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Fabrication of Microcylinder on Silicon

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In this paper, we describe a new fabrication method for a round microcylinder on a silicon substrate using polyvinyl alcohol (PVA) polymer and micro-electro-mechanical system (MEMS) technology. Silicon substrate is selectively etched using a LPCVD-Si_3N_4 mask and a HNA (hydrofluoric, nitric, acetic) acid mixture as an isotropic etchant, to fabricate the lower half of the microcylinder that has a hemicyclic cross section. PVA polymer is then selectively filled into the etched hemicyclic channel and covered by a gold layer. A following thermal treatment makes the polymer with the gold layer swell and decomposes the polymer filled in the channel when it reaches pyrolysis temperature, resulting in a cylinder-like channel. A polymer can be easily removed by heat treatment at the pyrolysis temperature so that it is used as a sacrificial layer. The fabricated microcylinder has a width of 80 mm and a length range of 100–500 mm. In principle, it is possible to control the diameter and shape of the microcylinder on demand by modifying processing conditions, such as hydrofluoric, nitric and acetic (HNA) and etching time, PVA coating, and thermal treatment. The microcylinder fabricated by this method may find various applications in the micro total chemical analysis system (μTAS) or Lab-on-a-Chip.

1. Introduction

Research on MEMS-based microfluidic devices about two decades ago was one of the first attempts to exploit the microelectromechanical systems (MEMS) technology for realizing miniaturized chemical analysis and biomedical instrumentation systems. Since that time, MEMS-based microfluidic devices underwent major developments in MEMS field, in which other functions have recently explored beyond what the name claims. Current researches on MEMS aim to produce a wide range of microfunctional devices, and use innovative materials and fabrication techniques combining with traditional semiconductor processes. The miniaturized fluidic devices not only reduce the cost of expensive agents and analyses, but also minimize the use of contaminated materials. Microfluidics

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therefore has become commercially available in biochips for genomics and proteomics.[1–3]

Microchannel is the basic component of microfluidic devices because it is essential for controlling fluid flowing through integrated micropumps, reservoirs, valves and mixers. Since a number of components should be assembled with each other into a complex microsystem, a channel is required to be electrically isolated, physically stable, and preferably optically transparent. Moreover, a simple fabrication is more desirable.[4,5]

In this paper, we propose a new method for fabricating a microcylinder on a silicon substrate using polymer and MEMS technologies. A hemicyclic-shaped channel is formed on a silicon substrate by isotropic etching using hydrofluoric, nitric and acetic (HNA) acid mixture and the microcylinder is completed by following thermal treatment of Au-deposited polyvinyl alcohol (PVA) polymer.[5,6] PVA is used as a sacrificial layer because it is decomposed at a specific temperature and can be easily removed by heat treatment.

2. HNA Etching

The mixture of hydrofluoric acid and nitric acid is a well-known isotropic etchant of silicon, and acetic acid is added to produce a HNA solution. Nitric acid oxidizes silicon, while hydrofluoric acid dissolves oxide; deionized water or acetic acid works as a buffer.

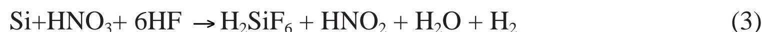
The isotropic etching of silicon in an acid solution can be achieved by hole injection into the silicon valence band by an electric field, photons and oxidants. Nitric acid is used as an oxidant in a HNA solution. The chemical formula is shown below. Holes are made by autocatalysis as shown in eq. (1). HNO_2 reacts again with HNO_3 to produce more holes.

$$HNO_3 + H_2O + HNO_2 \rightarrow 2HNO_2 + 2OH^- + 2H^+ \quad (1)$$

Equation (2) shows the process in which OH^- is absorbed into oxidized silicon species to form SiO_2 after inserting holes and hydrogen is produced.

