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Poly (dimethyl siloxane) micro/nanostructure replication using proton beam written masters

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Abstract

Proton beam writing (PBW) has been proven to be a powerful tool for fabricating micro and nanostructures with high aspect ratio. However, being a direct-write technique, and therefore, a serial process, PBW is not economic for low cost multiple component production. Techniques for replicating PBW structures with low cost are necessary for applications in for example nanofluidics, tissue engineering and optical devices. We have investigated casting poly (dimethyl siloxane) (PDMS Sylgard 184, Dow Corning Corp.) with PBW structures as masters. First, a 2 MeV focused H_2^+ beam was written into a 2 μm thick PMMA layer spin coated onto 50 μm thick Kapton film substrate. Next, these PMMA structures, with details down to 700 nm, were replicated with PDMS. Without any release coating treatment, PDMS circular pillars, 700 nm in diameter were successfully replicated. We also fabricated a nickel master with nanofeature dimensions and 2 μm depth using proton beam writing and sulfamate electroplating. The nickel master was used to successfully replicate a prototype DNA separation chip using PDMS.

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Keywords: Proton beam writing; PDMS casting; Replication

1. Introduction

The micro and nanofluidic device, which will provide integrated laboratory functionality on a single chip [1], is being promoted as a new area in biomedicine which may turn out to be as revolutionary as the IC in computing. By investigating, manipulating and exploiting micro, nano or picolitre scale liquid, unprecedented economies of scale with dramatically high speed, low cost, high sensitivity biological, chemical research and applications can be realized. Within nano channels, particles such as molecules and ions can be detected and manipulated individually [2].

The development and use of these fluidic chips rely on the fabrication of micro and nanostructures with increasingly low cost, which will in turn allow more and more researchers to access more efficient, reliable and automatic processes in biomedicine. The potential applications and challenges of exploiting micro and nanostructures have led to an increase in the research and development of new processes [3–7]. When fabrication feature dimensions approaches the sub-micron scale, traditional photo-lithography suffers from diffraction problems and becomes more and more expensive. New nano-lithographic processes are therefore required [3,5]. These processes include contact replication, such as imprint lithography, soft lithography and capillary lithography, where the contact replication resolution is determined by the quality of the mold or stamp feature dimensions. Charged particle focused beam writing such as electron beam writing (EBW), proton beam writing (PBW) and focused ion beam milling (FIB) are also finding niche roles in these new technologies. These direct-write processes are attractive because in general the fabrication resolution is not limited by diffraction limits as in

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the case of optical lithography, since the beam writing resolution is mainly determined by the ability to focus the charged particle beam.

In the last decade, materials such as silicon and glass have been the dominant choices for making micro and nanofluidic devices. More recently there has been increasing interest in polymer-based non-lithographic fabrication techniques using materials such as hydro gels, plastics and elastomers [4]. With these polymeric materials, the techniques of injection molding, embossing, thermal forming and replica molding can be applied and promise cheap components. For mass production these components will be inexpensive and disposable, while small quantity fabrication is also affordable. Another advantage of polymeric devices is the diversity of polymer materials available, providing extensive choices for different application requirements such as chemical resistance, optical transparency, mechanical flexibility and biological compatibility [8,9].

Currently the popular silicone elastomer poly-dimethyl siloxane (PDMS), which is 50 times cheaper than silicon per volume basis [4], is used for making microfluidic devices due to its desirable properties such as easy replica molding, good optical transparency, biological compatibility and ease of bonding to seal patterned structures [10,11]. However, most of these applications are with feature dimensions larger than 20 μm. Such structures can be realized with photo lithography using a low cost membrane mask and casting replication. Studies on PDMS fluidic structures at dimensions at the micron level and below is limited because of the difficulty in fabricating masters at these small dimensions.

