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Fabrication of metallic stamps for injection moulding applications by combining proton beam writing and UV lithography

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ABSTRACT

In this paper, we present the results of resist evaluation for the fabrication of metallic stamps used in the injection moulding of micro/nano fluidic devices. The resist was evaluated in terms of its suitability to combine direct proton beam writing (PBW) and UV lithography techniques for incorporating few tens of micron and micron- to millimeter sized features respectively. In a first step PBW is used to generate the fine features with smooth sidewall profiles in AR-P 3250, here the resist shows negative behavior. Following PBW, masked i-line UV lithography was used to create larger features to complete the device design, here the AR-P 3250 acts as a positive resist. After developing, the resist was used to generate the final mould through Ni electroplating, resulting in a high quality metallic stamp.

1. Introduction

Microfluidic systems have found exceptional success over a wide range of scientific fields including chemistry and biology [1–3]. The main advantages of microfluidic systems include high performance, versatility and fast processing. Conventionally microfluidic systems are fabricated on glass or Si substrates. However, the systems made of glass or Si are relatively expensive because of contamination that renders the devices not suitable for multiple usages. As a result, polymers gained attention as an attractive alternative to glass and Si as a substrate material due to their biocompatibility, disposability and low cost [4–6]. Moreover, replication techniques such as soft lithography, contact imprinting and injection moulding enable low cost mass production of polymeric microfluidic systems.

Apart from these advantages, polymers are suitable for rapid prototyping as well. For prototyping, direct write techniques have the advantage over the mass production techniques because masks or masters are not required [5]. Among the several next generation lithography methods (electron-beam writing, LIGA and UV lithography), proton beam writing (PBW), a novel technique developed at Centre for Ion Beam Applications (CIBA) [7], has attracted considerable attention. Compared to E-beam writing, PBW shows greatly reduced proximity effects [8], which allow the fabrication of high-density high aspect-ratio nano-structures, and secondly PBW has typically a 100 fold higher sensitivity compared with E-beam writing in the same resist material [9]. CIBA holds the world record for focusing protons down to $35 \times 75\,nm^2$ [10] and have produced 3D high aspect ratio walls down to 22 nm in hydrogen silsesquioxane HSQ [11].

In this paper we aim to study the suitability of the polymer resist AR-P 3250 as master mould for making Ni stamp for replication applications. This work is in continuation with the previous one [12] to look for possible resists in which PBW and UV lithography can be combined. The reason for combining two lithography techniques arise from the fact that the final chip design consists of few tens of micron sized pillars (about 60 μm) incorporated into the millimeter sized long channels (20 mm) with a final height of tens of microns (10–40 μm). The strategy is to write the micro pillars having smooth and straight sidewalls by PBW and link the fine structures to the large area by UV lithography. In this way the short patterning time of UV lithography and the reliability of PBW for fine features can be combined to produce the master mould for electroplating Ni stamps. It has been a well-established fact that the polymer PMMA [11,13] a commonly used positive tone resist, can be easily used for this kind applications. PBW and electroplating of PMMA resist can give smooth Ni moulds with sub-10 nm RMS side wall roughness and 20 nm details. Further, PMMA resist can be removed easily without compromising the fine details in the Ni stamp. The usage of PMMA resist for the present study is constrained by the fact that the maximum depth at which PMMA can be structured is limited to about 10 μm if a 248 nm deep UV lithography is used. Therefore, to complete the chip design with heights up to 30 μm or more, suitable resists have to be identified and thoroughly characterized for proton dosage, UV exposure conditions, developing, compatibility for electroplating metallic stamp and finally removal of the resist. To the best of our knowledge, the

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resist AR-P 3250 which is a positive tone i-line resist used in optical lithography is subjected to PBW for the first time, under which it shows negative tone resist behavior. The experimental procedures followed and the results obtained indicating its suitability for combining PBW and UV lithography are discussed in the following sections.