$$Si^{4+} + 4OH^- \rightarrow SiO_2 + H_2 \quad (2)$$

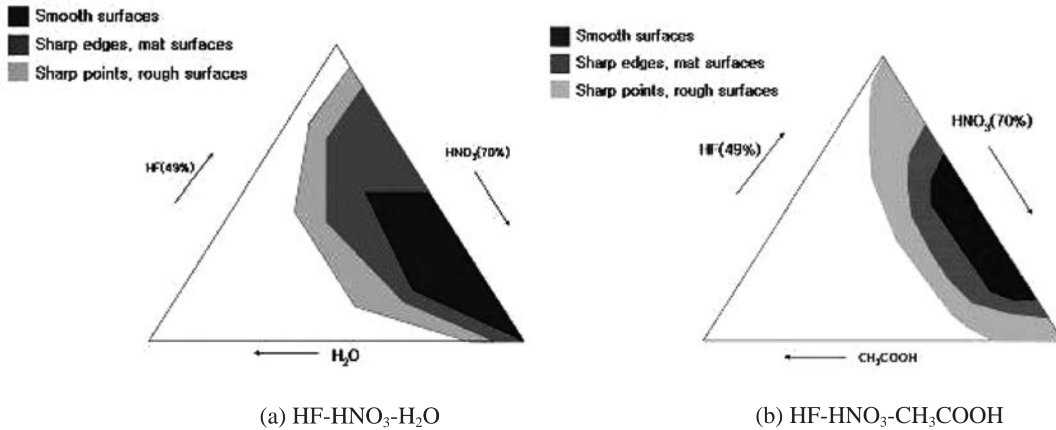
Hydrofluoric acid generates H_2SiF_6, which can be dissolved in water, and it dissolves SiO_2. Equation (3) indicates the whole process of HNA etching of silicon.



$$Si + HNO_3 + 6HF \rightarrow H_2SiF_6 + HNO_2 + H_2O + H_2 \quad (3)$$

The etched-surface morphology greatly depends upon the mixing ratio of the solution. The etching solution, which is prepared to have a maximum etch rate, produces a smooth surface with round corner, while the solution having a low etch rate produces a rough surface. Figure 1 shows the concentration dependence of surface roughness with respect to the HNA acid mixture.

Isotropic etching of silicon is a diffusion-limited process, i.e., the etch rate and shape of the structures are determined by the flow of reactants to the surface rather than the etch rate of different crystal planes. Therefore, solution agitation during HNA etching in principle may have considerable influence upon etching performance. It helps the bubbles to move



(a) HF-HNO_3-H_2O (b) HF-HNO_3-CH_3COOH

Fig. 1. Topology of etched silicon surfaces.

easily outward resulting in an enhanced etch rate and a more uniform hemicyclic structure. The cross-sectional etched shape without stirring may give an oval hemicycle. Figure 2 shows a conceptual image of the influence of stirring upon the etched shape.

3. Fabrication

Figure 3 shows the fabrication sequence of the microcylinder. For a masking layer during HNA etching, a 1500 Å Si_3N_4 is deposited on a p-type (100) silicon substrate by low-pressure chemical vapor depositions (LPCVD) and defined by reactive ion etching (RIE). Silicon is then isotropically etched using a HNA mixture (hydrofluoric acid:nitric acid: acetic acid =1:12:6) to form the bottom hemicyclic part of the channel. With the HNA mixture, silicon is etched for 40 min to achieve a bottom hemicyclic channel with a radius of 40 μm. After silicon etching, Si_3N_4 is removed from the HF solution. Silicon is then thermally oxidized at 1100°C for 5 h using wet-type oxidation. AZ9260 photoresist with a second mask patterns the oxide layer that covers the bottom part of the hemicyclic channel and PVA is applied to fill the bottom channel. Au/NiCr is deposited on top of the whole substrate and patterned for the top part of the channel. Au is chosen for the top cover material of a cylinder-type channel owing to its soft nature that is suitable for the expansion of PVA during the following heat treatment. To undergo pyrolysis, PVA is thermally treated up to 600°C with a ramp rate of 20°C /min in nitrogen environment.

