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A novel restricted-flow etching method for glass*

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Abstract: This paper presents a novel micro fabrication method based on the laminar characteristics of micro-scale flows. Therein the separator and etchant are alternatively arranged in micro channels to form multiple laminar streams, and the etchant is located at the site where the reaction is supposed to occur. This new micro fabrication process can be used for the high aspect ratio etching inside a microchannel on glass substrates. Furthermore, the topography of microstructure patterned by this method can be controlled by changing the flow parameters of the separator and etchant. Experiments on the effects of flow parameters on the aspect ratio, side wall profile and etching rate were carried out on a glass substrate. The effect of flow rates on the etching rate and the micro topography was analyzed. In addition, experiments with dynamical changes of the flow rate ratio of the separator and etchant showed that the verticality of the side walls of microstructures can be significantly improved. The restricted flowing etching technique not only abates the isotropic effect in the traditional wet etching but also significantly reduces the dependence on expensive photolithographic equipment.

Key words: Microfluidics, Micro fabrication, Etching, Laminar flow
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INTRODUCTION

Since Manz *et al.*(1992) successfully invented the first microfluidic device, microfluidic technology has been a focus in micro-nano research (Stroock and Whitesides, 2003; Atencia and Beebe, 2005; Dittrich *et al.*, 2006; Weibel and Whitesides, 2006; Whitesides, 2006). The materials that are widely used for micro fabrication include silicon, glass and some organic materials, among which glass has excellent light transmittance and a high strength (Lee *et al.*, 2002; Verpoorte and Rooij, 2003; Geissler and Xia, 2004; Paul *et al.*, 2005; Wouden *et al.*, 2005; Howlader *et al.*, 2006; Fu *et al.*, 2006). Glass is a typical isotropic material and when a micro device is fabricated with the chemical wet etching, the etching rates in all directions are almost equal. Therefore, the microchannels on a glass substrate processed by the photolithography and wet etching method usually have a lower aspect ratio (not higher than 0.4), which limits its application range greatly. Nowadays though new micro fabrication techniques are developing rapidly, like LIGA and soft lithography (Kim *et al.*, 2002; Malek and Saile, 2004; Khademhosseini *et al.*, 2004; Urbanski *et al.*, 2006), the limitation of the wet etching method still has not been overcome. Therefore, practical methods for fabricating microstructures on glass substrates are in urgent need.

In recent years, the studies on flowing etching techniques are at an exploratory stage. For example, Kenis *et al.*(1999; 2000) put forth the flow etching/deposit concept firstly and demonstrated some exploratory experiments of flow pattern or deposit process; but the emphases are to deposit organic fibers that possess biological compatibility and reactive etching at the interface between streams at nanoscale; the depths of the microstructure were only about several hundred nanometers and the shape of etching structure was uncontrollable. Yoon *et al.*(2005) studied the reorientation of the interface between two

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laminar flow liquids with different densities, as they flow through a microchannel under the action of gravity field. Lee *et al.*(2006) established the mathematical model for the hydrodynamic focusing effect inside rectangular microchannels and validated the accuracy by visualization experiments.

In this paper, we present a restricted flow etching method. Because the characteristic dimension of microchannels (usually several to several hundreds of microns) results in low Reynolds numbers (usually smaller than 100), the flow pattern in microchannels is often laminar. If flowing through a microchannel simultaneously, two parallel streams of miscible fluids with equal viscosities will stay side by side and diffuse across their interface. The principle of this method is that when injected into a microchannel, the separator and etchant can keep well separated for the distance considerably less than the characteristic diffusion length $\sqrt{Dt}$, where D is the diffusion coefficient (about 10^{-9} m^2/s); in that situation the etchant will react with the substrate on its own path and the separator can protect other areas of the substrate from being etched. Furthermore, we can fabricate the microstructure with high aspect ratios by changing the flow parameters of the separator and etchant.

