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Fabrication of high-transmission microporous membranes by proton beam writing-based molding technique

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ABSTRACT

Porous membranes are widely used as filters in a broad range of micro and nanofluidic applications, e.g. organelle sorters, permeable cell growth substrates, and plasma filtration. Conventional silicon fabrication approaches are not suitable for microporous membranes due to the low mechanical stability of thin film substrates. Other techniques like ion track etching are limited to the production of randomly distributed and randomly orientated pores with non-uniform pore sizes.

In this project, we developed a procedure for fabricating high-transmission microporous membranes by proton beam writing (PBW) with a combination of spin-casting and soft lithography. In this approach, focused 2 MeV protons were used to lithographically write patterns consisting of hexagonal arrays of high-density pillars of few μm size in a SU-8 layer coated on a silicon wafer. After development, the pillars were conformably coated with a thin film of poly-para-xylylene (Parylene)-C release agent and spin-coated with polydimethylsiloxane (PDMS). To facilitate demolding, a special technique based on the use of a laser-cut sealing tape ring was developed. This method facilitated the successful delamination of 20-μm thick PDMS membrane with high-density micropores from the mold without rupture or damage.

1. Introduction

The use of self-supporting porous membranes as filters for the separation and cultivation of biological species, blood filtration, and control of drug delivery systems has achieved great success [1–3]. The flow of liquid phase through a pore-channel is governed through the Navier-Stokes equation by the shape, size, and cross-section of the pore. In the case of a porous membrane used as a filter to block the transport of solid or soft-phase particles dispersed in the fluid medium, at least one cross-sectional dimension of the pore must be smaller than the minimum cross-sectional size of the particles. It follows that a membrane with a regular spatially dense array of slot-shaped pores will present a reduced hydrodynamic flow resistance for the same blocking capacity as circular pores of the same size. This requires that the size, shape, spatial density and regularity of the pores are precisely defined during the fabrication process. Conventional fabrication techniques for porous membranes are mostly based on semiconductor technology and, therefore, are restricted by the low mechanical stability of the thin film substrates [4]. Ion track etching, which is widely used for fabricating commercial porous membranes in polycarbonate and polyethylene terephthalate, is limited to the production of randomly distributed and randomly orientated round pores, some of which overlap and do not have uniform pore sizes [4]. Laser machining of pores produces conical shaped sidewalls, and the laser spot size is limited by optical diffraction to pores larger than about 1 μm. Plasma etching to make high-aspect ratio patterns is difficult to control and requires a complex mask deposition process.

Here we report the development of a procedure for fabricating high-transmission microporous membranes in polydimethylsiloxane (PDMS) by combining proton beam writing (PBW) and soft lithography. This takes advantages of the special capability of PBW for fabricating micro and nanostructures with straight vertical side walls, large height-to-width aspect ratios, and well controlled dimensions. These characteristics originate from the large momentum and penetration depth of MeV protons in resist materials, like SU-8 and poly(methyl methacrylate) (PMMA) [5,6]. In combination with soft lithography, PBW has been demonstrated well suitable for

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fabricating various micro and nanofluidic components and lab-on-chip devices for biomedical and analytical chemistry applications [7,8].

2. Materials and methods

2.1. Processing of SU-8

SU-8, a conventional negative photoresist for micro and nanolithography, was chosen for fabricating the mold in soft lithography. The substrate was a polished 2-inch silicon wafer treated by oxygen plasma (Plasmaline 415, TEGAL, USA) to increase its surface wettability. Then an approximately 20-μm thick SU-8 (GM1060, Gersteltec Sarl, Switzerland) layer was spin-coated on the Si substrate. The SU-8 layer was then subject to PBW irradiation and chemical development by immersion into propylene glycol monomethyl ether acetate (PGMEA, Gersteltec Sarl, Switzerland) for 2 min at room temperature, followed by a rinse with isopropanol and blow-dry with N_2.

2.2. Proton beam writing

PBW was carried out with 2 MeV protons deflected into the MeV ion microscope attached to the 1.7 MV Tandetron accelerator at Haute Ecole Arc Ingénierie, La Chaux-de-Fonds Switzerland. The lens system demagnification factors are 88 times and 15 times in horizontal and vertical directions, respectively.

Fine focusing was conducted by projecting and scanning the proton beam onto coper grids placed at the same focal plane as that of SU-8. Particle induced X-ray emission (PIXE) mapping of a corner of the grid by OMDAQ2007 was performed to verify the beam spot size, which was about 1 μm × 1 μm in the experiments. A pattern consisting of a hexagonal array of 4 μm × 8 μm holes, arranged at a center (of pillar)-to-center (of pillar) distance of 20 μm, was written by Ionscan software over a 560 μm × 560 μm scan area at a fluence of 1.9×10^{13} ions cm^{-2}, with a beam current of 1 pA. A scan-and-stitch method was adopted to fabricate a large area of pattern, which was composed of 12 individual scans over an area of 2 mm × 2.7 mm.