4. Results and Discussion

4.1 *Characteristics of HNA etching*

To achieve a bottom hemicycle for the cylinder-type channel, isotropic etching of silicon rather than anisotropic etching is preferable. The most well known isotropic etchant

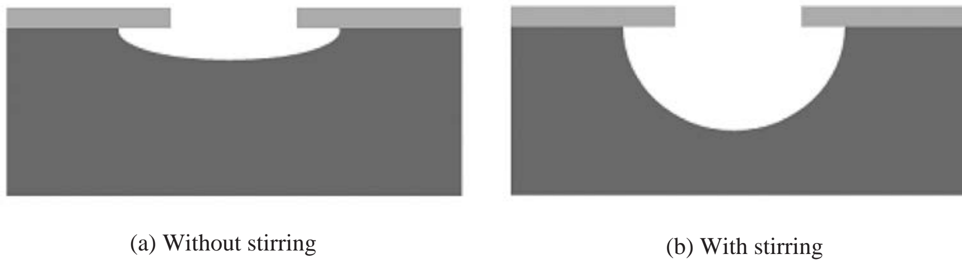


Fig. 2. Cross section of HNA isotropic etching on silicon.

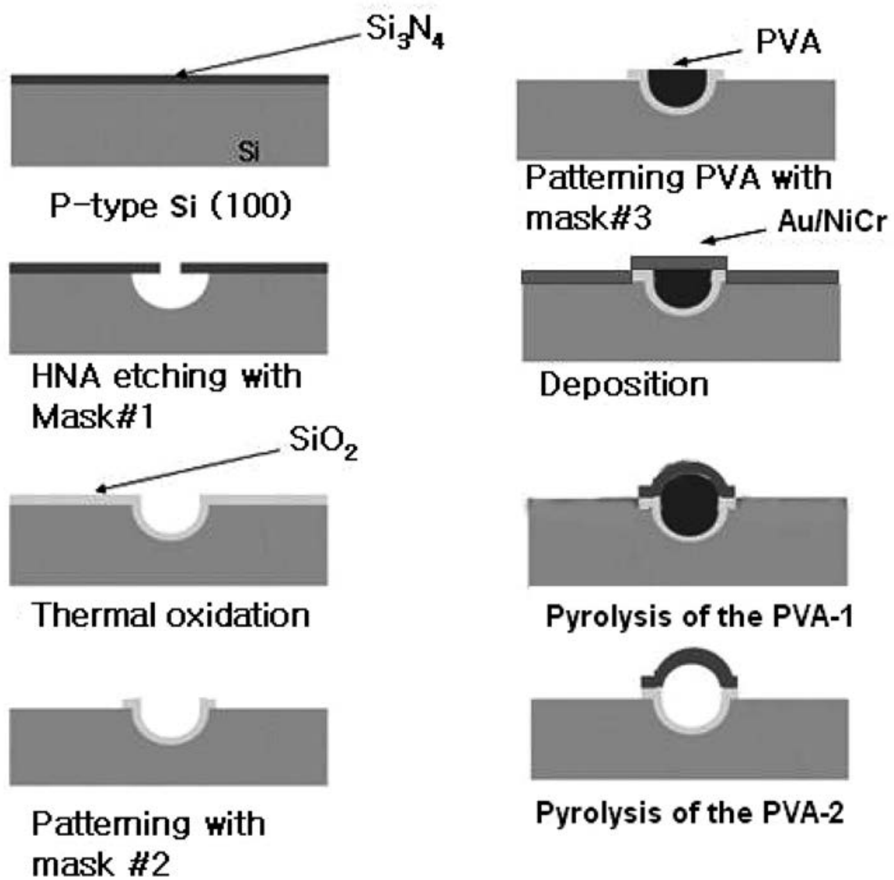


Fig. 3. Fabrication of round microcylinder.