Firstly we fabricated a microchannel with three inlets and one outlet via the glass plate by the standard photolithographic procedure and the chemical wet etching process. The etchant that can produce soluble matter by the reaction with the substrate was injected into the middle inlet; the separator that does not react with the substrate was injected into the two other inlets to restrict the effective reaction region. We intended to control the etching width by changing the flow rate ratio of the separator and etchant. After a period of reaction, the secondary microstructure would be patterned inside the original microchannel. We cut the microchannel at A-A section located 5 mm from where the separator and etchant converge to examine the topography of the secondary microstructure. Fig.1 shows the working principle and a resultant etching topographical feature.

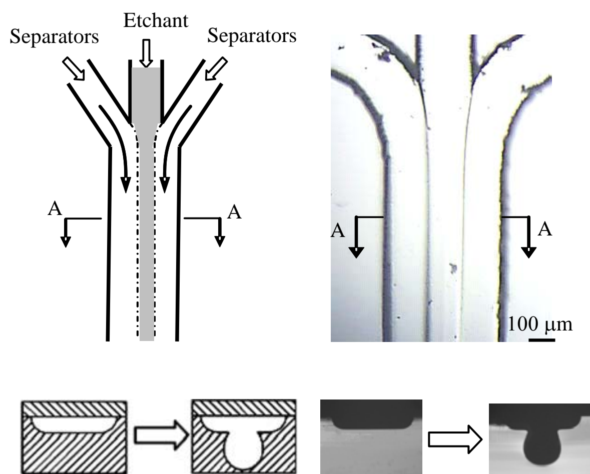


Fig.1 Theory of restricted flowing etching

DESIGN AND FABRICATION

The original microchannel used in this experiment, about 300 μm in width and 50 μm in depth, has three inlets and one outlet. To avoid sharp changing in the flow direction, arc connections at the inlets were adopted. The configuration of the microchannel is shown in Fig.2. To study the topographical features, we have to observe the cross-section of microchannel. Usually the microfluidic glass chips are bonded with the high temperature bonding technology (heat the glass plates up to above 500 °C, then cool them in the furnace naturally) and have a quite high bonding strength, which means the microstructures created by the flow etching method are sealed in the original microchannels and can hardly be observed and measured. Thus we bonded the glass substrate with the polydimethylsiloxane (PDMS) membrane for an impermanent packaging, and the substrate can be separated conveniently after experiments; the glass-PDMS bonding is relatively firm so that it can keep the fluid in the microchannel from seepage with the pressure difference no more than one atmosphere.

The original microchannel was formed on the glass substrates using standard photolithography and wet chemical etching. The fabrication procedure is outlined schematically in Fig.3. A commercially available blank photomask (Nanofilm Inc.) consisting of three layers of materials (1 μm UV-sensitive photoresist (PR), 0.1 μm chromium, and 2.3 mm quartz, respectively) was used to fabricate the microfluidic chips. The fabrication process is described as follows:

(1) The graphics were first made using a commercial software Adobe Illustrator (Adobe Inc.), and then the vectorgraph photofilm generated from a

high-resolution laser plotter (10000 dot/in) was chosen as the first photomask to transfer microchannel patterns onto the PR layer using standard photolithography process.

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

(3) Then the residual PR was stripped and the patterned Cr layer was used as an etch mask for glass etching.

(4) The special echant (the mole concentration ratio of $HF:HNO_3:NH_4Cl$ is 0.75:0.5:0.5) was chosen for glass etching considering that the fabricated microstructure will have a smoother appearance. The etching rate was about 1.7 μm/min at a constant temperature of 50 °C in water area.