To fabricate structures with feature dimensions of several microns or larger on glass or silicon, optical lithography is an ideal choice [3,4], with a beam of UV light passing through a mask and projecting the image of the mask on a layer of photo resist. For nanostructures, electron beam writing is often the choice to pattern an electron sensitive resist layer. The patterned resist layer, which in general is very shallow, acts as a mask for further etching the substrate to produce nanostructuring of silicon or glass. Recently imprinting, embossing and other contact replication technologies have been used for replicating nanostructures, where the imprinting or embossing molds are often fabricated using e-beam writing. Proton beam writing, which can be classed as the deep writing analogue of e-beam writing, has been proved recently to be a powerful tool for fabricating deep nano structures. P-beam writing is characterized by high aspect ratio structuring, exhibiting vertical and smooth walls, in resists such as PMMA, SU8 and HSQ [12,13]. Proton beam writing can realize much deeper structures than e-beam writing because the proton is much more massive than the electron, and therefore, can penetrate much deeper in materials whilst maintaining a straight path. PBW can therefore realize three dimension structuring directly without further etch steps. Like all direct-write processes, however, PBW is slow for fabricating devices at large quantities. In CIBA, research has been carried out to transfer PBW nanostructures to a nickel structure by electroplating, and using this nickel nanostructure as a mold to replicate polymer structure by hot embossing [14]. Because PDMS is soft material with low surface energy, this material promises low stress replication and easy release from the mold after replication, and so PDMS replication in principle should be much easier than hot embossing. In this paper, we report replicating PDMS nanostructures directly from proton beam written PMMA structures, as well as from nickel structures electroplated from PBW structures.

2. Experimental

To fabricate PMDS structure, it is important to fabricate a good quality mold or master and avoid strong adhesion between the master and the PDMS. Because silicon and glass has strong adhesion with PDMS, when the master is made of silicon or glass, the surface of the wafer should be treated with a silane-containing fluorinated functional groups since a monolayer of silane prevents irreversible bonding between the silicon and PDMS [10]. In our work, we use Kapton film instead of silicon wafer as substrate, which does not have strong bonding with PDMS.

The process of replicating PDMS structure from a PMMA master fabricated by PBW in CIBA is shown in Fig. 1, which involves following steps: (a) A thin 2 μm layer of PMMA resist (950 K molecular weight, 11 wt.% in anisole, from Microchem) was spin coated on 50 μm thick Kapton film (Kapton® HN from DuPon) which had been previously cleaned by rinsing with acetone and baked at 180 °C for 10 min. The resist was then patterned using proton beam writing using a 2 MeV H_2^+ beam focused into a 100 nm spot. At these resist thicknesses, the proton beam penetrates through the PMMA film, and stops in the Kapton film. (b) The exposed PMMA was developed, forming high aspect ratio structures in the PMMA but not in the Kapton film. The developer used was isopropyl alcohol IPA water (7:3) solution and developing time was 10 min at room temperature without agitation. (c) A piece of 170 μm think PTFE tape (3M™ PTFE Film Tape 5491) was fixed on the boundary of the patterned PMMA forming a reservoir for the PDMS precursor. The PTFE has low surface energy, and therefore, ensures easy release for the PMDS replicated component. (d) The PDMS polymer was made by combining a 10:1 ratio of PDMS Sylgard 184 base and PDMS Sylgard 184 cure agent (from Dow Corning, Midland, MI) and stirred rigorously until thoroughly combined. The mixture was then poured onto the patterned PMMA structure and put into a vacuum desiccator for degassing for 20 min at a vacuum of 5×10^{-1} mbar. (e) A microscope slide was put on to the PDMS and this stack was then cured at 60 °C in oven for 4 h. (f) The PDMS replica and the mold were separated.

We also used a nickel mold to replicate PDMS components. The nickel was made by plating a PBW patterned