2. Experimental details

The details of the schematic process for the fabrication of Ni stamp can be found elsewhere [12]. Briefly, in a first step, a 10 μm thick AR-P 3250 was spin coated onto the Si substrate with Cr/Au seed layer. The metal coated wafer was dry baked at 200 °C to remove any moist, next spin coated at 2000 RPM for 30 s, followed by a bake at 95 °C for 12 min to completely remove the solvent. Secondly, PBW was done using a beam of 2 MeV protons focused down to a spot size of about 250 × 250 nm^2, as measured by an indigenously made resolution standard [14], and magnetically scanned over an area of 100 × 100 μm^2 to form squares of 10 × 10 μm^2 and test the sensitivity of the AR-P 3250 resist to proton exposure. In a next experiment pillars with a 60 μm diameter were exposed. Every proton exposure is followed by an i-line (365 nm) UV exposure to remove the unexposed resist during PBW and create micron to millimeter sized features. The UV exposure was performed using a 100 W lamp for about 20 min. Following that the sample was developed in AR 300-26 (1:1 diluted with DI water) for 1 min followed by DI water rinse to observe the PBW and UV exposed structures. Next, the developed squares were used to determine the sensitivity of AR-P 3250 to proton exposure and the circular pillars were used as a master mould for Ni electroplating. Before the Ni electroplating process a thin (few nm) Ti conducting layer was coated on the surface using filtered cathodic arc vacuum deposition (<1 × 10^{-5} mbar). A 100 μm thick Ni layer was electroplated using a commercial plating system RD.50 from Technotrans AG. At the last step, Ni delamination and residual resist removal was done using the remover AR 300-73 under ultrasonic agitation at 60 °C for 15 min followed by DI water rinse. The samples that are developed after a combined proton and UV exposure as well as the electroplated Ni stamps were examined using SEM.

3. Characterization of the resist and Ni stamp

The AR-P 3200 series of photoresists from ALLRESIST [15] are positive tone resists that undergo chain scission with i-line UV exposure, i.e. the exposed parts will be removed during the development procedure. In order to characterize the AR-P 3250 resist for PBW, samples on Si wafers with seed layers of Cr/Au and a 10 μm thick layer of the resist were subjected to PBW with a 2 MeV proton beam. Array of squares with different proton doses ranging from 1 to 5 nC/mm^2 were written. This was done to identify whether the molecular bonds in the resist cross-link or chain scission under proton beam irradiation. Following PBW, the samples were subjected to flood i-line UV exposure. After development only the parts of the resist that have undergone enough chain scissioning are removed (i.e. the UV exposed areas) therefore the resist parts that are not exposed to proton beam exposure are expected to be removed. If the proton beam causes enough cross linking the resist will not be removed by the developer. A number of SEM micrographs were taken to investigate the developed structures after the combined PBW and UV lithography. Fig. 1a shows the SEM image of arrays of 10 × 10 μm^2 proton beam written squares at different proton doses (1–5 nC/mm^2) into 10 μm thick AR-P 3250 resist. As seen from the figure, the proton beam exposed patterns cannot be removed after development, which indicates proton induced cross-linking of the AR-P 3250 resist. Further, the figure indicates

