



Fabrication of nickel molds using proton beam writing for micro/nano fluidic devices

Fan Liu*, Kheng Boon Tan, P. Malar, S.K. Bikkarolla, J.A. van Kan

Centre for Ion Beam Applications, Department of Physics, National University of Singapore, Singapore 117542, Singapore

ARTICLE INFO

Article history:

Available online 7 June 2012

Keywords:

Proton beam writing
Nickel molds
DNA analysis

ABSTRACT

In this paper, we present the fabrication of micro/nano fluidic devices with the combination of proton beam writing and UV lithography. Proton beam writing was used to generate the fine features with smooth sidewall profiles on ma-N resist, 110 and 600 nm thick. UV lithography is used to fabricate the micron sized feeding channels properly aligned with the nanostructures on ma-P resist. To get a durable mold, we need to transfer the resist structure into a nickel mold. Nickel electroplating and re-electroplating have been carried out to replicate the polymer structure in a nickel mold with the desired geometry, resulting in a durable Ni master mold. Finally it is demonstrated that these Ni molds can be used to make high quality PDMS fluidic channels used for DNA lab on chip experiments.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The fabrication of micro and nanofluidic devices has been an emerging field of research in recent years. The increasing interest is largely due to the new opportunities offered by micro- and nano-technologies allowing the fabrication of well-defined networks of nano-channels [1]. A growing number of applications are found in the areas of nano-science and biological science such as biosensors, drug delivery systems and DNA analytical system [2]. One of the most obvious advantages of smaller fluidic devices is reduced reagent consumption. It becomes especially appealing for many of the biological applications where the reagents can be very expensive (e.g. antibodies), and the quantity of the sample volumes are often limited [3]. Another appealing aspect of such devices as lab-on-a-chip (LOC) is that they are able to carry out separation and detection with high resolution and sensitivity [4,5]. Thirdly, the small size makes it a portable analytical device without the need of access to a proper laboratory. Lastly, a less obvious characteristic of micro-fluidics, is that the flow of fluid is laminar [6], which basically sums up the various advantages that make LOCs so appealing today.

Often LOC devices for DNA analysis are fabricated in quartz [7]. The choice of PDMS as the material for micro-fluidic devices was based on various advantages offered by using this particular polymer. Firstly, PDMS can be easily replicated without the need of advanced etching steps which are required in the fabrication of fluidic devices in quartz. Secondly, it is biologically inert and

non-toxic, which makes it suitable for biological applications as well as safe to use. It is also optically transparent, therefore making it well suited for fluorescence analysis [8]. PDMS is now widely used in many micro-fluidic devices for a wide range of biomedical purposes [9,10].

Here we use proton beam writing in combination with UV lithography to fabricate resist molds. One way of achieving a fluidic device for DNA analysis is to cast PDMS onto a mold with inverted structures [11,12]. The disadvantage of a resist mold is that the structures are easily damaged during release of the PDMS from the mold. Nickel electroplating was used to produce robust, high quality Ni molds which can be used many times for PDMS casting. This is one of the possible ways to replicate the master mold with high fidelity.

As a promising fabrication process proton beam writing (PBW) was used to produce features in ma-N 2401 and ma-N 2410. When MeV protons interact with a resist, they scatter and lose energy through nuclear and electronic interaction processes. The probability that a proton interacts with electrons is several order of magnitude larger than nuclear interaction [13]. Because of the higher mass of the protons compared with electrons, any scattering of the proton beam due to electronic collisions is negligible and since electronic interaction is the most likely event, MeV protons will penetrate deep into the resist while maintaining a straight path [14]. The secondary electrons generated through the scattering process have a range of only a few nanometers [15,16], therefore proximity effects (exposure due to unwanted energetic secondary electrons) are very small. These characteristics make proton beam writing a promising process to fabricate smooth, straight and vertical sidewalls. Proton beam writing in combination with electroplating provides a unique technique for the fabrication of durable

* Corresponding author.

E-mail address: A0076593@nus.edu.sg (F. Liu).

high quality 3D metallic stamps and masks for nanofluidic lab on chip applications.

