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Fabrication of polymeric dual-scale nanoimprint molds using a polymer stencil membrane

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Abstract

We report on a simple and effective process that allows fabricating polymeric dual-scale nanoimprinting molds. The key for the process is the use of a thin flexible SU-8 stencil membrane, which was fabricated by either photolithography or thermal nanoimprint lithography (NIL). The stencil membrane with microscale pores was assembled into a nanopatterned substrate, producing a dual-scale structure. The assembled structure was used as a template to produce polymeric imprinting molds via UV-NIL. With this method, we demonstrated dual-scale nanoimprint molds having nano-pillars of 251 nm diameter and 146 nm high on top of microscale square protrusions of 5 μm wide and 3.6 μm high. The resin mold with the dual-scale structure was successfully used to produce a freestanding membrane with dual-scale perforated pores via UV-NIL. After metal coating and integrated into microfluidic devices, this freestanding membrane can potentially be used as a substrate for surface plasmon resonance sensors.

Graphical Abstract

Keywords

Nanoimprint Lithography (NIL); dual-scale molds; polymer stencil membrane; micropore; nanopore

1. Introduction

The ability to produce multi-scale or dual-scale hierarchical structures is important for the development of applications such as surfaces with directional wetting and spreading, dry

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adhesive motivated by gecko, and lab-on-chips [1]. One interesting hierarchical structure for the lab-on-chip application is a freestanding polymer membrane with nanoscale through-holes (nanopores) integrated with microscale fluidic compartments. Such a structure can be used as a platform for molecular separation and sorting [2], cell trapping and enrichment [3], and organs-on-chips [4]. After a metal coating, such a membrane structure can also be used as a substrate for surface plasmon resonance (SPR)-based biosensing [5, 6].

Nanoimprint lithography (NIL) is a promising method for the fabrication of the nanopore membrane with microscale compartments, due to its ability to produce large area structures at low cost and with high throughput [7]. Thermal-NIL has demonstrated sub-10 nm structures imprinted in a thin resist layer [8]. However, production of a nanopore membrane by thermal- and UV-NIL is more challenging than producing imprinted surface patterns, mostly because high aspect ratio NIL is usually required to achieve a membrane thickness for sufficient mechanical strength and easy handling of the membrane. Our group has demonstrated fabrication of a freestanding polymer membrane with nanopores with diameters less than 100 nm via thermal-NIL and used the membrane for detection of DNA molecules via transient current measurements across the nanopore membrane [9]. A Si mold with microneedles formed by wet chemical etching of Si was used, which makes it difficult to produce the membrane structure with high density nanopore arrays with microscale fluidic compartments. Such structures have never been realized by NIL, attributed mostly to the difficulty in fabricating a large area mold with the hierarchical structures.

There are mainly two top-down fabrication methods for the dual-scale hierarchical structures: one is a two-step photolithography and the other is a sequential thermal-NIL [1]. However, the two-step photolithography technique is limited to the fabrication of microscale patterns set by the wavelength of the light source used. For the sequential thermal-NIL, it is difficult to adjust the imprinting temperature to prevent collapse or reflow of predefined structures during the second imprinting. Two-step UV-assisted capillary molding technique was recently developed [10]. A partially UV cured microstructure was further molded to produce nanostructures on its top, making a monolithic hierarchical structure. However, controlling the degree of UV curing is exceedingly difficult. Here, we present a simple method to produce dual-scale nanoimprint molds using a polymer stencil membrane and single-step UV-assisted molding technique, which allow excluding two-step UV-assisted molding process.

2. Materials and methods

The first step of fabricating polymeric dual-scale nanoimprint molds is to fabricate a polymer stencil membrane with microscale through-holes via photolithography or thermal-NIL. For photolithography, a 1 μm thick lift-off resist (LOR) layer (LOR-7B, MicroChem) was first spin-coated on a silicon (Si) substrate as a sacrificial layer and baked. On the LOR layer, a thick SU-8 layer of different thickness (SU-8 2005, SU-8 2010, SU-8 2020, and SU-8 2035, MicroChem) was spin-coated and baked. The spin-coating speed, soft and post exposure baking temperatures, and UV exposing energy were selected according to the company protocol provided. After exposure and development of the uncured SU-8, the membrane was released via dissolving the sacrificial layer with a developer (Microposit

MF-319, MicroChem). For thermal-NIL, in the same combination of sacrificial and SU-8 layers the microscale pores were imprinted using a Si mold. Details of the process to form the polymer stencil mask via thermal-NIL have been published in [7].