is a mixture of HNO_3 and HF. The former component is an oxidizing agent and the latter dissolves oxide. When acetic acid (CH_3COOH) is added as a dilutent to this mixture, it is called HNA. Because the etch rate of a HNA solution depends on the composition of the mixture, an appropriate mixture ratio of the HNA etchant was determined experimentally as $HF:HNO_3:CH_3COOH$ = 1:12:6. Rounding and undercutting can be controlled to some degree by solution agitation. Figure 4 shows the variation in total etched width as a function of time for an open width of 40 μm. Figure 5 illustrates the etched depth for the same open width.(7–9) As shown in Figs. 4 and 5, the total etched depth is smaller than the etched width for the same etching window resulting in an oval hemicycle. The effect of the agitation was also studied and shown in Fig. 6. A faster spin rate of a stirring bar resulted in a more uniform hemicyclic structure as expected, but the formation of structure stopped with a rough etched surface.

4.2 *Characteristics of PVA*

Polyvinyl alcohol (PVA) is chosen as the sacrificial polymer material to form the cylinder-type channel. PVA is inexpensive, water soluble and has a negative photoresist by adding a sensitizer so that it could simply be patterned by standard photolithography. A PVA polymer in the form of white-colored powder has specific gravities in the range of 0.3–0.7 g/cm^3 and shows thermal stability as well as thermoplasticity in the temperature range of 100–140°C. In general, a PVA polymer does not change its appearance in a short period with heating. Its structure begins to change at around 150°C and dissolves at around 300°C. Moreover, it melts in warm water (> 75°C) and expands, but does not melt in cool water.

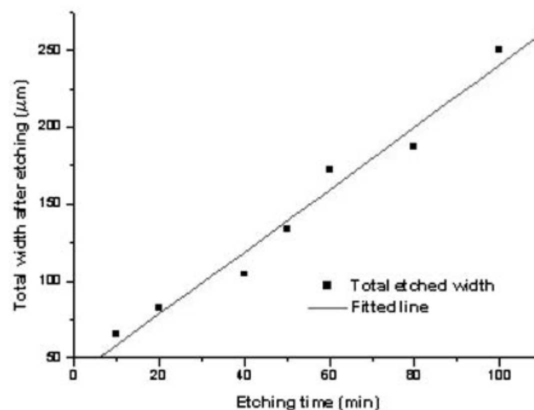


Fig. 4. HNA etching width as function of etching time.

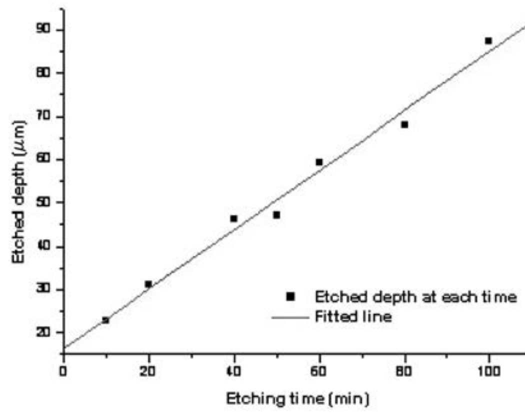
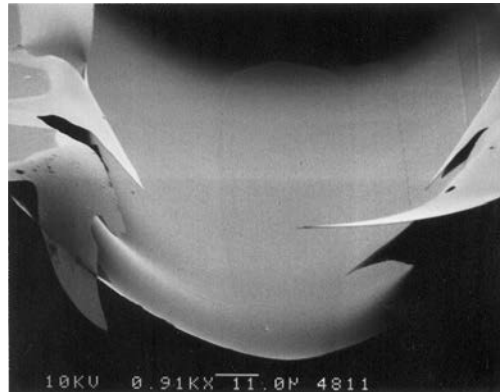
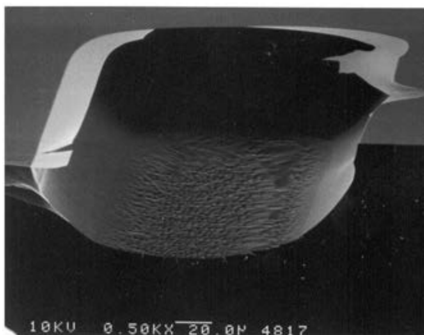
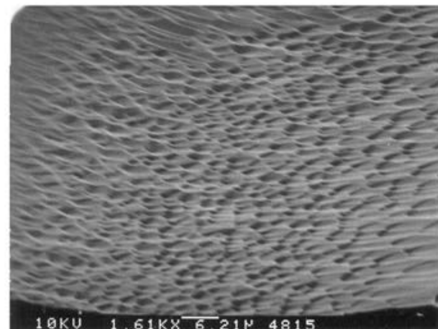