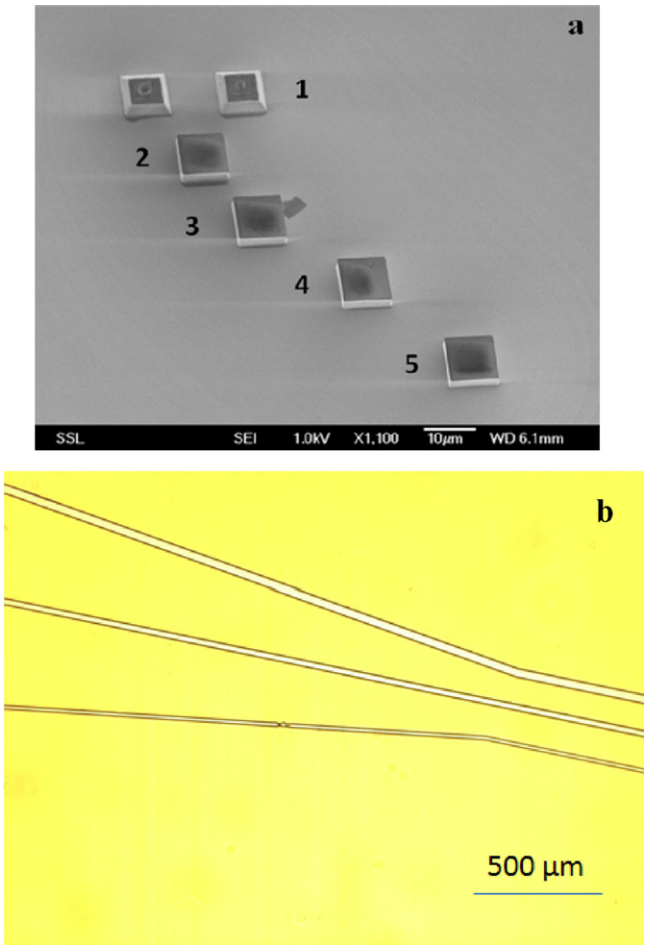

Fig. 1. (a) SEM images of 2 MeV proton beam written 10 × 10 μm^2 square pillars on AR-P 3250 with varying proton dose of 1–5 nC/mm^2 (PBW followed by flood UV exposure); (b) UV patterned ARP resist showing micron–millimeter sized features.

that the cross linking of the resist starts to happen at proton doses as low as 1 nC/mm^2 though the shape is not perfect. Pattering of the square pillars with a proton dose of 1 nC/mm^2 followed by a UV exposure results in ~3 μm tall tapered squares indicating that ~30% of the resist cross links. Square pillars standing 10 μm tall were obtained at doses of more than 2 nC/mm^2. Therefore an optimum dose of at least a few nC/mm^2 is required to fully cross-link the resist and withstand subsequent UV exposure and chemical development.

This test result suggests that the PBW and UV lithography can be successfully combined in AR-P 3250 to pattern small and large features respectively. The small features can be directly written using PBW and in the next step the larger features can be incorporated by UV lithography using a pre-patterned mask. Fig. 1b is presented here for illustration purpose to show how well the large arbitrary micron–millimeter sized features can be patterned on to AR-P 3250 through UV lithography.

Fig. 2 shows the contrast curve (height of the resist as a function of exposure dose) for AR-P 3250 to 2 MeV PBW followed by UV exposure and chemical development. The contrast curve was obtained by exposing the resist of given thickness (10 μm in this case) to a varying proton dose (1–25 nC/mm^2) and an optimized UV exposure. The SEM image shown in Fig. 1a reveals the height information of the developed resist. The contrast curve was obtained by measuring the height of the pillars for different proton doses using SEM images. The thickness is normalized to one, for fully cross

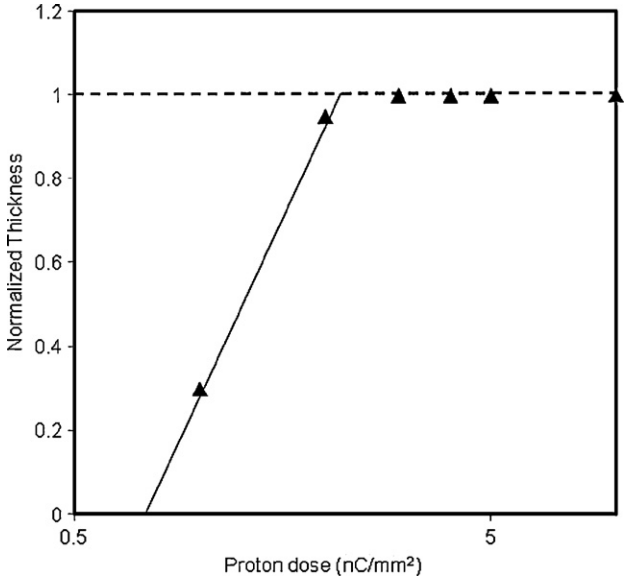

Fig. 2. Contrast curve for 10 μm thick AR-P 3250 using 2 MeV proton exposure. The thickness is normalized to one, for fully cross-linked resist.

linked resist. Here the contrast is defined as $\gamma = 1/[\log(D_f) - \log(D_i)]$ where D_f is the dose at which the resist is fully insoluble and D_i the dose where the resist becomes insoluble for the developer [16]. The measured contrast value of $\gamma = 2.0 \pm 0.2$ for AR-P3250 is comparable to the values reported for the negative tone resist HSQ for protons [17] and electrons [18]. Similar cross linking behavior for PBW and UV exposure is observed in maP1275 hv resist [12].