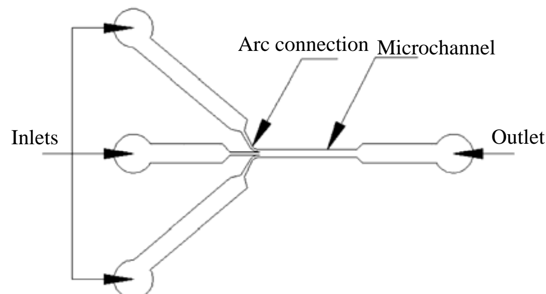


Fig.2 Pattern of the original microchannel

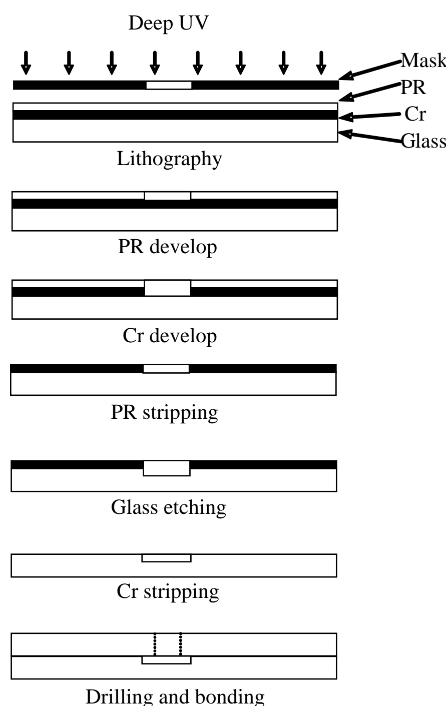


Fig.3 Fabrication process of the original microchannel

(5) Before the preparation of the PDMS membrane, the silicon wafer was firstly silanized by means of getting placed in a desiccator under vacuum for 15 min along with a vial containing a few drops of silanizing agent, such as dimethyloctadecylchlorosilane.

(6) A 10:1 (v/v) mixture of PDMS oligomer and crosslinking agent (Sylgard 184), which had been degassed under vacuum, was poured onto the silicon wafer. After at least 1 h of curing at 80 °C, the PDMS membrane was removed from silicon wafer.

(7) After drilling holes at certain places, the PDMS membrane was rinsed with ethanol and treated with ultraviolet for 25 min (light intensity is about 10 mW/cm^2). Then by placing the glass and PDMS membrane into conformal contact without additional pressure, the seal was achieved within 24 h.

EXPERIMENTAL

Etchant and separator were introduced into the microchannel from syringe pumps (minimum volume flow rate is 0.1 ml/h, precision ±1%), as illustrated in Fig.4. The etchant used here is the same as the etchant used for chemical wet etching, and the separator is deionized water. After finishing the etching process, the PDMS membrane can be easily torn down and the microstructures can be measured and analyzed expediently.

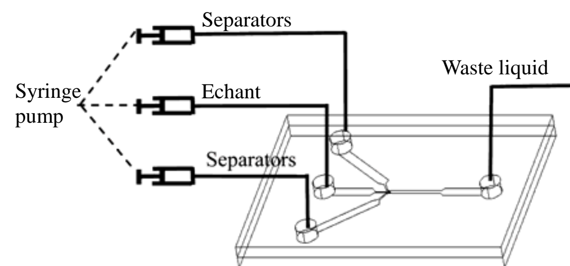


Fig.4 Schematic drawing of the experimental setup

We cut the microchannel at the section A-A in Fig.1 to get the whole profile of the microstructure. Scion image software (Scion, Frederick, MD) was deployed to measure the topographical details of the structure by image elements.

To reveal the relationship between the flow parameters and the topography of the microstructure, we carried out the experiments under the following conditions: the syringe pumps to ensure that equal flow

rates of the three inlets were adjusted and then at 0.2, 0.5, 1, 2, and 3 ml/h, respectively; each etching case lasted for 5 h. Under these conditions the *Re* number in the microchannels was 0.5~15, which ensured the laminar flow condition, so the stream of etchant was held at the middle of the microchannel, and the width of the etchant stream (about 100 μm) is about one third the width of the original microchannel. The schematic drawing of the A-A cross-section of the microchannel after etching is shown in Fig.5.