Fig. 5. HNA etching depth as function of etching time.



(a) Stirring at 350 rpm





(b) Stirring at 500 rpm

Fig. 6. Etched surface with agitation.

By adding ammonium bichromate ($(NH_4)_2Cr_2O_7$), PVA starts to have a negative-PR-like feature. The final PVA solution consists of a solvent, a polymer and a sensitizer. The added ammonium bichromate functioning as a sensitizer transforms the PVA into a macromolecular material that is not soluble in water when it is exposed to either ultraviolet rays or heat. The PVA, which is soluble in water before UV or heat exposure, does not melt at low temperatures but dissolves at 80°C by stirring. At this temperature, a mixture of ammonium bichromate and 5 wt% PVA solution is then prepared with a ratio of 1:40. Because the PVA solution mixed with ammonium bichromate is sensitive to heat, the soft baking step is skipped during its spin-coating process. To examine an adequate exposure time of the prepared 1-μm-thick PVA film, the dependence of the patterned shapes on exposure time has been investigated and the results are shown in Fig. 7. With an exposure time of 100 s, the developed PVA patterns were clearest.

Polymers can be easily removed by heat treatment at pyrolysis temperatures so that they are used as a sacrificial layer. Thermal gravity analysis (TGA) for measuring the pyrolysis temperature of PVA was conducted at a ramp rate of 20°C / min and the results are shown in Fig. 8. With this temperature ramp rate, a residue of 9 wt% PVA was observed at 520°C and only about 3 wt% PVA remained at 1,000°C.[10–12]

4.3 *Microcylinder structure*

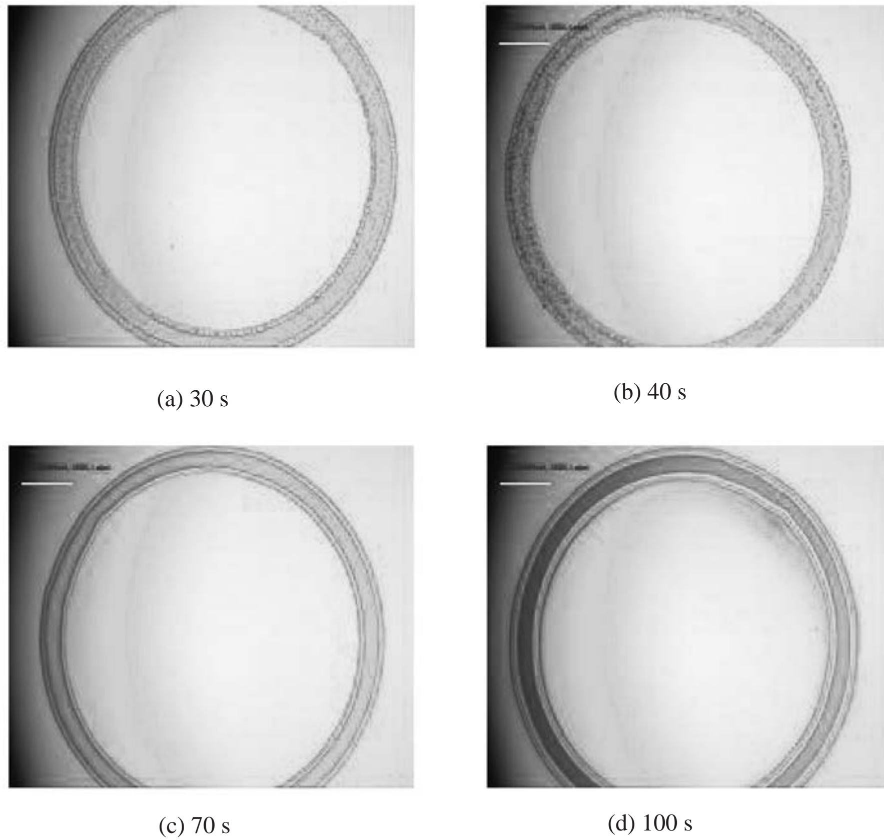
Figure 9 shows scanning electron microscope (SEM) images of the hemicyclic bottom part of the microcylinder etched by the HNA mixture for different etching times. The PVA was spin-coated on the substrate surface, which has an isotropically etched hemicyclic channel, to fill the channel and was patterned. A Au/NiCr layer was then deposited and patterned for the top cover of the microcylinder. Au is a soft metal, so that it is a suitable material for forming a round channel by PVA expansion during heat treatment. For PVA pyrolysis, the prepared sample was thermally treated in nitrogen atmosphere.

