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High aspect ratio PDMS replication through proton beam fabricated Ni masters

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Abstract

In application areas where multiple samples are required (for example tissue engineering substrates), proton beam writing (PBW) is a suitable technique to fabricate high quality metal masters. These masters can then be used to replicate multiple copies in polymers, either through nanoimprinting or softlithography. Since poly(dimethyl siloxane) (PDMS) is a compatible material in tissue engineering we explore PDMS casting on Ni masters as an alternative way to replicate high aspect ratio micro structures. Ni masters with grooves spaced 2.5 μm apart, and 13 μm deep were successfully replicated in PDMS: These PDMS structures, which have aspect ratio of more than 5, are comparable to the best high aspect ratios reported in PDMS replication.

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Keywords: Proton beam writing; Ni stamps; High aspect ratio; Soft lithography; PDMS

1. Introduction

Cellular developments such as proliferation, differentiation, migration or apoptosis are guided by multiple surface cues that are potentially remodeled during cell culture assays. The cell responses are controlled by intra-cellular signaling pathways that are originally triggered by transmembrane proteins interacting with the engineered surface [1]. The surface chemistry characterized by the type of cell-binding ligands (peptides, proteins, etc.), their surface density [2–4] and spatial distribution [1,5,6] as well as their conformation [7], have been demonstrated to be important surface cues.

A popular technique for micro scale patterning of cells is microcontact printing. Here molecules of interest are first adsorbed onto a PDMS stamp and then transferred to a chemically activated substrate by direct contact of the substrate with the stamp. Regions that are not stamped are treated with another molecule that inhibits cell adhesion [8]. PDMS stencils are also used as a physical barrier to inhibit cell adhesion at specific areas on an underlying substrate [8]. PDMS has also been used successfully for cell culture in complicated geometries [9].

A challenge for the future will be the systematic exploitation of cell culturing in patterns on compliant substrates such as high elasticity PDMS or poly(acryl amide), that will be likely to provide more detailed insights into the interplay between cell shape, substrate compliance and forces exerted by the cell. In addition, flexible substrates also provide opportunities to study the effect of external forces on cell development and function [10]. One of the challenges here is the fabrication of high aspect ratio masters since they are not readily available. PBW has shown to be a technique for the production of high aspect ratio Ni masters [11,12]. In earlier studies three dimensional proton beam fabricated PMMA structures were successfully used for cell culture [13–15]. Since PBW is a direct write and therefore a relatively slow technique, and in cell studies

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typically many substrates are required, a fast replication method is desired to reproduce multiple copies of a high aspect ratio metallic master produced through PBW. Here we discuss the fabrication of high aspect ratio Ni masters through PBW and their successful application in PDMS replication.

2. Experimental procedures

The PBW has been performed at the Centre for Ion Beam Applications in the Physics department of the National University of Singapore. A more detailed description of the set-up can be found in elsewhere [16–18].

2.1. PMMA prototype

To test the feasibility of the intended geometry (see Fig. 1) a prototype was fabricated in a 3 mm thick layer of PMMA using a 1 MeV proton beam. Here the cell culture area is a $5 \times 5\ mm^2$ square flat area which is surrounded by a 30 μm wide and 20 μm deep corral. At the four sides of the cell culture area different link-ways have been fabricated to see how specific cell-types react to different sized connections. The inset in Fig. 1 represents an optical micrograph of the right bottom section of the PMMA prototype corral (15 μm wide link-way, 50 μm long) fabricated with a 1 MeV proton beam. One of the fabrication problems concerned the smallest connections (2.5 μm wide) which were not very stable. In thick resist samples, at the end of range the proton beam not only spreads but also deposits more energy compared to the surface. This leads to an undercut which weakens the narrower walls, resulting in collapse after substrate cleaning.