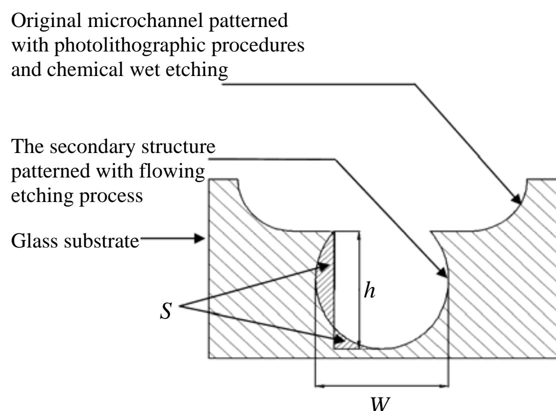


Fig.5 Schematic drawing of the A-A cross-section of the microchannel

To quantitatively describe the characteristics of the microstructures, the distance from the bottom of the original microchannel to the bottom of the secondary structure is defined as the maximum etching depth h (μm); the largest distance between the side walls of the secondary structure is defined as the maximum etching width W (μm); the ratio of h to W is the aspect ratio denoted by δ. The ideal secondary structures should possess vertical side walls, while the secondary structure patterned by the flow etching was an outstretched arc. We define a parameter σ (μm) to depict the average departure from the ideal vertical side wall by the ratio of the dense shadowed part areas S to the maximum etching depth h. When σ=0, the side wall is completely vertical, and σ will increase with the growth of the departure-from-vertical of the actual side walls.

RESULTS AND ANALYSIS

Fig.6 depicts the profiles of the structures under the conditions of 5 h' etching time and the inlet flow rates from 0.2 to 3 ml/h. From the micrographs of the cross-sections in Fig.6, we can conclude that the flow rate in the channels affects the topographical features greatly. The side wall etching rate increased as the inlet flow rate augmented; etching rates in different directions resulted in varied aspect ratios. Fig.7a is the curves of maximum depth and width versus the inlet flow rate after the same etching time (5 h). Fig.7b is the curve of the aspect ratio of the secondary microstructures. Fig.7c is the relationship between the departure-from-vertical σ and the inlet flow rates. These results reveal that the etching rates at both the depth and side directions increased with the flow rate. Higher flow rate means higher velocity of the liquid at the etching surfaces; the etchant, of which the concentration has been reduced by the reaction with the glass substrate, can be replaced more quickly by the fresh etchant; and a higher velocity is also beneficial for scouring away the insoluble deposit produced by the chemical reaction. Both of the effects increase the etching rate. It should be noticed in Fig.7b that the secondary microstructures have the largest aspect ratio at the flow rate of ca. 1 ml/h.

According to Fig.7c, we can conclude that the departure-from-vertical at lower flow rates is smaller than that at higher flow rates, except for the flow rate of 0.2 ml/h where the etching speed is so small that

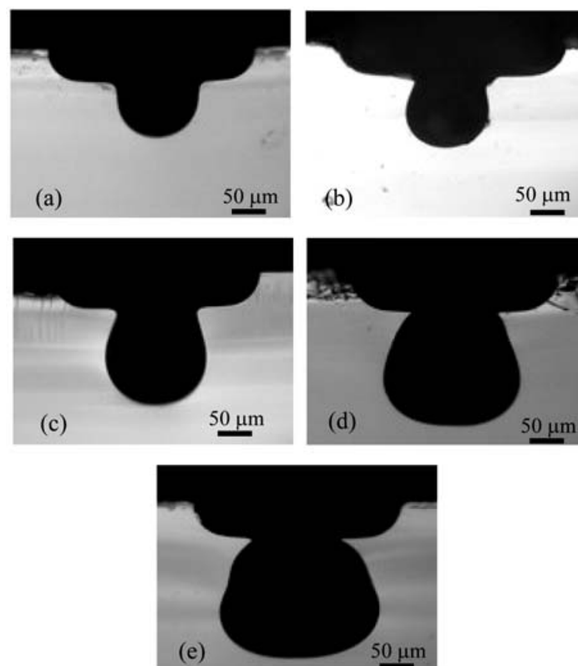


Fig.6 Profiles of secondary structures at different inlet flow rates. (a) 0.2 ml/h; (b) 0.5 ml/h; (c) 1 ml/h; (d) 2 ml/h; (e) 3 ml/h

