Fabrication of enclosed nanochannels in poly⟨methylmethacrylate⟩ using proton beam writing and thermal bonding

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We report a technique for fabricating enclosed nanochannels in poly(methylmethacrylate) (PMMA) using proton beam writing coupled with thermal bonding. Using proton beam writing, straight-walled high-aspect-ratio channels can be directly fabricated through a relatively thick PMMA resist layer spin coated on a Kapton film. By thermally bonding the fabricated structures onto bulk PMMA, peeling off the Kapton substrate, and bonding the remaining exposed side to PMMA, enclosed high-aspect-ratio nano/microchannels can be fabricated. Such enclosed channels can be incorporated into fluidic polymeric devices, and the process is compatible with the fabrication of multilevel three-dimensional fluidic chips with vertical interconnects. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2181631]

The fabrication of micro/nanofluidic systems represents a critical technology for the efficient development of cheap lab-on-a-chip systems for applications in chemistry, biology, and medicine.[1–7] These fluidic systems typically consist of three-dimensional (3D) channels and are conventionally fabricated from silicon or glass using optical lithography. This technology has been adopted mainly as a consequence of the expertise gained during decades of research and development in the integrated circuit (IC) industry.[8] Alternative technologies are being explored for IC fabrication and also for different kinds of nanostructure development for applications in biological sciences, biophysical sciences, and chemistry.[9–12] The use of polymeric materials for lab-on-a-chip technology is increasing due to its resistance to aggressive chemicals, its optical transparency, and the ability to be mass produced using imprinting technology, thereby leading to cheap disposable devices.[13–15] Fluidic channels in polymer can be fabricated by hot embossing, promising molecule-scale resolution.[16] Sealing these channels to form enclosed microchannel systems using adhesive bonding,[17] thermal bonding,[18] and microwave bonding[19] have been demonstrated successfully, but so far bonding techniques for sealing 3D polymer channels at the submicron scale have not been reported, although Han Cao *et al.* have utilized nonuniform deposition as a sealing technique at nanodimensions.[20] Adhesive bonding is not considered an efficient option at smaller submicron dimensions because of the possibility of adhesive clogging the channels.

For mass production of polymer lab-on-a-chip devices, a stamp or mold for each design is a prerequisite. For rapid prototyping of devices with feature dimensions of several microns or larger, casting poly(dimethylsiloxane) (PDMS) with a lithography master using a mask, represents a convenient way of fabricating a rapid and cheap prototype.[21] However, for prototyping submicron devices it is more convenient and efficient to use direct writing, thereby avoiding the more complex procedures of fabricating a high resolution stamp or mold.

In this letter we report a rapid prototyping process for fabricating enclosed micro/nanochannel systems in poly (methylmethacrylate) (PMMA) using the direct-write technique of proton beam writing (PBW) coupled with thermal bonding. In recent years, PBW has been demonstrated as a successful one step process for direct writing high aspect ratio structure with smooth vertical walls in PMMA and SU8 resist at sub-100 nm resolutions.[22] Compared with electron beam writing, PBW can realize a straighter and deeper structure because a proton is more massive than an electron and therefore deviates much less as it penetrates matter. The deviation from a straight line path of the proton trajectory is very small, especially in the initial part of its trajectory, e.g., a 1 MeV proton beam traveling through a 2 μm PMMA resist layer will experience less than 12 nm spread in the beam profile according to a Monte Carlo calculation using the SRIM code.[23] This means that p-beam writing is capable of writing straight-walled high-aspect-ratio channels completely through a relatively thick (e.g., up to 10 μm) layer of resist. Experimental results have also demonstrated that PBW is capable of writing high-aspect-ratio structures with low surface roughness of 2.5 nm (rms), at dimensions down to 30 nm.[22]

PBW is a fast fabrication method for serial production of high quality 3D structures. With in-house software, prototype designs can be programmed into computer code and a focused proton beam can be magnetically or electrostatically scanned over a resist material. The scanned area in the prototype p-beam writer at the Centre for Ion Beam Applications, National University of Singapore, is currently limited to 500×500 μm^2. However, larger patterns of up to 25×25 mm^2 can be realized by coupling proton beam scanning with stage scanning.[24] Depending on the spatial resolution of the pattern, a pattern of 25×25 mm^2 can be realized in a few hours. However, being a direct-write technique, and therefore a serial process, PBW is not economic for multiple component production, although it does have unique advantages. PBW has the ability to fabricate high aspect ratio, smooth structures with high resolution, and as such has great potential for rapid and cheap prototyping of 3D micro/ nanostructures for research and development purposes. It
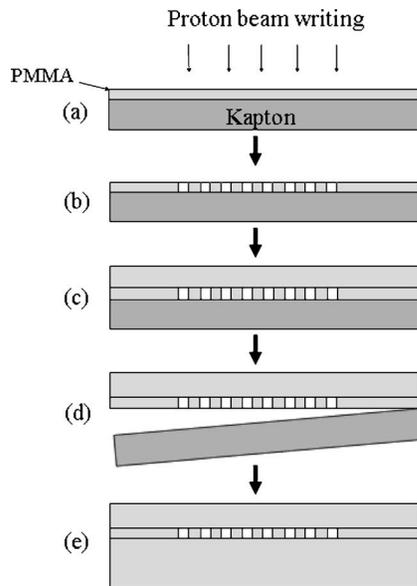