2. Fabrication procedures

A schematic representation of the fabrication process is shown in Fig. 1. The fabrication process was started by coating a clean Si wafer with 30 nm Cr and 60 nm Au consecutively. The Cr and Au layers ensure adhesion as well as electrical conductivity for electroplating. The Au/Cr/Si wafer was prebaked at 120 °C for 5 min to dehydrate before coating the resist to ensure a good adhesion between the resist and wafer. After that, a layer of 110 nm ma-N 2401 was spin coated on the substrate at 3000 rpm for 30 s (sample one). On a second sample a layer of 600 nm ma-N 2410 was spin coated at 8000 rpm for 1 min. The PBW for nano-lines was conducted in the Centre for Ion Beam Applications at the National University of Singapore using 2 MeV protons [17]. Here the proton beam was focused down to around $130 \times 200 \text{ nm}^2$ and magnetically scanned to produce the nano-lines. After the fabrication process, both samples were developed in ma-D 331 for about 25 s. It was observed that after coating ma-P resist, the channels became invisible under the optical microscope. To facilitate alignment of the nanochannels and UV exposure of the micro-channels, a thin Ti layer (1.5 nm) was deposited onto the ma-N layer before coating the ma-P resist using filtered cathodic arc vacuum (FCVA) deposition. Sample one was coated with a 4 μm thick layer of ma-P 1240 resist (3000 rpm for 30 s). Sample two was coated with a 10 μm thick layer of ma-P 1275 HV resist (3000 rpm for 30 s). An optical mask with 5 μm wide lines (1.5 mm long) was aligned with respect to the nano-lines using an Oriol UV mask aligner (i-line). Next sample one and two were exposed for 60 and 240 s respectively. Both samples were developed in 2.38% TMAH for about 2 min. To get a durable mold for PDMS casting, we carried out electroplating of nickel on the resist samples. Before electroplating, a thin layer of Ti (1.5 nm) was deposited via FCVA on the samples to create an electrically conductive seed layer for plating. These metal molds were used in a metal-on-metal plating process to get replicas of the original polymer structures in Ni. Before the second plating step, the Ni mold is immersed in 30% hydrogen peroxide for 90 s [18]. A layer of oxide will form on the surface of the Ni mold and

therefore facilitates easy separation of the two Ni molds without damaging the structures. After this, PDMS casting was conducted using the final Ni mold.

Single T4 GT7 DNA (T4-DNA, 165.65 kbp) molecules stained with YOYO-1 dye at the ratio of 1:40 were prepared for observation of DNA in the PDMS fluidics chip. These DNA molecules were then dispersed into a buffer solution of condition $1 \times$ TBE (90 mM tris,

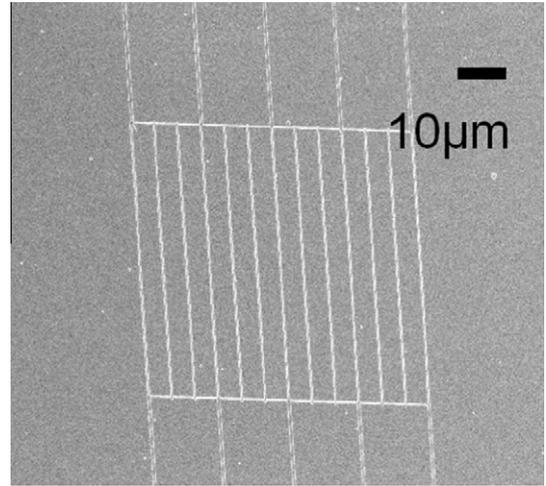


Fig. 2. SEM image of nanolines fabricated by PBW in ma-N 2401.