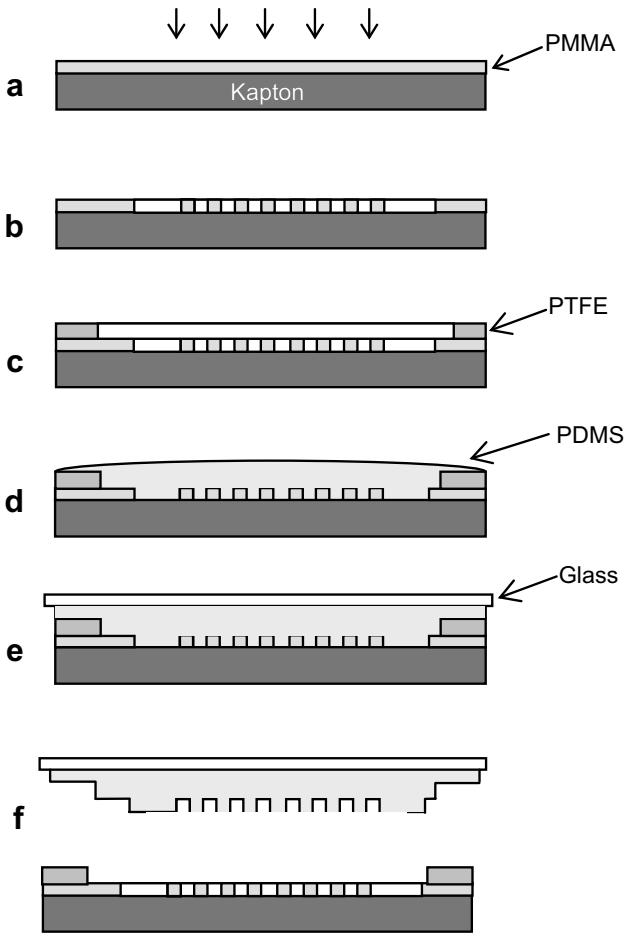

Fig. 1. A schematic representation of the process of PDMS replication used at CIBA.

structure of PMMA on a silicon wafer with a metal seed layer. For the electroplating process details please refer to [14]. After the nickel mold was fabricated, a prototype PDMS DNA separation chip was replicated using a process similar to that shown in Fig. 1.

3. Results

In many applications of micro/nanofluidics, bio analytical assays and sensors etc., it is important to realize PDMS structures with small feature dimensions and high aspect ratios. As shown in Fig. 2, we have fabricated an array of holes of sub-micron diameter in 2 μm thick PMMA layer on Kapton substrate and then cast PDMS on this array to produce an array of submicron PDMS pillars. This array has been fabricated for investigations into the interaction between biological cells and various 3D geometries fabricated in PDMS [15]. As shown in Fig. 2, all PMMA holes with diameter of 700 nm and depth of 2 μm (aspect ratio around three) in an array were successfully replicated to PDMS pillars. Experimental results show that aspect ratios less than three can be easily replicated while at these sub-micron dimensions replication becomes increasingly more difficult for aspect ratios higher than three. Under our current experimental conditions, PMMA holes with diameter of 300 nm and depth of 2 μm could not be replicated with PDMS since the pillars fractured inside the holes during separation of the master and the PDMS (step (f) in Fig. 1). Low aspect ratio structures in general have higher resistance to fracture because the contact interface area between the master and replicated structures is small compared to the cross-sectional area. A poor alignment in vertical direction during separation of the high aspect ratio PDMS structures also increases the failure rate, and therefore, it is important not only to reduce the interface adhesion between master and replica but also to improve alignment during separation. In the quest for improving the aspect ratio of PDMS replicated structures, we intend to investigate both surface modification of the master to reduce adhesion forces, and the methodology for improving the separation alignment.

Proton beam writing is fast direct writing process, and fabricating a PMMA master coupled with casting and curing a PDMS replica can be realized in a few hours depend-

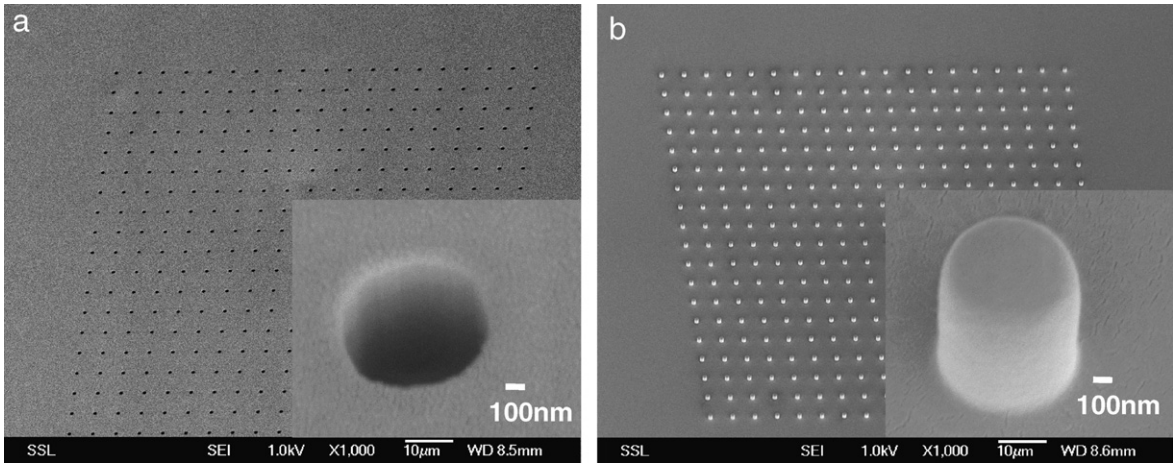

Fig. 2. (a) Hole array in PMMA on Kapton substrate and (b) PDMS pillars replicated from (a).

