Fabrication of Perforated Membranes in Polymers using Imprint Lithography

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ABSTRACT

This study presents fabrication of mechanically stable, free-standing membrane structures in polymers down to 1.5 μm pore diameter by using all parallel patterning processes. Imprint lithography was used to define microscale patterns, which was combined with a sacrificial layer technique where double resist layers were spin-coated on Si substrates. A lift-off resist (LOR) and a low molecular weight poly(methyl methacrylate) (PMMA) were used as the lower sacrificial layer and a UV-curable SU-8 was used for the active membrane layer. The mechanical stability for the thin SU-8 membrane layers was achieved by employing a modified imprinting process which combines thermal imprinting with a post UV-curing process. The membrane was not released when PMMA sacrificial layer was used, however a clean and fully-released SU-8 membrane was obtained when LOR was used instead. We will also discuss some technical challenges to achieve the membrane structures such as stamp fabrication and high aspect ratio imprinting of SU-8. The development of a fast and low cost fabrication process for perforated polymer membranes will help open new vistas in several research fields, especially in biomimetic and bioanalytic devices.

Keywords: nanoimprint, polymer, freestanding, perforated, membranes.

1 INTRODUCTION

The ability to imitate architecture of naturally existing systems in an economical way is important because this will provide a platform for various fundamental and applied research activities. Among the various architectures, perforated membrane structures, which allow access from both sides, are among the most promising as they play an important role in various biological systems. The various applications of the membrane structures include biomaterials, lab-on-a-chip systems, separations**,** transport behavior, and polymer optics [1-3]. Membrane technologies have been used particularly in modeling cell membranes to study specific biological phenomena occurring at the cell membranes such as the formation and structure of lipid micro-domains of rafts [4], peptide/lipid interactions [5], cell-adhesions [6]. As an example, Mardilovich and Kokkoli constructed mica-supported lipid bilayer membranes from biomimetic peptide-amphiphiles and their binary mixtures with lapidated polyethyleneglycol molecules using the Langmuir-Blodgett technique [7]. Even though such supported membrane structures that are accessible from only one side are useful to study cell-adhesion behavior, it is the perforated membrane structures which represent the real biological system in which the adhesion and transport behaviors are determined by the environments on both sides.

Membrane structures with perforated micro- and nanoscale pores have been produced by a number of methods. Commercially available membranes are fabricated by ion track etching in polycarbonate [8] or anodization of aluminum [9] which produces randomly distributed or a hexagonal array of nanopores, respectively, with pore diameter as small as 10 nm. Perforated micro- and nanopores in specific locations in a membrane were produced using micro- and nanofabrication techniques. Lo et al. demonstrated fabrication of sub-5 nm pores using focused ion beam and electron beam techniques [10]. Electron beam in the transmission electron microscope followed by a size shrinkage by laser heating was also used to produce nanoscale pores in SiO_2 [11]. However, those methods are slow and expensive, and thus are not able to provide many identical samples, which are often required for study of many biological events. Recently, Shift et al. [12] reported fabrication of sustained polymer membranes using imprint lithography. Imprint lithography is a high throughput and low cost micro- and nanofabrication method using molding. The main drawback faced in their work was low mechanical stability of traditional imprint polymers such as PMMA or PC. Their membrane structures were sustained by polymeric columns for mechanical stability and thus were not free-standing.

In this study we have developed a fast and high throughput process to produce free-standing polymer membranes down to 1.5 μm pore diameter by using imprint lithography and a sacrificial layer technique. In order to achieve self-supporting mechanical stability, a UV-curable polymer SU-8 was used as the membrane layer and a modified imprinting process combining thermal imprinting with a UV-curing step was employed.