A few types of microcylinder and a representative cross-sectional view after PVA thermal decomposition are shown in Fig. 10. As shown in the figure, a perfect round cross section could not be achieved. This is because the shape of hemicyclic space on the substrate formed by HNA etching was not perfectly isotropic and the amount of PVA filled inside the hemicyclic space could not be controlled properly. If the Au top layer is replaced by a soft material, it would also result in a better round shape. By optimizing all these parameters, a perfect round microcylinder could be produced.

5. Conclusions

A round microcylinder has been realized on a silicon substrate by isotropic HNA etching following PVA thermal treatment. The width and length range of the fabricated microcylinder are 80 μm and 100–500 μm, respectively. It is possible to control the diameter and shape of the cylinder on demand by modifying the processing conditions, such as HNA etching time, PVA coating, and thermal treatment.

From the results of this study, it is expected that the proposed fabrication method can be applied to microfluidic systems for varous bio-MEMS applications and chemical analyses.



(a) 30 s (b) 40 s

(c) 70 s (d) 100 s

Fig. 7. PVA patterns depending on exposure time.

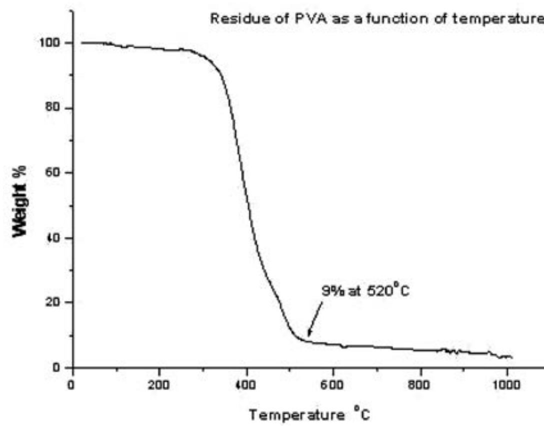
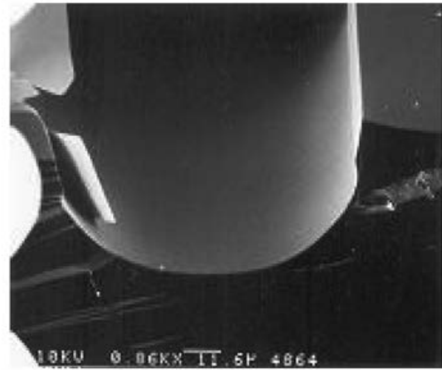
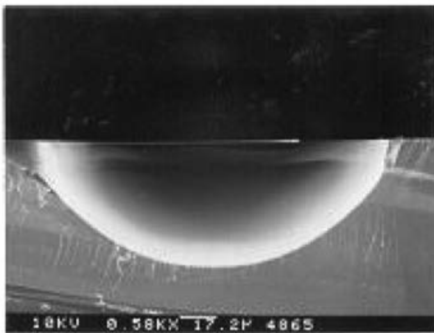


Fig. 8. Thermal gravity analysis at 20°C /min.