The second step involves producing a nanostructured substrate, which has been done via thermal-NIL into poly(methyl methacrylate) (PMMA) substrate (750 μm thick sheet, Goodfellow). The thermal-NIL was carried out at the imprinting temperature and pressure of 130 $^{\circ}\text{C}$ and 3.5 MPa, respectively, for 5 min by using a commercial nanoimprinter (Eitre6, Obducat). Demolding was performed at 70 $^{\circ}\text{C}$ manually. The nanostructured substrate has nanoscale cavity patterns with the pitch, diameter and depth of 450 ± 30 nm, 240 ± 30 nm, and 200 ± 40 nm, respectively.

The released membrane was dipped into isopropyl alcohol (IPA) (isopropyl alcohol, Sigma-Aldrich) and then laid on a nanostructured substrate, which allowed achieving a good conformal contact between the membrane and the nanostructured substrate. (**Fig. 1a, Step 1**). It should be noted that neither glue nor any sort of adhesive was used between the released membrane and the nanostructured substrate. The assembled substrate with dual-level pores, i.e. the microporous membrane on the nanostructured substrate, was treated with a thin polydimethylsiloxane (PDMS) layer in the liquid phase [11] or a fluorinated silane ((Heptadecafluoro-1, 1, 2, 2-Tetrahydrodecyl)Trichlorosilane, Gelest) in the vapor phase to reduce adhesion during the subsequent UV-NIL process.

A UV-curable resin (PUA511RM, Minuta technology) was used to transfer patterns on the assembled substrate into UV-cured polymers via UV-NIL (**Fig. 1a, Step 2–4**). Drops of the UV-curable resin were dispensed against the assembled substrate. Then, a flexible polycarbonate (PC) film (~ 250 μm thick polycarbonate sheet, ePlastics) was slightly pressed against the liquid drop and used as a supporting backplane. In the curing process, the sample was exposed to flash-type UV light (250–400 nm) for 10 s, at an intensity of ~ 1.8 W/cm^2 by using the nanoimprinter. Lastly, the UV-cured sample was peeled off from the assembled substrate using a sharp tweezer. The UV-cured sample was used as a master mold and replicated twice by UVNIL to make a replica with the same polarity. This step is not necessary when the UV-cured sample from the assembled substrate with dual-level pores is directly used as the mold for the final UV-NIL process to produce a membrane with perforated dual-level pores.

In order to produce a membrane with perforated dual-level pores, the resin mold and polycarbonate (PC) substrate was first coated with a thin PDMS layer to avoid an adhesion problem between substrates (e.g. the resin mold and PC substrate) and a membrane to be created (**Fig. 1b, Step 1**). Then, a drop of the UV-curable resin (PUA511RM, Minuta technology) was dispensed between the resin mold and the PC substrates (**Fig. 1b, Step 2**) and UV-NIL was performed in the same NIL system with the UV exposure time of 10 s under 1 MPa (**Fig. 1b, Step 3**). Finally, the freestanding membranes having dual-scale pores were gently peeled off from the PC substrate (**Fig. 1b, Step 4**). Fig. S1 in the supplementary document shows schematics of the entire pattern transfer processes for UV-resin master molds and UV-resin molds with dual-scale pores and dual-scale pillars.