2 FABRICATION PROCESS

Figure 1 shows the process scheme developed in this study for producing perforated membranes in polymers. The process involves a number of sub processes:

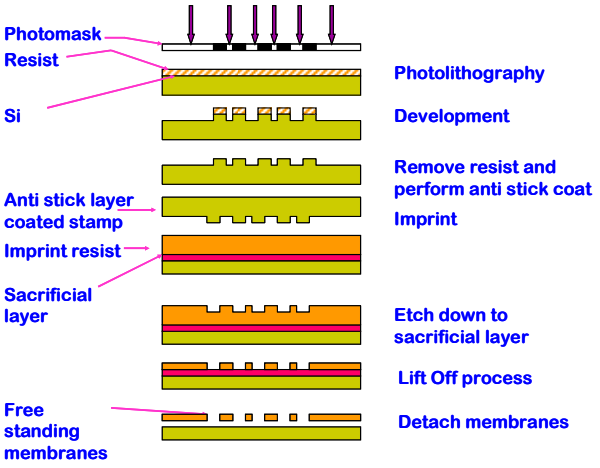

Figure 1. The process scheme for producing perforated polymer membranes.

photolithography and deep reactive ion etching (DRIE) for stamp fabrication, a modified imprinting process, and lift-off.

2.1 Stamp fabrication

The Si stamps were fabricated using a combination of photolithography and semiconductor micromachining techniques. Si wafers were initially spin-coated with a thin layer of HMDS used as an adhesion promoter [13]. After drying for 5 min, a 2 µm layer of S1813 photoresist was applied by spin-coating and subsequently a pre-exposure bake was performed at 95°C for 90 s. Photolithography was performed with a custom designed photomask in a 'Quintel' UV exposure station. The exposed wafer was then developed in MF 319 developer solution for 120 s, which was followed by washing in DI water bath for 2 min and drying with a N_2 gun.

The pattern transfer down to the Si substrate was achieved using a DRIE process. The Si etching was performed using an inductively coupled plasma (ICP) machine from STS systems at Micro Electronics Research Center (Georgia Institute of Technology). The gas chemistry and the power used were SF_6:O_2:C_4F_8 =130:13:100 sccm and 600 W, respectively. The DRIE process involved alternate etch and passivation cycles to etch down and subsequently passivate the sidewall so as to maintain a high degree of anisotropy, thus resulting in almost vertical sidewall profiles. The Si was etched to various depths ranging from 5 to 20 µm (Figure 2).

2.2 Anti-adhesion treatment of stamps

In order to improve imprint quality, i.e. a better demolding with little or no resist sticking to the Si stamp, a silane coating [14] was performed. An in-house designed CVD chamber was used to coat a fluorinated silane onto the Si surface. Prior to the coating, the stamp surface was

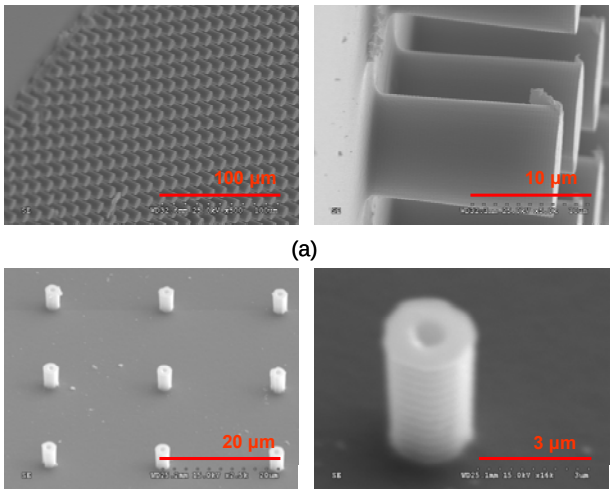

Figure 2. SEM images of Si stamp structures with different diameters: (a) 9 µm and (b) 2 µm diameter posts. They were produced by photolithography and DRIE.

exposed to an O_2 plasma for 30 seconds, leading to the formation of silanol groups at the Si surface. The silane coating resulted in hydrophobicity of the Si surface with the contact angle of 107°.

2.3 Imprint process

Si wafers are diced to 2×2 cm^2 and subsequently cleaned with acetone, isopropanol, and DI water followed by blow-drying with clean dry air. In order to achieve a release of the membrane layer, a sacrificial layer technique using double resist layers was employed. The cleaned wafer pieces were first spin-coated either with a lift-off resist (LOR 3B from Microchem) or a low molecular weight poly(methyl methacrylate) (PMMA, M_w=25 kg/mol) at 3000 rpm for 60 s resulting in 300nm in thickness. A post-baking was performed at 150°C for 3 min and 100°C for 3 min for LOR and PMMA, respectively. The samples are then spin-coated with SU-8 (Microchem) at 2000 rpm for 60 s, which results in a 5.5 µm thick SU-8 layer. A post bake is performed at 95°C for 5 min. Imprinting was performed with Si stamps under various conditions using a 6" nanoimprinter (Obducat, Sweden). Best imprint results for SU-8 were achieved at the imprint temperature of 135 °C and 40 bar pressure.