2.3. Anti-adhesion coating

After PBW, the sample was chemically developed without post-exposure baking to yield a mold consisting of SU-8 pillars. The SU-8 mold was then coated conformally with an approximately 100-nm thick poly-*para*-xylylene (Parylene)-C (Daisan Kasai CO., Japan), which was used as a release layer for PDMS demolding. Parylene-C was deposited by thermal evaporation of a solid Parylene precursor in a low pressure chemical vapor deposition (LPCVD) process [9,10]. This allowed the coating of a smooth Parylene film conformably onto the top surface and side walls of SU-8 pillars to stiffen the mold structures and to facilitate the removal of PDMS from the mold.

2.4. Spin casting PDMS

PDMS pre-polymer (Sylgard 184 Silicone Elastomer, Dow Corning, USA) was prepared at a 10:1 base-to-curing agent weight ratio, degassed, and poured onto the SU-8 mold. Then, a spin-coating process was performed at 4800 rpm for 60 s to purge excess pre-polymer and to generate a 15-μm thick PDMS membrane, which was estimated to be thin enough to form through-holes because the SU-8 pillars were 20 μm in height. Subsequently, the sample was treated thermally on a hotplate at 50 °C for 4 h. This step was performed to accelerate the polymerization process, while the relatively low temperature minimized polymer shrinkage effects after cooling down to room temperature.

2.5. Tape-ring method for demolding

A piece of 60-μm thick polyolephin tape (Model Nunc Sealing Tapes, Thermo Scientific, USA) was cut into a ring-shape by a Nd:YAG laser (Model Mephisto Q, Coherent Lasers Inc., USA) at a wavelength of 1064 nm and pulse energy of 90 μJ. The ring has an inner diameter of 4 mm and outer diameter of 9 mm to fit both the patterned area and the diameter of microfluidic tubing, respectively, for the subsequent membrane-to-chip integration. By using a piece of glass coverslip as a support, the tape ring was transferred onto the cured PDMS and pressed firmly against the membrane surface. The PDMS beyond the periphery of the tape ring was removed by a razor blade. Subsequently, the PDMS membrane, supported by the tape ring, was carefully lifted up by loosening up the edge towards center with the aid of sharp tweezers. When the membrane was completely peeled off, another tape ring was glued to the other side of the membrane to provide extra support.

3. Results and discussion

Optical inspection and measurements were conducted on a high-magnification optical microscope (Model Axioskop, Carl Zeiss AG, Germany) equipped with a digital colour camera (Model DCF420, Leica Camera AG, Germany) in clean-room environment. Fig. 1(a) shows an optical image of the pillars written in SU-8. The size of the pillars is about 4 μm × 8.5 μm, and it is increased to 4.5 μm × 9 μm after Parylene coating, as shown in Fig. 1(b). The increase in the pillar dimensions is probably due to the underestimation of Parylene layer thickness during the coating process, or the fact that Parylene layer was not conformally coated onto the bottom of the SU-8 pillars. The size of the pores in PDMS membrane are about 5.5 μm × 10 μm (Fig. 1(c)), which is slightly larger than that of the coated SU-8 pillars. Thermal relaxation from cooling from the curing temperature of 50 °C is unlikely. Apart from the PDMS shrinkage effects, the origin of this is unclear but might result from plastic flow on delamination.

Fig. 2(a) shows an optical image of the pattern consisting of large-scale SU-8 pillars for use as a mold. As a comparison, an optical image of the PDMS membrane containing through-holes after peeling off the mold is shown in Fig. 2(b). Fig. 2(c) shows the membrane being partially sandwiched between two tape rings, demonstrating the good mechanical stability supplied by the tape rings against rupture during demolding process. The tape ring also provided rigidity which helped maintain the thin PDMS film flat and allowed it to be readily handled using forceps (Fig. 3(c)).

To confirm the suitability of the porous membrane for fluid transmission. A piece of membrane was vertically sectioned, and its side profile was inspected under the microscope (Fig. 3(a)). The scanning microscopy image shows the straight vertical sidewalls of holes inside PDMS, implying a straight proton trajectory inside SU-8 (Fig. 3(b)). The thickness of the membrane is about 20 μm, which is larger than the expected value estimated from literature [11]. This might be associated with capillary forces from the pillars of the mold, which can be very large in microfluidic structures, acting to enhance the PDMS film thickness compered to a flat surface.

The 20-μm thickness also corresponds to a 5:1 height-to-cross sectional width aspect ratio of PDMS holes, which is slightly larger than that generally achievable in PDMS fabrication [12]. High-magnification microscopy of the high-density pore area (Fig. 3(c)) also revealed that the majority of pores remain open at both ends after demolding; whereas a few are covered by about 1 μm-thick