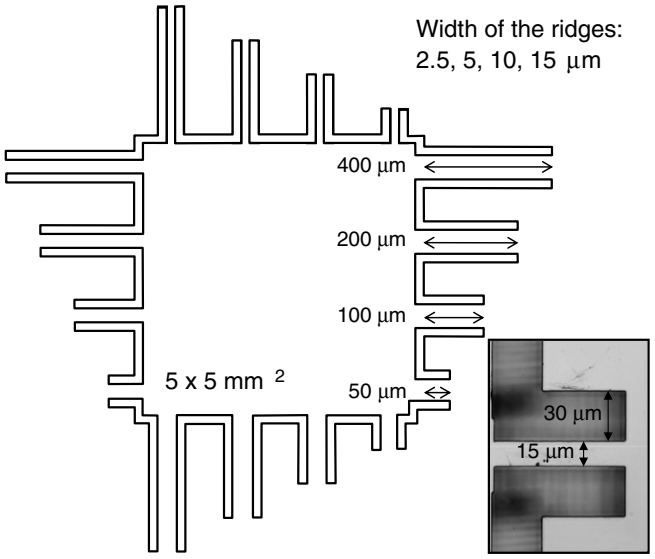

Fig. 1. Layout of the 3D microstructure corral. The inset shows a section of a prototype corral in thick PMMA, written with 1 MeV protons here the barrier is 20 μm deep.

2.2. Production of the Ni master

After evaluating the prototype it was decided to fabricate a Ni master in order to replicate multiple copies through nanoimprinting and softlithography. The design was kept the same as in Fig. 1. A Si wafer was coated with 20 nm Cr and 200 nm Au followed by six spincoating steps with PMMA (13 μm thick) (950 k molecular weight) dissolved in anisole (11 wt%). Here a spin speed of 2000 rpm (45 s) and a 5 min. curing bake at 150 °C in between the coats were used. After the last coat the wafer was baked at 180 °C for 30 min. To avoid end of range beam broadening this 13 μm thick layer of PMMA was exposed with 2 MeV protons. These protons have a range of 60 μm in PMMA and deviate less than 100 nm from their original straight path at a depth of 13 μm [19,20]. Next the sample was developed in IPA + DI water (7:3) followed by a DI water rinse. In a next step the sample was plated up to a thickness of 400 μm. This has been carried out using a typical Ni sulfamate bath solution in a Technotrans AG, RD.50 plating system [21]. In Fig. 2 two SEM photos of