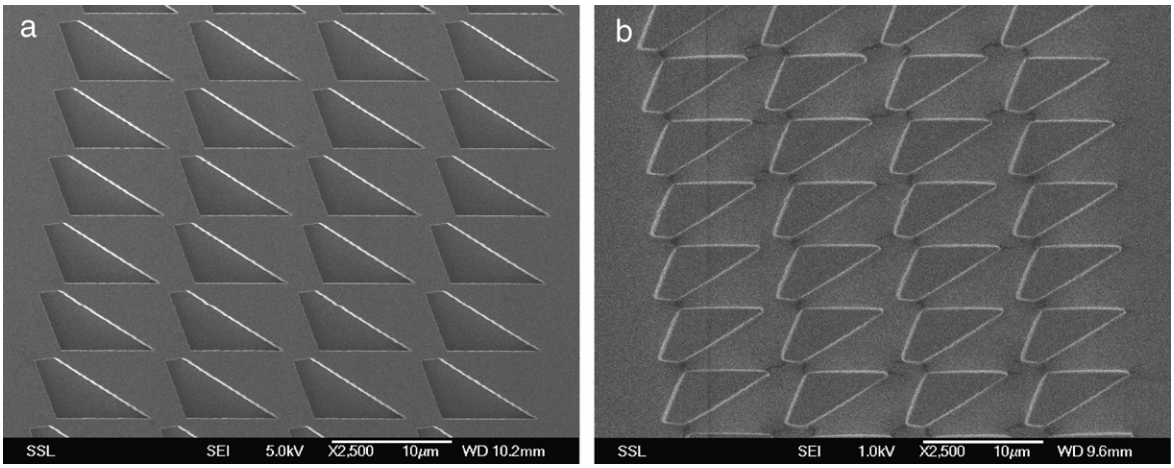

Fig. 3. (a) Nickel master of a DNA separation chip and (b) PDMS structure replicated from (a).

ing on the complexity. This rapid fabrication process is not only suitable for rapid prototyping of small quantities of components and devices, but there is also potential to increase production speed for PDMS curing by increasing the temperature. However, the PMMA master will lose its shape above 100 °C, and therefore, the temperature for curing PDMS with PMMA master is limited because high temperature can induce deformation in the PMMA master. Further reducing curing time, therefore, requires a more thermally stable master. If the casting quantity is large, it is also necessary to clean the master with a solvent such as teterabutylammonium fluoride 1 M solution in tetrahydrofuran after several replicating cycles. Therefore, we also require a master resistant to organic solvents, and a nickel master fabricated by plating a PBW pattern may be the ideal solution [16]. After optimizing a device by replicating PMMA masters of different designs, a nickel master can therefore be fabricated and used for mass production. Because of the low Young's modulus of PDMS, less stringent processing conditions are required, and replicating PDMS for many applications may be a much easier and cheaper solution than hot embossing. In CIBA we have previously investigated fabricating a nickel master or stamp with micron or nanofeature dimensions using PBW and electroplating. Here we have fabricated a nickel master with sub-micron structuring for a prototype DNA separation chip, with 100 nm feature sizes and a depth of 2 μm (Fig. 3(a)). With this nickel master, PDMS was cast and then cured at 100 °C for 60 min and then the replica was separated from the master. As shown in Fig. 3(b), the replicated PDMS structure has good precision.

4. Conclusion

We have demonstrated a process to replicate PDMS structures from a PBW PMMA master on a Kapton film substrate. The structures, exhibiting an aspect ratio of three and diameter of 700 nm, were successfully replicated, although replicating structures of similar dimensions but with larger aspect ratio has proved difficult due to the failure of separating the PDMS replica from the master. A more robust nickel master, with nano feature dimensions and a 2 μm depth, was also fabricated and used for replication. The PDMS structures replicated from the nickel master also exhibit good precision.

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