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FIG. 1. Schematic representation of the process of the enclosed channel fabrication using proton beam writing.
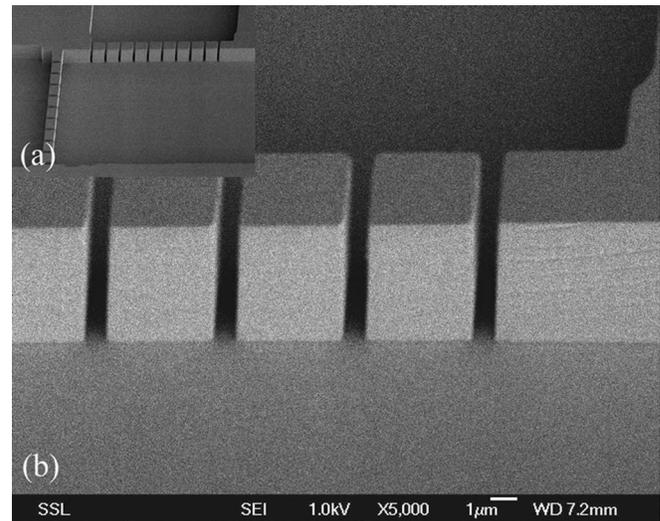

FIG. 2. (a) PMMA micropillars transferred to bulk PMMA using a Kapton substrate, (b) high resolution image of 2 (a). The grooves are 800 nm wide and 8 μm deep.

should be noted, however, that PBW combined with electroplating has been demonstrated successfully as a technique for fabricating high resolution 3D stamps for hot embossing at the nanolevel,[25] which can meet the high efficiency and low cost prerequisite to access the commercial market. Therefore, it is possible for proton beam writing to become a critical technology for fabricating micro/nanofluidic systems from prototype to mass production.

For a working fluidic system, it is critical to seal any open micro/nanochannel, otherwise rapid fluid evaporation will occur, particularly at small dimensions. We have developed a simple yet effective way of channel sealing by bonding a top housing on proton beam written structures to form enclosed channels. In this process we have used Kapton film (Kapton® HN from DuPont) as a carrier substrate. The process steps, shown schematically in Fig. 1, are as follows: (a) PMMA (1–10 μm) is spin coated onto 50 μm Kapton film, and patterned using proton beam writing. At these thicknesses, the proton beam penetrates through the PMMA film, and stops in the Kapton film. (b) The exposed PMMA is developed, forming high aspect ratio structures through the PMMA (but not in the Kapton film). (c) A flat uniform PMMA sheet is thermally bonded onto the topside of the PMMA structures. (d) The Kapton substrate is gently peeled off the bottom side of the PMMA structures. (e) A flat uniform PMMA sheet is then thermally bonded onto the bottom side of the PMMA structures, yielding a PMMA sealed device with enclosed nanochannels.

This procedure uses proton beam writing to produce the straight walled channels through the PMMA and Kapton as a carrier substrate. The process utilizes both the strength and flexible qualities of Kapton, and relies on the bonding strength of Kapton-PMMA being smaller than the bonding strength of PMMA-PMMA, enabling the Kapton substrate to be easily peeled from the PMMA. We used a 50 μm Kapton commercial film as the carrier substrate, cleaned with acetone, spin dried, and then baked at 170 °C for 10 min. A layer of PMMA resist (950k molecular weight, 11 wt % in anisole, from Microchem) was spin coated onto the Kapton substrate as a single layer (e.g., 1 μm thick).

The lithographic patterning was carried out using the PBW facility at the Centre for Ion Beam Applications, National University of Singapore.[22,26] A 2 MeV H_2^+ beam (equivalent to a 1 MeV proton beam) focused down to small spot sizes was scanned over the PMMA resist layer. We used a H_2^+ beam because of the reduced proton halo in our system created by this type of beam compared with 2 MeV protons, and also because of the lower dose requirement: The optimum doses for PMMA are 85 nC/mm^2 for 2 MeV H_2^+ and 140 nC/mm^2 for 2 MeV protons.