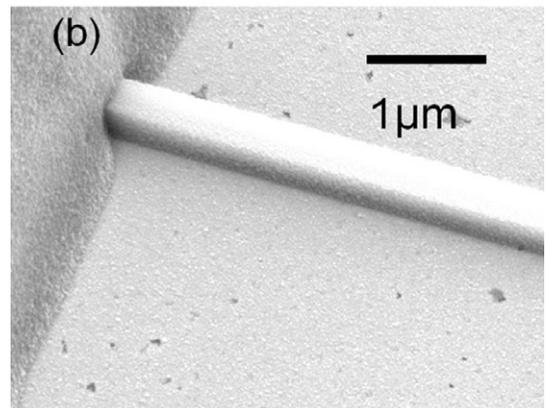
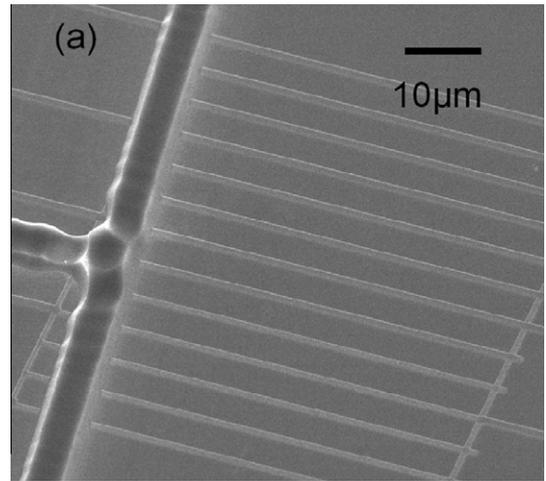


Fig. 3. (a) Double resist structure featuring micro and nano-lines (110 nm thick ma-N 2401), the size is about $4.5 \times 4 \text{ μm}^2$ and $130 \times 800 \text{ nm}^2$ (height \times width) for micro and nano-lines respectively. (b) High resolution SEM image of a nano-line (600 nm thick ma-N 2410).

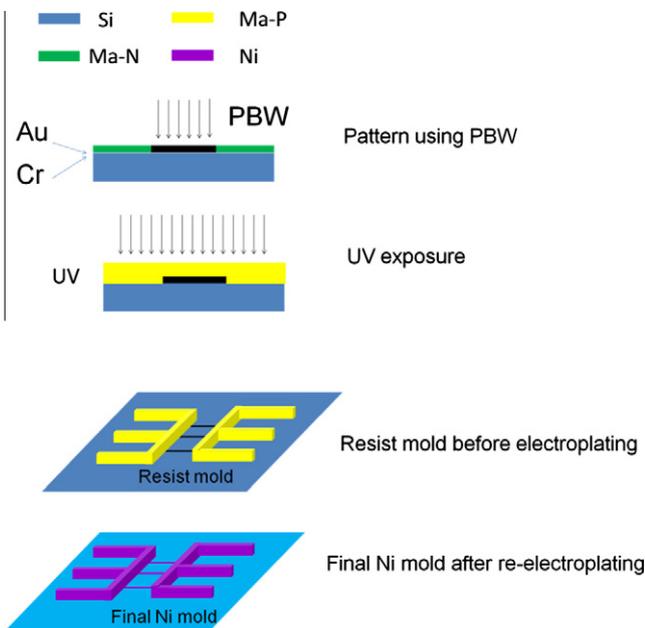


Fig. 1. Schematic representation of the experiment procedures for the fabrication of a Ni mold featuring nano lines for PDMS casting.