Following the results obtained for proton beam written $10 \times 10\ \mu m^2$ squares, 60 μm sized circular pillars were written starting from proton dosages of 10–60 nC/mm^2. A higher dose is chosen to guarantee sufficient cross linking of the resist. SEM results show that a proton dose of 20 nC/mm^2 or higher is required for writing the 60 μm circular features. Fig. 3a and b shows the pillars on AR-P 3250 with doses 10 nC/mm^2 and 30 nC/mm^2 respectively. From Fig. 3a it is clearly seen that a proton dose of 10 nC/mm^2 was not sufficient to fully cross link the resist. This difference could be attributed to various experimental conditions such as UV exposure timing, ratio of developer with DI water and developing time. Besides this to guarantee structural integrity during electroplating a nominal proton dose of 30 nC/mm^2 was chosen. As can be seen from Fig. 3b, smooth and vertical sidewalls are obtained at this nominal dosage. Inset to the figure is a high magnification image indicating smooth and straight sidewalls.

The developed resist is then coated with a very thin (few nm) Ti layer which acts as a seed layer for Ni electroplating. The Ni electroplating system available in CIBA employs a commercial plating system RD.50 from Technotrans AG, with a nickelsulfamate bath solution at pH 3.5 and a temperature of 50 °C. A 500 μm thick Ni stamp was plated. The Ni mould was delaminated from the Si wafer using the remover AR 300-73 under ultrasonic agitation at 60 °C for about 15 min followed by DI water rinse. Fig. 4 shows the high magnification image of the features present in the Ni stamp with the complete feature replication given as inset. It is clearly seen from the figure that the pillars in the resist master mould is well replicated into the metallic stamp as deep holes. The depth of the holes was about 10 μm matching with the height of the pillars in resist mould. These initial results on 10 μm AR-P 3250 are promising to continue with the fabrication of Ni stamp having deeper features (up to 30 μm) to achieve the final height requirement.

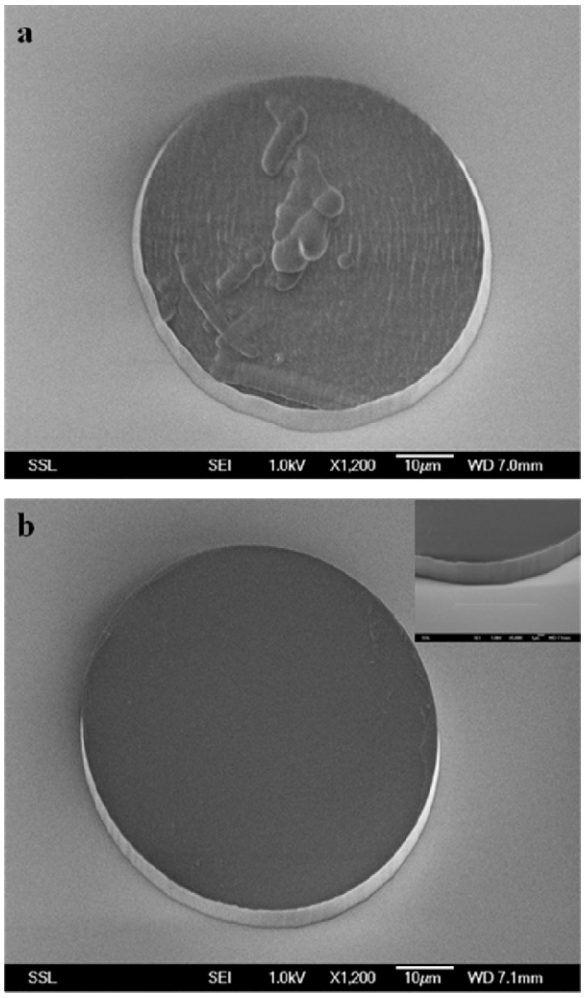

Fig. 3. SEM images of proton beam written AR-P3250 pillars with flood UV exposure: (a) 10 nC/mm^2 and (b) 30 nC/mm^2. Inset to (b) is high magnification electron micrograph indicating smooth side walls.