After PBW exposure, the PMMA resist was developed in isopropyl alcohol (IPA)-water (7:3) developer for 10 min at room temperature without agitation. We used the IPA based developer because it is much less aggressive to the unexposed 950k PMMA resist than the conventional developer (60% diethylene glycol monobutyl ether, 20% morpholine, 5% ethanolamine, 15% water),[27] and this ensured that the precision of the structures at the nanometer scale was defined by the dimensions of the focused proton beam, and not due to etching of unexposed resist. In addition, the IPA-water (7:3) developer is less viscous, thereby enabling efficient and rapid diffusion of the developer into the high aspect ratio 3D channels.

Various bonding conditions were investigated by varying the temperature and applied pressure between the surfaces to be bonded. The crucial part of this bonding process is to produce a stronger bond between the bulk PMMA and the patterned PMMA compared with the PMMA-Kapton substrate, while maintaining minimum distortion of the proton beam fabricated structures due to the applied temperature and pressure. In a preliminary experiment, a 2 MeV H_2^+ beam focused to a spot size of 300×300 nm^2 was written into a 10 μm thick PMMA resist layer spin coated onto a Kapton substrate. The proton beam was scanned such as to fabricate a test pattern of two orthogonal rows of 4 $\times 4$ μm^2 pillars with a spacing of 1 μm. The exposed resist was developed, bonded to a PMMA substrate, and the Kapton removed as described earlier in procedures (a)–(d). The final part (e) of the process (bonding the final PMMA sheet) was not carried out in order to visualize any distortion at this stage in the procedure. We observed that at a bonding pres-
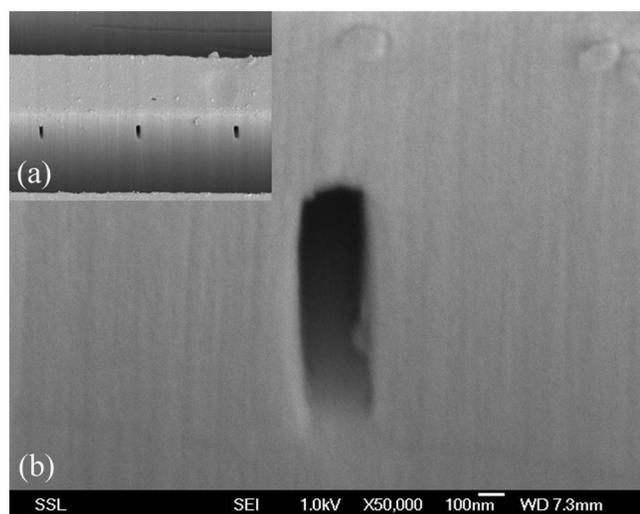
FIG. 3. (a). PMMA enclosed nanochannels fabricated using proton beam writing coupled with thermal bonding, and (b) close up of one of the buried channels. The channels are 200 nm wide and 2 μm deep.

sure of 1.2 bar and an interface temperature of 105 °C, the resulting structure could be transferred from the Kapton substrate and bonded to a PMMA substrate with minimal distortion. The transferred structures are shown in Figs. 2(a) and 2(b).

In a more exacting experiment, a 2 MeV H_2^+ beam was focused into a 200×300 nm^2 spot size and scanned as a series of linear channels over a 2 μm PMMA resist layer spin coated onto a 50 μm Kapton film. The full procedures (a)–(e) were carried out as described earlier. In order to visualize the enclosed channels, the final structure was laterally micromachined at a depth of around 20 μm using proton beam writing in order to expose the cross sections of the buried channels. As can be seen in Figs. 3(a) and 3(b), the channels are well formed with minimal deformation.

During these investigations, several other points were noted. For thermal bonding over large areas, a uniform pressure on the whole area is critical because uneven pressure will cause deformation in the high pressure area and bonding failure in the low pressure area. This is the reason why we utilize a flexible Kapton film instead of the more rigid glass or silicon wafer as substrate. We also found that to promote uniformity of contact pressure over large areas, a 3 mm thick sheet made of PDMS (Sylgard 184, Dow Corning Corp.) can be loosely attached beneath the Kapton substrate.

We have not considered retaining the Kapton carrier substrate thereby fabricating a bimaterial (Kapton-PMMA) fluidic chip, since using different materials in a fluidic device may create additional problems, e.g., with fluidic flow due to the different zeta potentials exhibited by contact with different adjacent walls of the channel, an effect which becomes more pronounced at nanodimensions. In addition, our research program is concerned with the fabrication of polymer lab-on-a-chip systems that utilize integrated optics, and unfortunately Kapton, unlike PMMA, exhibits high levels of fluorescence and is therefore unsuitable for integrated optical devices. However, there is a further potentially interesting advantage of using proton beam writing as the fabrication process, and Kapton as a transfer substrate. During the transfer and bonding process we have shown that uniform sheets of PMMA can be bonded onto the *p*-beam written structures to form enclosed channels. If instead of bonding using uniform PMMA sheets we use through-patterned PMMA film coated on Kapton, then by peeling off the Kapton substrate we have the possibility of fabricating stacked 3D fluidic structures with vertical interconnects. We plan to investigate this in future experiments.