3. Results and discussion

The key feature of this fabrication process for dual-scale NIL molds is to use a polymer stencil membrane that forms a good contact with a nanostructured substrate. SU-8 was chosen as the membrane material because of its high mechanical stability after UV curing. In order to obtain the polymer stencil membrane with perforated micropores, a sacrificial layer was coated on Si substrate prior to spin-coating the SU-8 layer. After forming microstructures via either photolithography or thermal-NIL, the membrane was released by dissolving the sacrificial layer. SU-8 membrane with various thicknesses can be readily produced. Considerations in determining the thickness of the SU-8 layer include mechanical strengths for designed applications, handling of the thin membrane as well as the ability to achieve a good conformal contact with the underlying nanostructured substrate. A thick membrane after release can be easily handled but the contact to the underlying nanostructured substrate becomes worse. A 3.6 μm thick membrane was initially used because it is a thickness without posing any issues in handling the membrane [7]. Fig. S2a in the supplementary document shows a photograph of a large area SU-8 membrane (4-inch diameter) fabricated by thermal-NIL. The SU-8 membrane was fully covered with square shaped cavities of 5 μm width. Fig. S2b-c show scanning electron micrograph (SEM) images of an example SU-8 membrane from the top and cross-sectional view. The SU-8 membrane was folded before putting on a SEM sample holder, so that we can observe both sides of the membrane at the same time.

SEM analysis of the UV-resin master, UV-resin mold, and UV-resin freestanding membrane were carried out to evaluate the pattern fidelity during pattern transfers. It should be noted that about 5 nm thick gold/palladium (Au/Pd) layer was deposited for SEM imaging. Fig. 2 shows SEM images of fabricated UV-resin master, UV-resin mold with negative polarity, and UV-resin mold with positive polarity. All replicas were successfully formed with dual-scale structures. No considerable dimensional variations in the microstructures were observed. However, small dimensional variations were observed for nanostructures. For the UV-resin master, the nanopillars were 254 nm wide and 146 nm high. The nanopores in the UV-resin mold with negative polarity were 255 nm wide. The nanopillars in the UV-resin mold with positive polarity were 251 nm wide and 142 nm high. Overall, small variations occurring in each step may be attributed to the shrinking of the UV-resin during curing, the relaxation of the cured UV-resin after demolding, and the dimension change of nanostructures after coating the thin PDMS layer [12]. Also, it is observed that the nanostructures in the peripheral area of the microstructures were not replicated well. We attribute it to the use of a thin PDMS layer for anti-adhesive coating; upon imprinting residual PDMS molecules are pushed towards the peripheral area of the micropores, which fills the nanopores in the area. The residual PDMS could be removed via sonication after the PDMS coating. However, in our process, sonication could not be carried out because the SU-8 membrane put on the nanostructured substrate would then be separated. As an alternative to the PDMS coating, a fluorinated silane was coated in the vapor phase. Indeed, replicating nanostructures at the peripheral location was significantly improved as shown in Fig. 3. Another alternative solution would be the use of a hydrophobic UV-curable resin, e.g. perfluoropolyether (PFPE), which does not require an anti-adhesive coating layer.

Since a thin membrane can be easily torn due to its feeble mechanical strength, it may be a problem to use the thin membrane in practical fields [5]. The membrane thickness corresponds closely to the height of UV-resin molds, which can be simply controlled by using different thick SU-8 membranes. The SU-8 membrane thickness was tuned by using different SU-8 solutions and adjusting the spin-coating speed. In addition to 3.6 μm , thicker membranes with three different thicknesses of 10 μm , 20 μm , and 30 μm were prepared and put on a nanostructured substrate without using adhesives as previously, followed by coating the fluorinated silane as an anti-adhesive coating layer. After UV-NIL, UV-resin master molds were obtained, as shown in Fig. 4. For thick SU-8 membranes of 20 and 30 μm thickness, defect in the peripheral area on top of micropillars ripping out of entire micropillars were observed. It is attributed to the large gap formed between the SU-8 membrane and the nanostructured substrate into which UV-resins are squeezed during UV-NIL, forming sidewall protrusions. This is schematically illustrated in Fig. S3 in the supplementary document. During demolding, the sidewall protrusions prevent the cured UV-resin layer being properly demolded (Fig. S4 in the supplementary document). The length of the sidewall protrusions increased with increasing the membrane thickness. The results are summarized in Fig. S5 in the supplementary document.