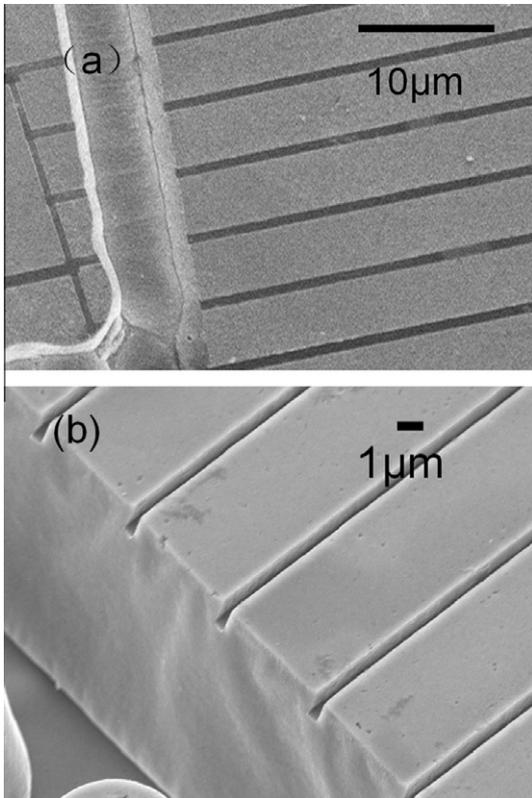


Fig. 4. (a) SEM image of Ni mold after first time plating (using ma-N 2401). (b) SEM image of Ni mold after first time plating (using ma-N 2410).

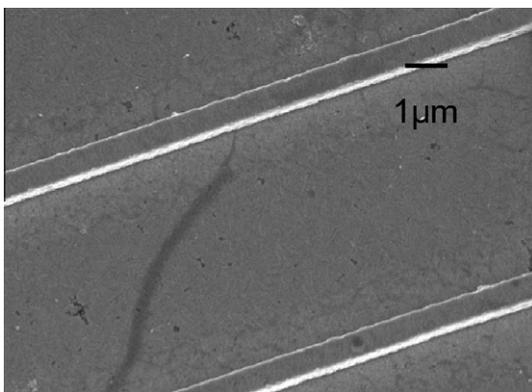


Fig. 5. Final Ni mold after twice plating (using ma-N 2410), featuring the nano-lines.

90 mM boric acid, and 2 mM EDTA, with pH of 8.5) and injected into the 2 reservoirs of the PDMS fluidic chip that connect the micro and nano-channels. Two platinum electrodes were immersed in the reservoirs and used to drive the DNA molecules into the micro and nano-channels. Once the DNA molecules were confined inside the nano-channels, the power supply was switched off to stop the flow of the DNA and allow for better observation. The analysis of the DNA molecules was done using an Olympus IX71 inverted fluorescence microscope.

3. Results

After the whole fabrication process, we get the resist and Ni mold showing as follow. Fig. 2 is the scanning electron micrograph

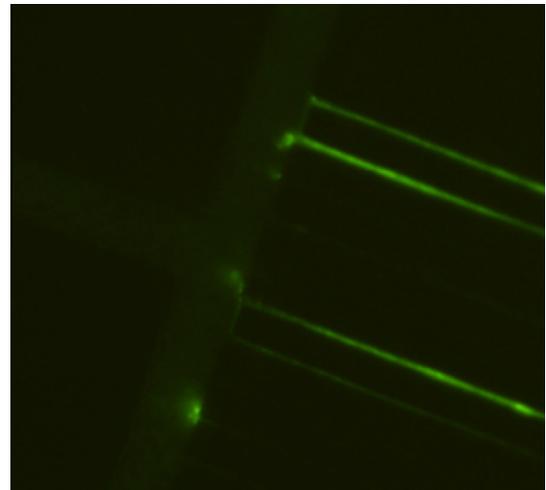


Fig. 6. Fluorescence image of the DNA in a bonded PDMS chip featuring micro and nano-channels.

(SEM) image of nano fabrication pattern for sample one. Fig. 3(a) shows a SEM image of the polymer structure featuring the micro and nano-channels of sample one. The size of the micro-channel is $4.5 \times 4 \mu\text{m}^2$ and the size of the nano-channels is $110 (\pm 15) \times 800 (\pm 80) \text{nm}^2$ (height \times width). Fig. 3(b) shows a high magnification SEM image of one of the nano-channels of sample two, which indicates a vertical, straight and smooth side-wall. After the first time plating, we can see from Fig. 4 that the resist inside the Ni mold is clearly removed by immersing into acetone. This suggests that the ma-N resist is a very promising resist for two level mold fabrication using PBW and UV lithography in combination with Ni electroplating. Fig. 5 shows the final Ni mold for sample two. The size of the nano-lines is $600 (\pm 15) \times 700 (\pm 15) \text{nm}^2$ (height \times width). We can see from the image that the top surface is very smooth while the sidewall is a little bit rough. This is probably because the first nickel mold has been oxidized too much by the hydrogen peroxide before the final plating step. This process will be further optimized to achieve smoother sidewalls. The green fluorescence image in Fig. 6 represents the DNA molecules stained with YOYO-1 dye in the long and straight nano-channels casted in PDMS.

