

Etching time 2 h

Etching time 3 h

Etching time 3 h

Etching time 4 h

Etching time 4 h

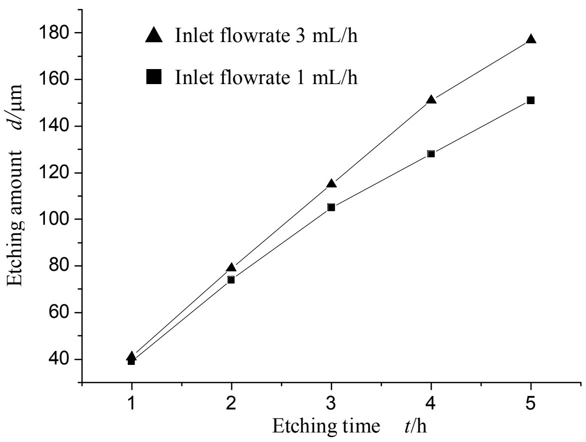
Etching time 5 h

Etching time 5 h

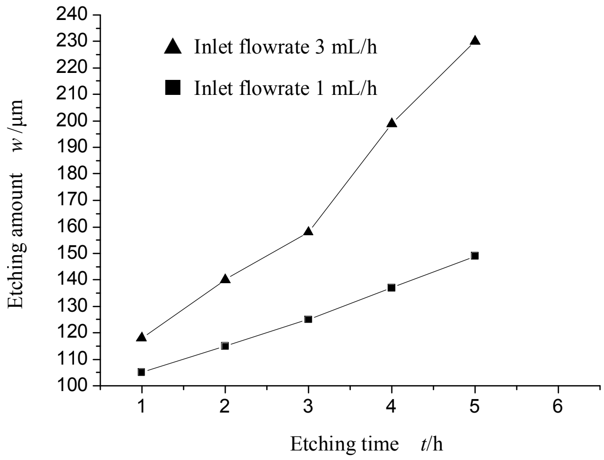
(a) Micrographs

(b) CFD results

Fig. 5. Profiles of secondary micro structures developed with time at the inlet flowrate of 3 mL/h



(a) Max depth of the secondary structures at the inlet flowrates of 1 mL/h and 3 mL/h



(b) Max widthof the secondary structures at the inlet flowrates of 1 mL/h and 3 mL/h

Fig. 6. Max depth and max width vs. etching time

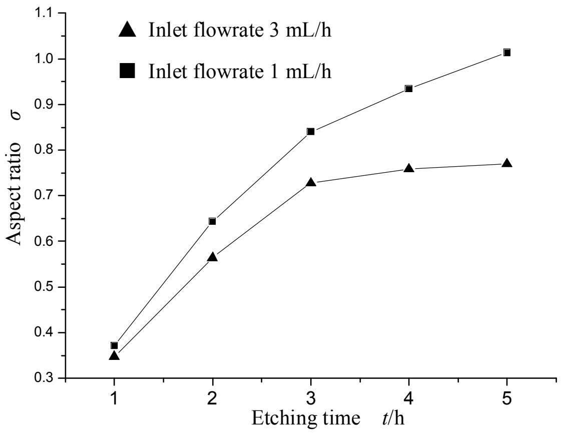
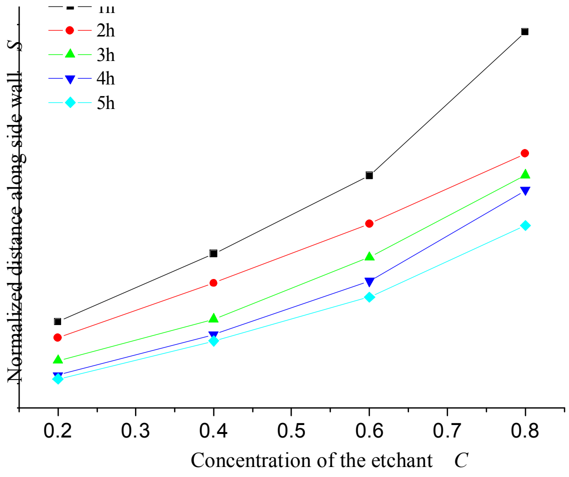
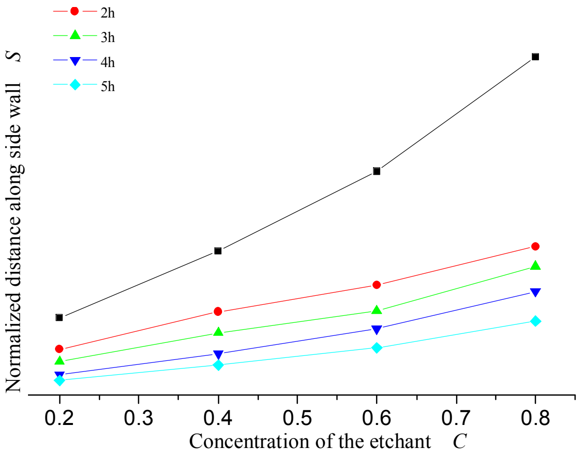


Fig. 7. Aspect ratios vs. etching time at different flow-rates

We did quantitatively estimation of the concentration distribution along the side wall, in which the distance taken by the concentration steps of 0.2, 0.4, 0.6 and 0.8 at the wall was normalized by half length of the side wall; the normalized concentration distributions along the side wall are shown in Fig. 8. From Fig. 8, one can derive that the arc shape of secondary micro structures is due to the concentration variation of etchant; the etchant sinks to the bottom of the micro channel immediately after entering the inlet, thus the etching rate at the bottom is faster; the upper part of secondary structure is mainly in the transitional region with lower concentration and etching rate than that at the bottom. The diffusion distance of the inlet flowrate of 1 mL/h larger than that of 3 mL/h, with most part of the secondary structure is in the transitional region, which leads to a more vertical side wall.