The dual-scale UV-resin mold was evaluated as imprinting molds by fabricating a freestanding membrane having dual-scale perforated pores in a UV-resin layer. Fig. 5a-c show SEM images of a fabricated UV-resin freestanding membrane. Both the microstructures with 15 μm pitch and 5 μm width and the perforated nanopores of 251 nm diameter were uniform. A cross-sectional image shows that the membrane thickness at microstructures and nanostructures were 2.7 μm and 74 nm, respectively. The membrane thickness was slightly different with the height of mold structures, which is attributed to the high-wettability difference between the PDMS coated substrate and the PUA resin and also to the use of a hierarchical structure as a mold, resulting in a non-residual layer of the PUA resin after UV-NIL [13]. Our results indicate that the UV-resin mold with dual-scale pores is useful to produce perforate dual-scale structures in a freestanding membrane with good replication fidelity via UV-NIL.

4. Conclusions

We have developed a simply and highly efficient method for fabricating dual-scale nanoimprinting molds by using a polymer stencil membrane. Using this approach, the polymeric dual-scale molds have been produced within several minutes. We found that the surface treatment procedure as well as the SU-8 membrane thickness play important roles to fabricate dual-scale imprinting molds. The polymeric dual-scale nanoimprinting molds have demonstrated fabrication of a freestanding membrane having dual-scale perforated structures. This membrane can be integrated into polymer-based microfluidic devices and used as SPR based sensor after metal coating [5].

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Highlights

- A simple and effective process of fabricating polymeric dual-scale nanoimprinting molds was developed.
- The process for the dual-scale molds consists of the assembly of a thin flexible SU-8 membrane with microscale pores into a nanopatterned substrate, followed by the replication into a UV curable resin by UV-NIL.
- A freestanding membrane having dual-scale perforated structures was fabricated by the dual-scale nanoimprinting mold.

Fig. 1.

(a) Schematics of fabricating dual-scale nanoimprint molds: place a piece of SU-8 membranes over a nanostructured substrate. Then, treat with a thin PDMS layer or a fluorinated silane (1); dispense drops of UV-curable resin and slightly press with a flexible PC substrate. Then, expose to flash-type UV-light (2); peel off the UV-cured sample (3); and coat a thin PDMS layer on the UV-cured sample for self-replicating (4). **(b)** Schematics of fabricating UV-resin freestanding membranes having dual-scale perforated structures: dispense drops of UV-curable resin on a PC substrate coated with the thin PDMS layer (1); slightly press with the UV-resin mold self-replicated from the UV-resin master and coated with the thin PDMS layer. Then, expose to flash-type UV-light (2); peel off the UV-resin mold (3); and gently peel off the UV-cured membrane from the PC substrate (4).

Fig. 2. SEM images of fabricated UV-resin master (a)-(c), UV-resin mold with a negative polarity (d)-(f), and UV-resin mold with a positive polarity (g)-(i), correspondingly, in the top, middle, and bottom row. The UV-resin mold with a positive polarity was used to fabricate UV-resin freestanding membrane as shown in Fig. 5.

Fig. 3. SEM images of the replicated UV-resin master. In this case, a fluorinated silane in the vapor phase was treated on the assembled substrate (e.g. a SU-8 membrane on a nanostructured substrate) instead of coating the thin PDMS layer.

Fig. 4.

SEM images of the replicated UV-resin masters by using different thick SU-8 membranes. 10 μm , 20 μm , and 30 μm thick SU-8 membranes were used, correspondingly, in the left, center, and right column. A sidewall protrusion was appeared when thick SU-8 membranes were used (Supplementary Fig. S3). Also, there were uncompleted replications by formatting air-pockets and defects, respectively, during molding and demolding. Details are shown in supplementary Fig. S4.

Fig. 5. SEM images of the fabricated UV-resin freestanding membrane. The total size of the membrane is $2\text{ cm} \times 2\text{ cm}$. The UV-resin mold with a positive polarity as shown in Fig. 2 was used to fabricate the UV-resin freestanding membrane.