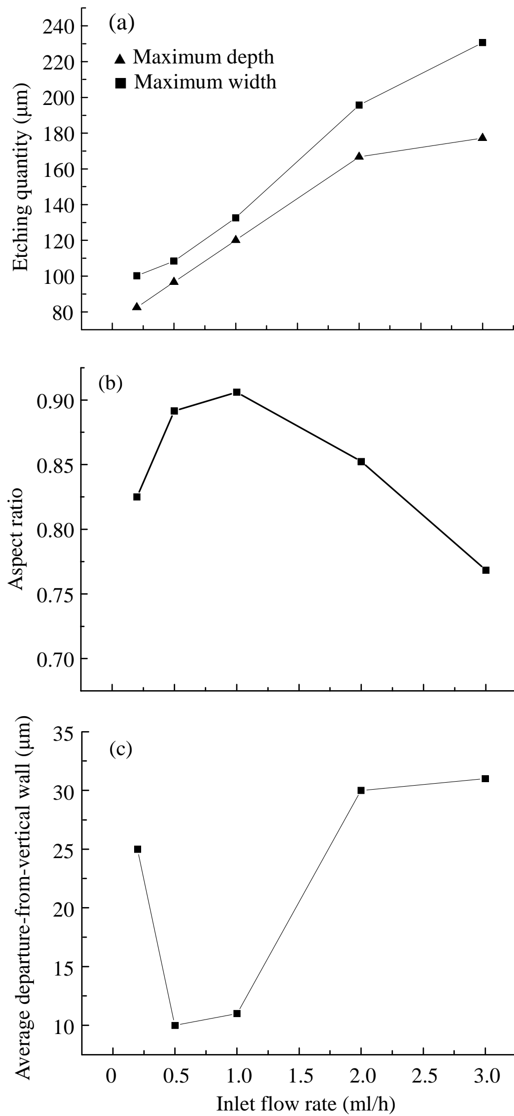


Fig.7 (a) Maximum depth and width; (b) Aspect ratio and (c) Average departure-from-vertical wall of the secondary structures vs inlet flow rates

the secondary microstructure had not fully developed. The topography of the side walls is the closest to the ideal vertical form with the inlet flow rate of 1 ml/h.

For further analysis of the etching process, two typical cases were selected: the inlet flow rate of 1 ml/h which is the closest to optimum condition and the inlet flow rate of 3 ml/h which has the largest etching rate. We kept the inlet flow rates 1 and 3 ml/h constant, and examined the profile of the cross-section every 1 h during the 5 h' etching process. The micrographs of the cross-section are shown in Fig.8, reflecting the detailed developing processes of the structures in Fig.6.

The developments of the maximum depth and width versus the etching time are presented in Figs.9a and 9b. Fig.9 indicates that the etching amount (maximum width and maximum depth) varied approximately linearly with the etching time. That is to say, though the topography was changing during the etching process and the concentration distribution