(a) Etchant flowrate 1 mL/h



(b) Etchant flowrate 3 mL/h

Fig. 8. Normalized distance within certain concentration along side wall at different etching time

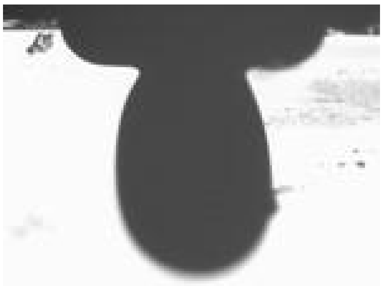
4.2 Cases with changing flowrate

With constant etchant flowrates and long enough etching time, the profile of the etched micro structures tends to be a circle and the aspect ratio is about 1. However, if we change the ratio of the flowrates of etchant and separant and prolong the etching time appropriately, the profiles of the etched structure can be improved considerably. According to the analysis above, in order to weaken the side etching, the etchant flowrate should be reduced gradually in time, thus the stream of etchant should be narrowed, centered in the middle of the secondary channel, and consequently the concentration of etchant near the side wall will be lower resulting lower etching rate there.

Specifically, we kept etchant flowrate 1 mL/h for 3 h and then changed it to 0.5 mL/h for 5 h. The final secondary micro channel with an aspect ratio of about 1.3 was obtained. The topographies of the microchannels patterned by the timely adjusted etchant flowrate are shown in Fig. 9, and the development of the aspect ratio in Fig. 10. CFD simulations of the concentration distributions for the case of timely changed flowrate of etchant are shown in Fig. 11. Because the flowrate of etchant is only half of that of separant, the etchant concentrates at the bottom, and most part of the side wall is in the transitional region.

After 3 h etching under the condition of 1 mL/h

After another 2 h etching under the condition of 0.5 mL/h



After total 8 h etching

Fig. 9.　Micro structures patterned by changing etchant flowrate

5　Conclusions

Summing up the experiment and CFD results, we conclude that the flowrate has three effects on the etching process.

(1) Higher flowrate is beneficial to scouring out the polymer, accordingly increasing the etching rate.

(2) The flowrate determines the concentration distribution of the etchent in the microchannel through molecule diffusion between the streams, and the secondary microchannel is formed into an arc shape.

(3) The restricted flow etching method can obtain micro structures with higher aspect ratios on glass substrate.

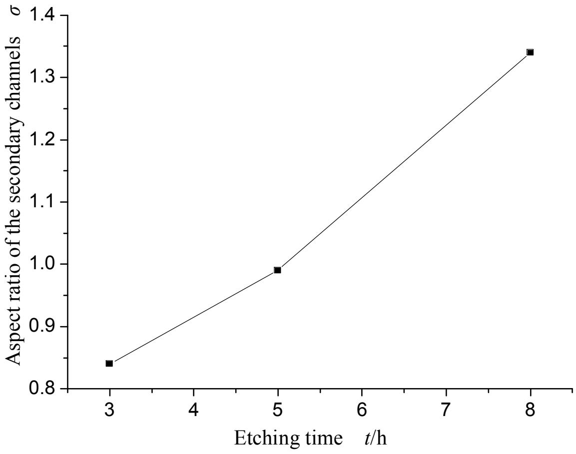
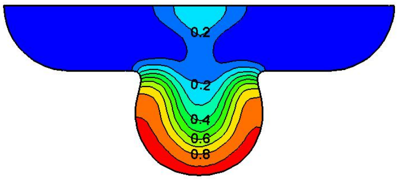
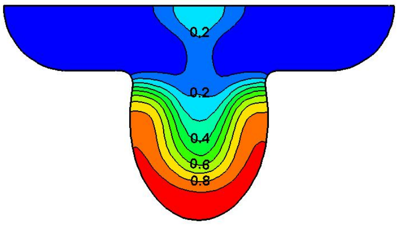


Fig. 10.　Development of aspect ratio vs. etching time under the condition of changing flowrate



Flow pattern when changing the etchant flowrate to 0.5 mL/h after 3 h etching under the condition of 1 mL/h



Flow pattern after 3 hetching under the condition of 1 mL/h and 2 h etching under the condition of 0.5 mL/h

Fig. 11.　CFD results of the flow pattern in the etching process

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Biographical notes

XIE Haibo, born in 1975, is currently an associate professor in The State Key Lab of Fluid Power Transmission and Control, Zhejiang University, China. He received his doctoral degree on mechatronics in Zhejiang University, China, in 2004. His main research interests include microfluidics and fluid power transmission and control.
Tel: +86-571-87953395; E-mail: hbxie@zju.edu.cn

ZHENG Yi, born in 1983, is currently a master candidate in The State Key Lab of Fluid Power Transmission and Control, Zhejiang University, China. His main research interests include microfluidics and fluid power transmission and control.
Tel: +86-571-87953395; E-mail: yizheng@zju.edu.cn

FAN Yurun, born in 1947, is currently a professor in The State Key Lab of Fluid Power Transmission and Control, Zhejiang University, China. His main research interests include microfluidics,computational fluid mechanics and rheology.

FU Xin, born in 1961, is currently a professor and a PhD candidate supervisor in The State Key Lab of Fluid Power Transmission and Control, Zhejiang University, China. His main research interests include mechachonics engineering, fluid power transmission and control, applied hydrodynamics .

YANG Huayong, born in 1961, is currently a professor and a PhD candidate supervisor in The State Key Lab of Fluid Power Transmission and Control, Zhejiang University, China. He received his PhD degree from Bath Universtiy, United Kingdom of Great Britain, in 1988. His main research interests include mechachonics engineering, fluid power transmission and control.