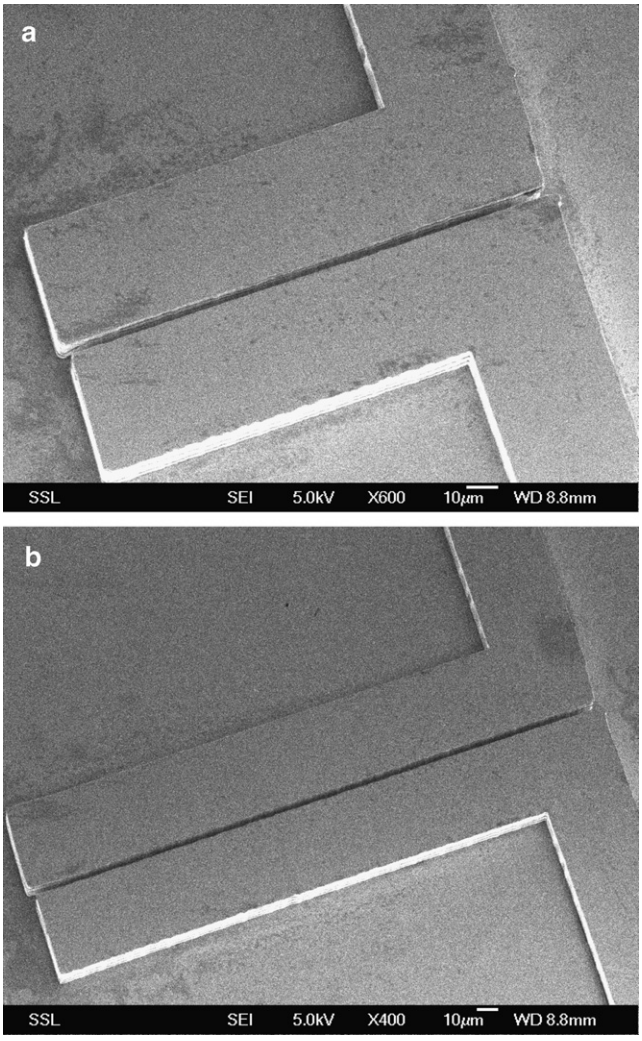

Fig. 2. SEM photo of two narrow exits (2.5 μm wide) in the Ni mold. In (a) the confinement is 100 μm long and in (b) 200 μm long.

2.5 μm wide gaps in the Ni stamp are shown for the 100 and 200 μm long link-ways. This stamp has 13 μm raised walls which are 30 μm wide.

2.3. Nanoimprinting in PMMA

Nanoimprinting was carried out with a commercial nanoimprinter (Obducat Technologies AB, NIL-2-PL 2.5 in. nanoimprinter) using 125 μm thick sheets of PMMA (Goodfellow). Some areas are reproduced correctly while other areas show a shift, see Fig. 3. This shift is attributed to two main factors; firstly back-side curvature of the Ni stamp gives rise to lateral forces during imprinting, and secondly neither the polymer film nor the stamp can be fixed during imprinting which gives rise to lateral movement between the stamp and polymer substrate. These shifts can be avoided by applying a more parallel stamp and polymer coated Si substrate [21]. However, transparent substrates are required for cell mobility investigations utilising optical microscopy, and therefore more research needs to be done to implement nanoimprinting to reproduce this type of structures in transparent polymer films.

2.4. PDMS replication

A 10:1 ratio of elastomer monomer:curing agent (Sylguard 184 Silicone Elastomer, Dow Corning) was thoroughly mixed and degassed in a glass desiccator. The PDMS was poured onto the Ni mold and degassed again using a vacuum pump to remove the trapped air bubbles generated during the casting inside the deep and narrow trenches. Next the PDMS casted Ni mold was placed in an oven and cured at 60 °C for 4 h. The PDMS replicas were manually peeled off from the Ni mold insert, and as can be observed in Fig. 4 the PDMS faithfully replicates the Ni mold. The 2.5 μm wide wall is strong enough and remains standing for the 50 μm long connection, see Fig. 4(b). However, at a length of 100 μm (2.5 μm wide) the wall is not strong enough and collapses into the trench, not shown here. This suggests that an aspect ratio of more than 5 is difficult to support in PDMS over relatively long dimensions. Similar limitations have been reported for PDMS replications by other groups [22]. The cracks observed in Fig. 4(b) were also observed in some parts of the original PMMA layer, they are reproduced in the Ni mold and also in the PDMS. These cracks are probably due to stress in the 13 μm thick PMMA layer, these cracks are not observed in thinner PMMA layers. The spincoating