2.4 Post processing

The imprinted samples are subject to O_2 plasma etch to remove the residual SU-8 layer from the imprinted trenches, so that the LOR sacrificial layer can be exposed to the developer during lift-off. The O_2 plasma etching was performed at 250 mTorr and 150 W for 30 s. The etched samples are then cured with a UV lamp (λ = 346 nm) for 5 min and post baked at 95°C for 5 min. The UV curing

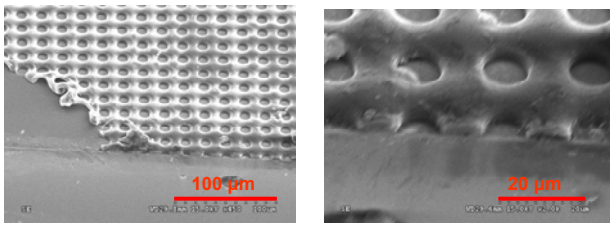

Figure 3. SEM images of imprinted SU-8 on Si substrate.

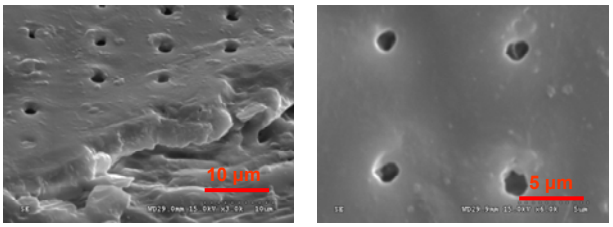

Figure 4. SEM images of a SU-8 membrane with PMMA as a sacrificial layer.

results in a crosslinking of the SU-8 resist, thus rendering it the desired mechanical strength and stability to be free-standing. The free-standing membrane was achieved by dissolving the LOR or PMMA sacrificial layer by placing the cured sample in an MF319 or acetone bath for 3 hours, respectively.

3 RESULTS AND DISCUSSIONS

A key challenge to fabricate free-standing membranes with micro- and nanopores is to select polymer materials that allow for imprinting of high aspect ratio structures with good replication fidelity and at the same time have enough mechanical stability to be free-standing. Thermoplastic polymers such as PMMA and PC, which are widely used for imprinting, do not provide enough mechanical stability [15]. SU-8 was chosen as the membrane layer because it is the resist widely used for high aspect ratio microstructures in the LIGA process and thus high mechanical stability was expected.

We first determined imprint parameters for SU-8 by performing imprints without having a sacrificial layer. Since the hard-baking temperature of SU-8 is 150°C, the flow at this temperature will be impeded by partially-cured SU-8. On the other hand, imprinting at a lower temperature below 120°C also resulted in incomplete filling of trench cavities. We achieved best imprint results when imprinting was performed at 135°C and 40 bars for 20 min. Figure 3 shows SEM micrographs of imprinted SU-8 without a sacrificial layer under these imprint conditions. Uniform and ordered pore patterns are observed. Even at the optimized imprint conditions, however, the replication fidelity was not as good as that for PMMA or PC, as observed in the sagging around pores. The increased mechanical strength forfeits decreased replication fidelity. Nonetheless, those parameters were used for imprinting of SU-8 with either a PMMA or LOR sacrificial layer underneath.

A slight resist adhesion to the Si stamp surface was observed during SU-8 imprinting, which did not occur when PMMA was used as resist. This increased adhesion is attributed to the highly negative charge of SU-8 and its partial curing. After each imprinting, the stamp was cleaned again by sonification in an acetone bath.

Initial testing with the sacrificial layer technique was performed by using a low molecular PMMA because the PMMA is known to be easily dissolved in acetone. The depth of pillars in the stamp was chosen to be slightly larger than the thickness of the SU-8 layer in a hope that there is no residual SU-8 at the bottom of the imprinted holes. Nevertheless, an O_2 plasma treatment was performed in order to make sure that the LOR layer is exposed.