[1] B. H. Weigl and P. Yager, Science **283**, 346 (1999).
[2] J. Han and H. G. Craighead, Science **288**, 1026 (2000).
[3] M. Baba, T. Sano, N. Iguchi, K. Iida, T. Sakamoto, and H. Kawaura, Appl. Phys. Lett. **83**, 1468 (2003).
[4] P. K. Wong, T. H. Wang, J. H. Deval, and C. M. Ho, IEEE/ASME Trans. Mechatron. **9**, 366 (2004).
[5] S. M. Stavis, J. B. Edel, K. T. Samiee, and H. G. Craighead, Lab Chip **5**, 337 (2005).
[6] Q. S. Pu, J. S. Yun, H. Temkin, and S. R. Liu, Nano Lett. **4**, 1099 (2004).
[7] W. Reisner, K. J. Morton, R. Riehn, Y. M. Wang, Z. Yu, M. Rosen, J. C. Sturm, S. Y. Chou, E. Frey, and R. H. Austin, Phys. Rev. Lett. **94**, 196101 (2005).
[8] F. Watt, Nucl. Instrum. Methods Phys. Res. B **158**, 165 (1999).
[9] G. M. Whitesides and J. C. Love, Sci. Am. **285**, 38 (2001).
[10] D. Mijatovic, J. C. Eijkel, and A. van den Berg, Lab Chip **5**, 492 (2005).
[11] F. Watt, A. A. Bettiol, J. A. Van Kan, E. J. Teo, and M. B. H. Breese, Int. J. Nanosci. **4**, 269 (2005).
[12] S. Quake and A. Scherer, Science **290**, 1536 (2000).
[13] M. Noerholm, H. Bruus, M. H. Jakobsen, P. Telleman, and N. B. Ramsing, Lab Chip **4**, 28 (2004).
[14] J. Kameoka, H. G. Craighead, H. Zhang, and J. Henion, Anal. Chem. **73**, 1935 (2001).
[15] S. A. Soper, S. M. Ford, S. Qi, R. L. McCarley, K. Kelly, and M. C. Murphy, Anal. Chem. **72**, 643A (2000).
[16] F. Hua, Y. Sun, A. Gaur, M. A. Meitl, L. Bilhaut, L. Rotkina, J. Wang, P. Geil, M. Shim, J. A. Rogers, and A. Shim, Nano Lett. **4**, 2467 (2004).
[17] W. K. Schomburg, R. Ahrens, W. Bacher, J. Martin, and V. Saile, Sens. Actuators, A **A76**, 343 (1999).
[18] J. Li, D. Chen, and G. Chen, Anal. Lett. **38**, 1127 (2005).
[19] A. A. Yussu, I. Sbarski, J. P. Hayes, M. Solomon, and N. Tran, J. Micromech. Microeng. **15**, 1692 (2005).
[20] H. Cao, Z. Yua, J. Wang, E. Chen, W. Wua, J. Tegenfeldt, R. Austin, and S. Chou, Appl. Phys. Lett. **81**, 174 (2002).
[21] J. M. Ng, I. Gitlin, A. D. Stroock, and G. M. Whitesides, Electrophoresis **23**, 3461 (2002).
[22] J. A. Van Kan, A. A. Bettiol, and F. Watt, Appl. Phys. Lett. **83**, 1629 (2003).
[23] J. Biersack and L. G. Haggmark, Nucl. Instrum. Methods **174**, 257 (1980).
[24] J. A. van Kan, A. A. Bettiol, and F. Watt, Mater. Res. Soc. Symp. Proc. **777**, T2.1.1 (2003).
[25] K. Ansari, J. A. van Kan, A. A. Bettiol, and F. Watt, Appl. Phys. Lett. **85**, 476 (2004).
[26] F. Watt, J. A. van Kan, I. Rajta, A. A. Bettiol, T. F. Choo, M. B. H. Breese, and T. Osipowicz, Nucl. Instrum. Methods Phys. Res. B **210**, 14 (2003).
[27] S. V. Springham, T. Osipowicz, J. L. Sanchez, L. H. Gan, and F. Watt, Nucl. Instrum. Methods Phys. Res. B **130**, 155 (1997).