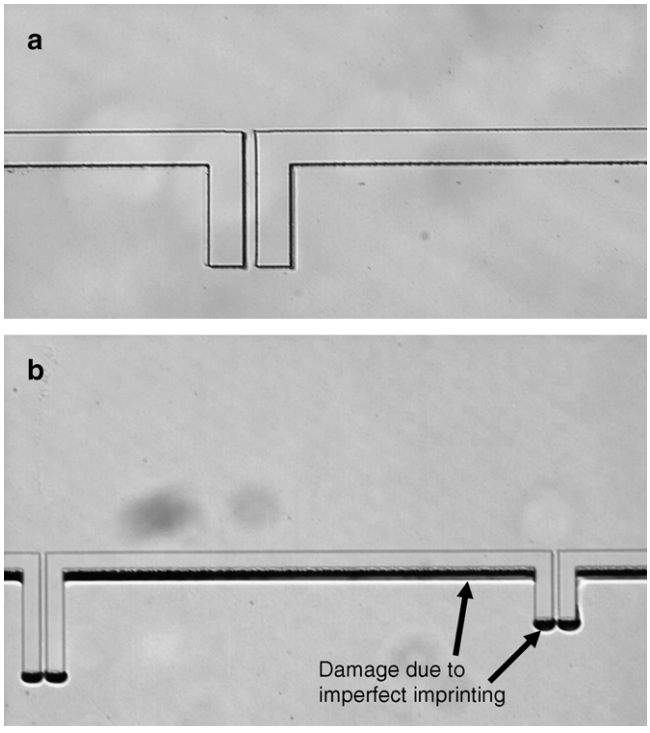

Fig. 3. Optical micrograph of two sides of the corral imprinted in a 125 μm sheet of PMMA, (a) one side shows faithful reproduction, and (b) the other side shows shift during imprinting.

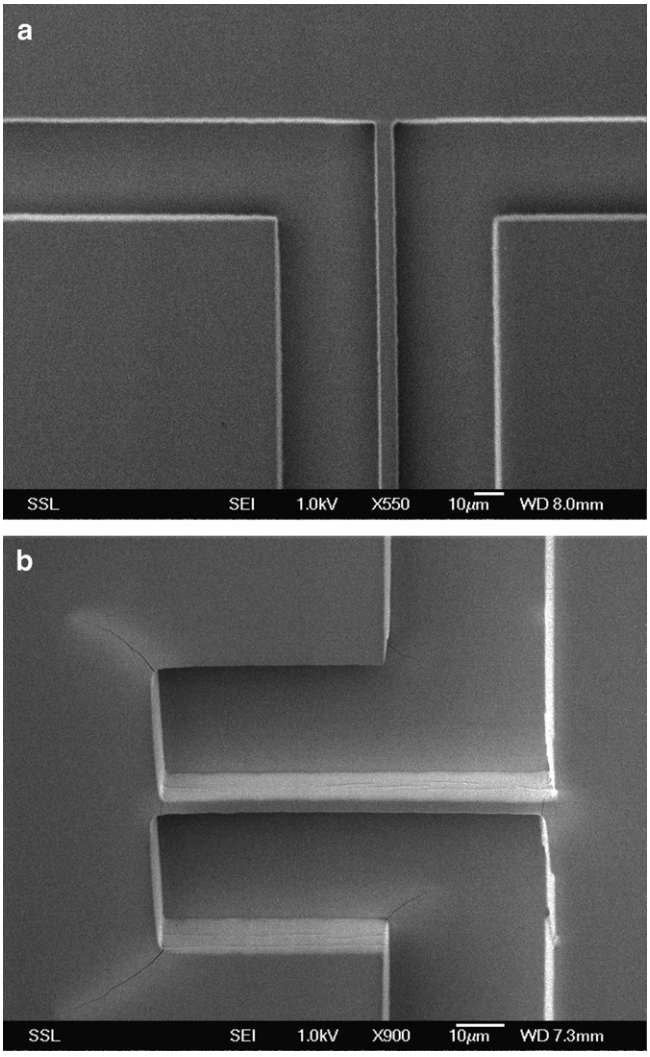

Fig. 4. SEM photo of (a) a 5 μm wide and (b) 2.5 μm wide exit channel of the corral replicated through PDMS casting on the Ni mold.

and backing procedure has to be optimized to reduce the stress in thick PMMA layers.

3. Discussion

In this paper we have demonstrated the successful fabrication of a Ni mold which can be used in nanoimprinting and softlithography to generate multiple polymer copies. More research is needed to improve the high aspect ratio nanoimprinting in PMMA polymer films. Aspect ratios of more than 5 have been achieved in the PDMS replication of the Ni mold, similar to state of the art PDMS replication. These molded PDMS structures will be used in future cell culture experiments. The curing time and temperature can be adjusted to minimize the curing time and improve the strength of the PDMS structures. Research is ongoing to improve the release of the PDMS through release layer coating on the Ni mold.

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