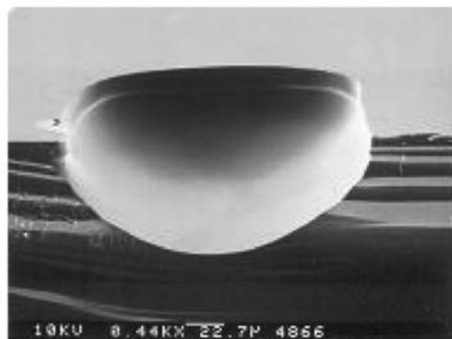
(a) 20 min



(b) 40 min

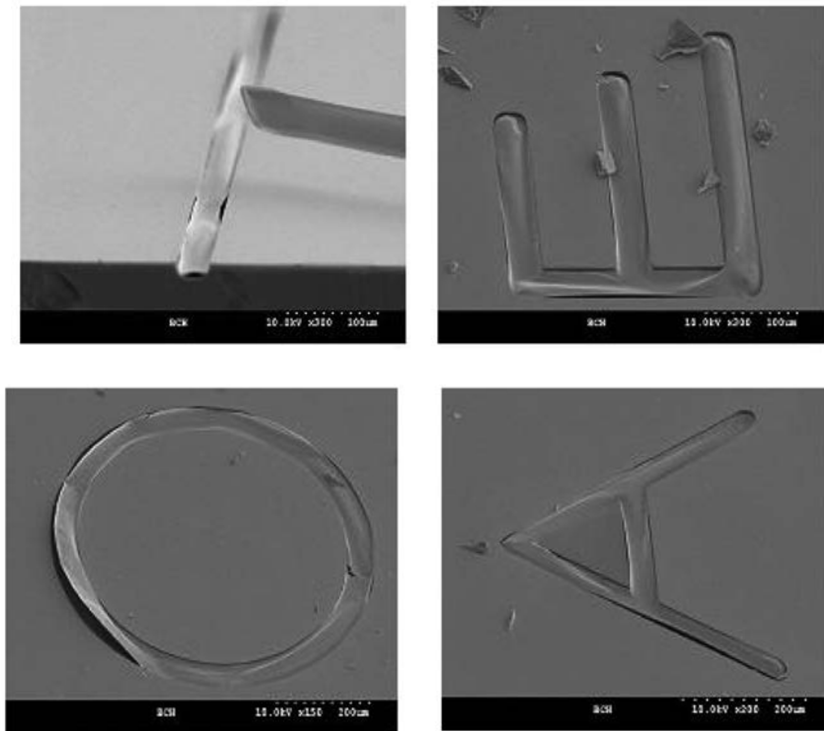


(c) 60 min

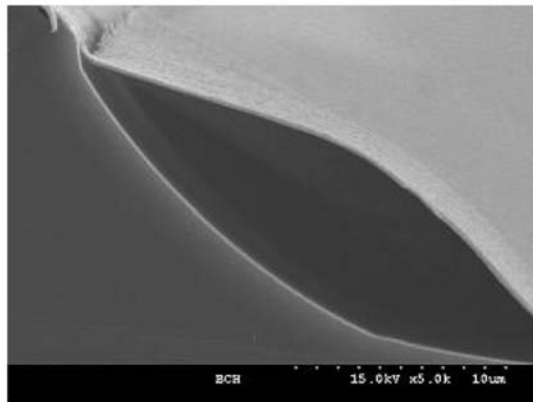


(d) 80 min

Fig. 9. Cross-sectional view after HNA etching (open window, 40 mm).



(a) Various types of channel



(b) Cross-sectional view

Fig. 10. SEM image of microcylinder after thermal decomposition of PVA.

Acknowledgement

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