Figure 4 shows the UV-cured SU-8 membrane with 1.5 µm diameter pores after attempting to remove the PMMA sacrificial layer in an acetone bath for 3 hours. Even after 1 day, the SU-8 membrane layer was not fully released. This is due to the insufficient solubility of PMMA to acetone and insufficient transport of acetone through the micropores.

When LOR was used as the sacrificial layer, however, a clean and fully-released SU-8 membrane was obtained, as is shown in Figure 5(a). The thickness of the membrane is expected to be slightly less than 5 µm. Even though the SU-8 membrane was a bit brittle after UV curing, it was mechanically stable enough to be self-supporting. In order to confirm perforation of the pores through the membrane, a 20 nm Au layer was deposited to both sides of the membrane and the SEM micrographs were taken. For that, the membrane was cut through the middle of a patterned area and one of the portions was reversed before placing on a Si dummy wafer in order to study the back side of the imprinted wafer. Figure 5(b) and (c) show the SEM micrographs for the SU-8 membranes from the top and bottom surfaces, respectively, clearly confirming the formation of perforated structures.

Figure 6 shows SEM images for the SU-8 membrane

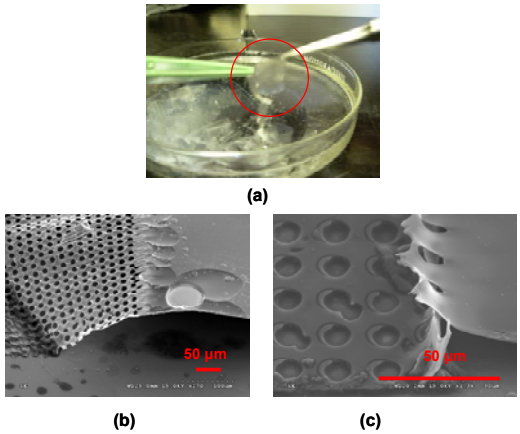

Figure 5. (a) Photograph for a SU-8 membrane after released from substrate and SEM images from (b) top and (c) bottom surfaces of the released membrane.

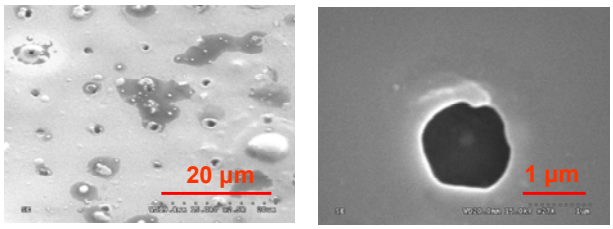

Figure 6. SEM images of a free-standing SU-8 membrane with 1.5 µm diameter pores fabricated by using a LOR sacrificial layer.

with the smallest pore structures we have achieved. The diameter of the pore was 1.5 µm. This was fabricated with a stamp containing pillar structures with 2 µm diameter. The pore structures are less sagged than the larger pores depicted in Figure 3. This can be attributed to different filling behavior for structures with different diameter/period ratios. Considering the sub-10 nm resolution of imprint lithography, the method developed in this work can be extended to the nanometer scale. However, imprinting of much higher aspect ratio structures and development of a new resist complying with both easy filling and enough mechanical strength are prerequisites.

4 CONCLUSIONS

A novel low cost and high throughput fabrication technique to fabricate free-standing perforated membranes in polymers was developed by combining imprint lithography with a sacrificial layer technique. The use of LOR as a sacrificial layer helped reduce fabrication time and cost by eliminating any backside etching procedures to make the membranes free standing. The mechanical stability issue of membranes has been addressed by using a UV curable resist allowing for greater stability than traditional imprint polymers like PMMA or PC. Such a high throughput fabrication process for perforated polymer membranes will help open new vistas in many research fields especially in biomimetic and bioanalytic devices.

5 ACKNOWLEDGEMENT

This research was supported by the Louisiana Board of Regents - Research Competitive Sub-program (RCS) (Contract No. LEQSF(2006-09)-RD-A-09 and by the LSU Faculty Research Grant in 2005-2006. We also thank the LSU Center for Advanced Microstructures and Devices (CAMD) for technical support, Profs. M.C. Murphy and D. Nikitopoulos for fruitful discussions, and the staff at Micro Electronics Research Center (Georgia Institute of Technology) for assistance with DRIE work.

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