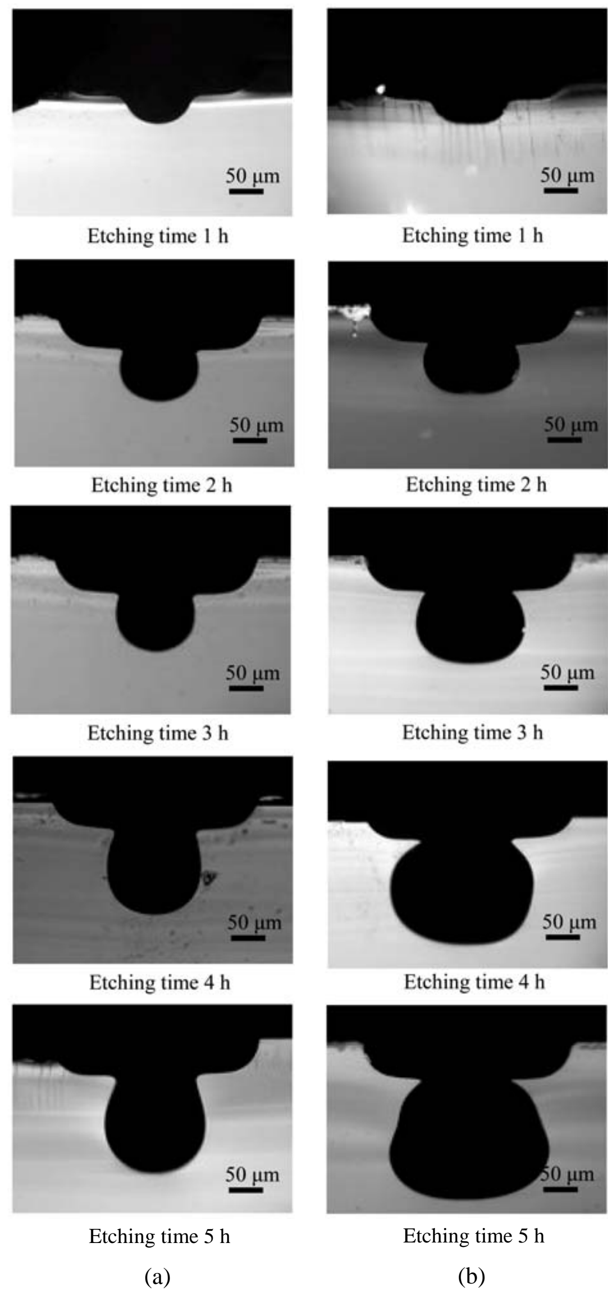


Fig.8 Development process of the secondary microstructures. (a) Inlet flow rate of 1 ml/h; (b) Inlet flow rate of 3 ml/h

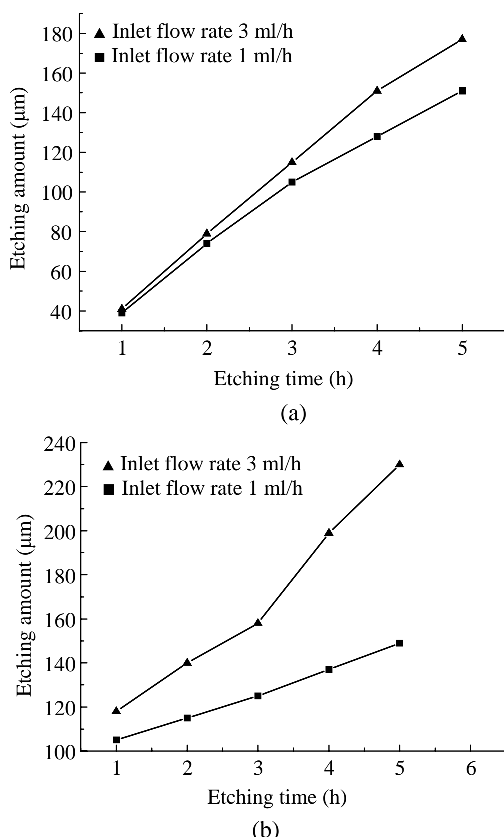
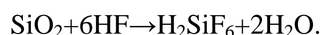


Fig.9 (a) Maximum depth and (b) maximum width vs etching time at the inlet flow rates of 1 and 3 ml/h, respectively

was also altering, the rates of etching amount were almost constant in different time intervals. As shown in Fig.9, for the inlet flow rates of 1 and 3 ml/h, there was little difference in the depth etching rates (approximately 28 and 32 μm/h); but the side etching rates varied considerably (approximately 11 versus 27 μm/h). This may help us to understand the effects of flow rate on the aspect ratio and departure-from-vertical.

Since glass is isotropic, the etching rates in the depth and side directions should be equal. In fact when the flow rate in the microchannels was 3 ml/h, the etching rates in various directions turned out to be nearly equal. However, when the flow rate was in a decline, the side etching rate considerably reduced. Since the flow in the microchannel was laminar, the mixing between the etchant and separator (deionized water) was restricted to molecular diffusion in the direction normal to the interface. Obviously, a lower flow rate induces a larger diffusion time at a fixed cross-section; thus the etchant concentration thereat is lower than that with higher flow rate, and the reduced etchant concentration leads to a lower etching rate on the side walls. We can estimate the characteristic diffusion length $\sqrt{Dt}$ with the flow rate 0.2 ml/h at the cross-section checked to be 10~30 μm. When compared with the width of the etchant stream of about 100 μm, the etchant concentration in the central portion of the etchant flow clearly underwent little effect by the molecular diffusion, and so did the etching rate in the depth direction. These differences of topography are mainly caused by the resultant of the chemical reaction; the etchant reacts with glass substrate to form H_2SiF_6:



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

H_2SiF_6 is a kind of complex compound adhering to the side wall, which can block the reaction process. Though we have added a certain amount of HNO_3 to weaken this effect, most complex compounds will still rely on the fluid pressure to sweep out the microchannels. Therefore, a smaller flow rate means a lower etching rate on side walls and larger aspect ratios.