4. Conclusion and future work

PBW & UV lithography have successfully been used to fabricate a multi level resist mold for nanofluidic lab on chip devices with smooth and vertical sidewalls. After Ni plating and re-electroplating, we get a Ni mold with almost the same fidelity as the original resist mold. We have also demonstrated successful DNA observation in PDMS nanofluidic lab on chip devices down to 700 nm.

In the future, the oxidation process will be further optimized aiming for Ni molds with even smaller feature sizes for PDMS nanofluidic lab on chip devices down to 100 nm.

Acknowledgements

We acknowledge the support from A*STAR (R-144-000-261-305).

References

- [1] Patrick. Abgrall, Ana. Chem. 80 (2008) 2326–2341.
- [2] Patrick Abgrall, Nam Trung Nguyen, Nanofluidics, Boston, London, 2009, pp. 1–7.

- [3] Tian, W.-C., E. Finehout, *Microfluidics for Biological Applications*, Springer, 2009.
- [4] S.E. Ong, S. Zhang, H. Du, Y. Fu, *Front Biosci.* 13 (2008) 2757–2773.
- [5] F. Persson, P. Utko, W. Reisner, N.B. Larsen, A. Kristensen, *Nano Lett.* 9 (4) (2009) 1382–1385.
- [6] J.P. Brody, P. Yager, R.E. Goldstein, R.H. Austin, *Biophys. J.* 71 (6) (1996) 3430–3441.
- [7] W. Reisner, K.J. Morton, R. Riehn, Y.M. Wang, Z. Yu, M. Rosen, J.C. Sturm, S.Y. Chou, E. Frey, R.H. Austin, *Phys. Rev. Lett.* 94 (19) (2005) 196101.
- [8] Walter. Schrott, Milos. Svoboda, Zdenek. Slouka, Michal. Pribyl, Dalimil. Snita, *Microelectron. Eng.* 87 (5–8) (2010) 1600–1602.
- [9] T. Fujii, *Microelectron. Eng.* 61–62 (2002) 907–914.
- [10] Sara. Thorslund, Rolf. Larsson, Fredrik. Nikolajeff, Jonas. Bergquist, Javier. Sanchez, *Sens. Actuators B: Chemical* 123 (2) (2007) 847–855.
- [11] C Zhang, F Zhang, J.A. van Kan, J.R.C. van der Maarel, *J. Chem. Phys.* 128 (2008) 225109.
- [12] C. Zhang, P.G. Shao, *Proc. Natl. Acad. Sci.* 106 (2009) 16651.
- [13] J.F. Ziegler, *The Stopping and Range of Ions in Matter*, vols. 2–6, Pergamon, Oxford, 1977–1985.
- [14] J.A. van Kan, T.C. Sum, T. Osipowicz, F. Watt, *Nucl. Instrum. Methods Phys. Res. B* 161–163 (2000) 366.
- [15] J.A. van Kan, A.A. Bettiol, F. Watt, *Appl. Phys. Lett.* 83 (2003) 1629.
- [16] C.N.B. Udagama, A.A. Bettiol, F. Watt, *Nucl. Instrum. Methods Phys. Res. B* 260 (2007) 390–395.
- [17] F. Watt, J.A. van Kan, I. Rajta, A.A. Bettiol, T.F. Choo, M.B.H. Breese, T. Osipowicz, *Nucl. Instr. and Meth. B* 210 (2003) 14.
- [18] K. Ansari, J.A. van Kan, A.A. Bettiol, F. Watt, *J. Micromech. Microeng.* 16 (2006) 1967.