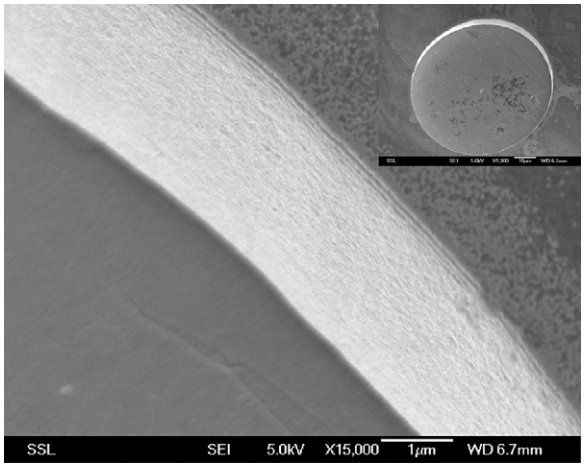

Fig. 4. High magnification SEM image of Ni stamp fabricated from AR-P 3250 resist mould that was exposed to a 30 nC/mm^2 proton dose. Inset to the figure is the overview of the complete hole replicated into Ni from a pillar in the resist mould.

4. Conclusion

PBW has shown great advantages in writing fine features with smooth and straight sidewalls in the newly tested resist AR-P 3250.

UV lithography could be combined to achieve short production time. The resist behaves as a negative resist under PBW, in contrast to i-line UV lithography where a positive resist behavior is observed. The optimum dose for PBW experiments in combination with UV lithography on AR-P 3250 resist is around 30 nC/mm^2. Ni moulds formed on these resist moulds are completely free of resist and are identical in smoothness and size compared to the polymer master mould.

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References

[1] P. Yager, T. Edwards, E. Fu, K. Helton, K. Nelson, M.R. Tam, B.H. Weigl, Nature 442 (2006) 412.
[2] E.A. Ottesen, J.W. Hong, S.R. Quake, J.R. Leadbetter, Science 314 (2006) 1464.
[3] Helene Andersson, Albert Van den Berg, Sens. Actuator B 92 (2003) 315.
[4] Stephen R. Quake, Axel Scherer, Science 290 (2000) 1536.
[5] Holger Becker, Laurie E. Locascio, Talanta 56 (2002) 267.
[6] M. Heckele, W.K. Schomburg, J. Micromech. Microeng. 14 (2004) R1.
[7] Frank Watt, Mark B.H. Breese, Andrew A. Bettiol, Jeroen A. van Kan, Mater. Today 10 (2007) 20.
[8] C.N.B. Udalagama, A.A. Bettiol, F. Watt, Nucl. Instr. Meth. B 260 (2007) 384.
[9] J.A. van Kan, A.A. Bettiol, S.Y. Chiam, M.S.M. Saifullah, K.R.V. Subramanian, M.E. Welland, F. Watt, Nucl. Instr. Meth. B 260 (2007) 460.
[10] F. Watt, J.A. van Kan, I. Rajta 1, A.A. Bettiol, T.F. Choo, M.B.H. Breese, T. Osipowicz, Nucl. Instr. Meth. B 210 (2003) 14.
[11] J.A. van Kan, A.A. Bettiol, F. Watt, Nano Lett. 6 (2006) 579.
[12] Liu Nan Nan, Shao Peige, Shripad R. Kulkarni, Jianhong Zhao, Jeroen A. van Kan, Key Eng. Mater. 447–448 (2010) 188.
[13] J.A. van Kan, A.A. Bettiol, F. Watt, Appl. Phys. Lett. 83 (2003) 1629.
[14] F. Zhang, J.A. van Kan, S.Y. Chiam, F. Watt, Nucl. Instr. Meth. B 260 (2007) 474.
[15] http://www.allresist.de/.
[16] Cui Zheng, Micro-nanofabrication Technologies and Applications, Springer-Verlag, 2005.
[17] J.A. van Kan, F. Zhang, C. Zhang, A.A. Bettiol, F. Watt, Nucl. Instr. Meth. B 266 (2008) 1676.
[18] Michael J. Word, Ilesanmi Adesida, Paul R. Berger, J. Vac. Sci. Technol. B 21 (2003) L12.