In the experiments described above, the etchant and separator flow rates were kept constant during the etching process. When the inlet flow rate was 1 ml/h, the etching structure showed the preferable topography with the highest aspect ratio (about 1). It is much higher than the limit ratio of the traditional chemical wet etching method.

Suppose that the etchant flow rate is kept constant and the etching time is long enough, the profile of the secondary microstructures tend to be a circle, the departure-from-vertical is large and the aspect ratio remains at ca. 1. However, it was found that if we changed the ratio of flow rates of etchant and separators and prolonged the etching time appropriately, the profiles of the secondary structures could be improved greatly. Specifically, to weaken the effect of side etching, the etchant flow rate should be reduced during the etching process, because under constant separator flow rates, reducing the etchant flow rate means to narrow the etchant stream, focus it at the middle of the etched groove and reduce the etchant concentration near the side wall. In this way, we can not only reduce the side etching rate but also keep the depth etching rate. In this study we designed 3 groups of experiments to keep the separator flow rate con-

stant and timely change the etchant flow rate during the etching process. The experiment conditions are listed as follows:

(1) Group 1: Keep the etchant flow rate at 1 ml/h for 3 h, change to 0.7 ml/h for 1 h, and then to 0.5 ml/h for 1 h.

(2) Group 2: Keep the etchant flow rate at 1 ml/h for 3 h, then change to 0.5 ml/h for 2 h.

(3) Group 3: Keep the etchant flow rate at 1 ml/h for 3 h, then change to 0.5 ml/h for 5 h.

The topographies of the microchannels patterned from the three groups of experiments are shown in Fig.10, and the parameters of the secondary structures are listed in Table 1. From Table 1, properly reducing the etchant flow rate during the etching process is very useful to etch microstructures with higher aspect ratios and more vertical side walls.

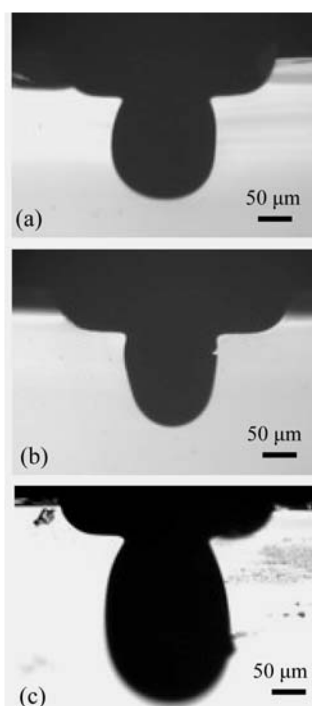


Fig.10 Influence of etchant flow rate. (a) Group 1; (b) Group 2; (c) Group 3

Table 1 Parameters of the secondary structures patterned with the timely changing etchant flow rate method

Group No.	h (μm)	w (μm)	S (μm^2)	δ	σ (μm)
1	140	141	1320	0.99	8
2	124	121	1364	1.03	11
3	240	175	4964	1.34	15

Note: h is the maximum depth, w is the maximum width, S is the shadowed part areas, δ is the aspect ratio, and σ is the departure-from-vertical

CONCLUSION

We present a novel micro fabrication method based on restricted laminar flow and quantitative studies on the topography of the secondary micro-structures. The restricted flow etching method, using two separator streams to restrict the etchant reaction area, aims to obtain microstructures with high aspect ratios. The experimental results revealed that the topographies of microstructures patterned by the restricted flow etching are mainly determined by the flow rates of the separator and etchant. At high etchant flow rates the etching rates in the depth and side directions were almost equal, and after a long enough etching time, the side wall profile of the microstructure tended to be a circle. At low etchant flow rates, the etching rate in the depth direction—due to protection effect of the chemical reaction compound—was higher than that in the side direction, resulting in structures with high aspect ratios and nearly vertical side walls. The experiments also showed that timely reducing the etchant flow rate during the etching process can effectively protect the side walls and increase the aspect ratios of the secondary structure. The restricted flow etching method proposed here overcomes the deficiency of the standard chemical wet etching method and can pattern microstructures with high aspect ratios on glass substrates.

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