

# Nanofeature-Patterned Polymer Mold Fabrication toward Precisely Defined Nanostructure Replication

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A simple strategy for patterning and replicating high aspect ratio nanostructures onto a polymer mold is reported. A mercapto ester type UV-curable prepolymer has been introduced as a choice of material for manufacturing polymer molds having nanopatterns with physical barriers sufficiently hard and robust enough to preserve firm and concrete nanostructures. In addition, a simple surface treatment technique for easy release of coated film from the polymer mold has been introduced. A polymer mold having precise nanoscale patterns of high aspect ratio with high feature density was successfully fabricated, and its nanopatterns were properly transferred onto the surface of a thin replica film, demonstrating the potential of this polymer material as a stamp for rapid replication of accurate nanostructures with great simplicity.

## Introduction

The establishment of an easy and practical strategy for patterning micro- and nanostructures is key toward establishing reservoirs for many electronic/optical devices, biomedical applications, and biosensor applications. Photolithography has been a dominant technology for micro- and nanostructure fabrication. However, as the cost of short-wavelength light source systems and photosensitive polymers increases significantly and the required feature size is reduced, photolithographic technology will eventually reach its limit. For these reasons, extensive efforts have been made to replace photolithography with simple techniques employing a replica mold for patterning micro- and nanometer-scale features.

Over the past 10 years, simple techniques such as imprint lithography,<sup>1–5</sup> soft lithography,<sup>6,7</sup> capillary force lithography,<sup>8,9</sup> polymer transfer printing,<sup>10</sup> and others<sup>11–17</sup> have been developed for patterning micro- and nanoscale features, and

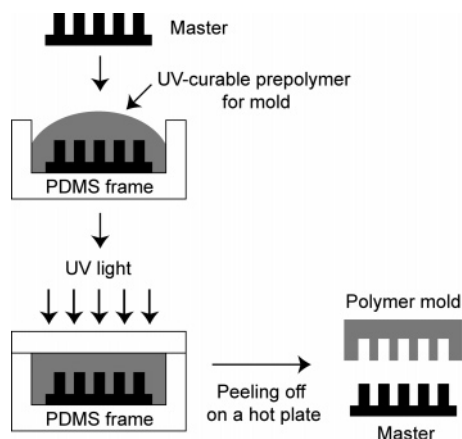
displayed substantial results. Particularly, imprint lithography (IL)<sup>1–5</sup> based on a hard mold has been utilized successfully as an alternative for nanostructure fabrication applicable for manufacturing integrated circuits, nanofluidics, photonics, and optical devices. However, hard molds are vulnerable to high pressure, leading to formation of cracking during processing, and they are also easily contaminated. Soft lithography,<sup>6,7</sup> which is based on a soft polymer mold, has also been successfully used in microscale patterning and fabrication of fluidic devices. Poly(dimethylsiloxane) (PDMS) rubber has been widely adopted as a stamp for transferring patterns onto various surfaces owing to its high elasticity and ease of replication. However, the softness of the mold itself could lead to the collapse of nanostructures<sup>6</sup> when applied to nanostructure fabrication.

Recently, the applicability of soft polymer molds has been extended to the field of nanostructure fabrication.<sup>9–17</sup> In previous studies,<sup>9–11</sup> the potential of fabricating nanostructures of various shapes and sizes using photocurable soft replica molds has been reported. Although these soft replica molds have displayed good performance for nanostructure fabrication, some challenges still remain such as transferring nanostructures with high aspect ratio onto thin polymer film, reduction of thick residual polymer layer, unnecessarily strong adhesion between the mold and the pattern-transferred polymer layer, and swelling in organic solvent which limits its potential application toward the fabrication of highly accurate nanostructures to be applied to the manufacturing of integrated circuits, fluidic devices, and biosensors.

In this study, we used a commercialized mercapto ester type prepolymer, Norland Optical Adhesives (NOA) 63 (Norland Products Inc.), as the polymer mold material. This is a clear, colorless, and photocurable prepolymer that cures under UV light ( $\lambda = 365$  nm). Owing to its high adhesiveness and transparency, it is generally used as UV-curable optical adhesive<sup>18–22</sup> for purposes such as cell immobilization<sup>18</sup> and film coating<sup>19</sup> on solid substrates. Although NOA 63 is not

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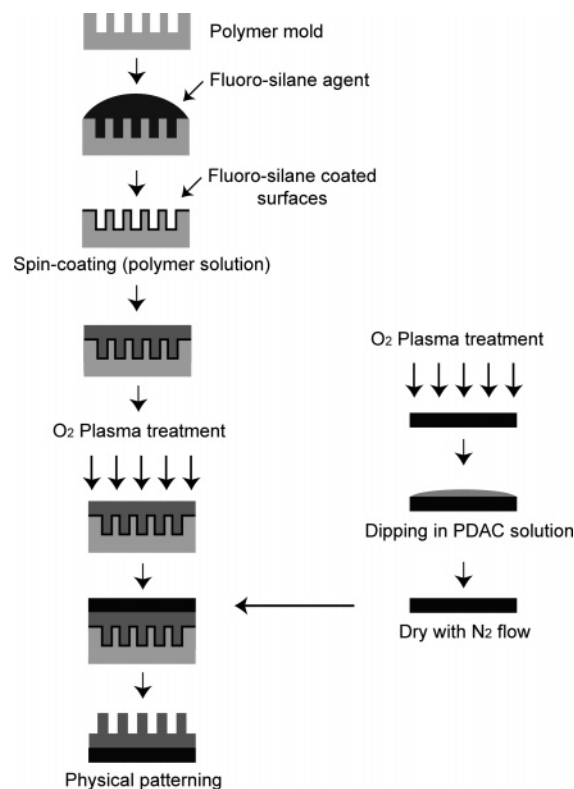
**Figure 1.** Schematic illustrations for the fabrication of NOA 63 based polymer mold.

considered to be an appropriate material for constructing a mold because its strong adhesion to a rigid support to which it is glued prevents its release from the support due to its high surface energy, its very unique thermal property lowers the surface energy at increased temperature, facilitating its easy release from the solid support. Here, we introduce this material as a candidate for fabricating a polymer mold for patterning nanostructures of high aspect ratio. Also, a simple technique is introduced for modifying the surface of polymer mold using fluorosilane as an adhesion reducer to accurately transfer topographical features onto polymer film on various substrates.

## Experimental Section

**Materials.** A commercialized mercapto ester type UV-curable prepolymer, NOA 63 (Norland Optical Adhesives 63), was purchased from Norland Products Inc. (Tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-1-trichlorosilane was purchased from United Chemical Technologies. Poly(dimethylsiloxane) (PDMS, Sylgard 184) was purchased from Dow Corning. Poly(diallyldimethylammonium chloride) (PDAC, 20 wt %, MW 100 000–200 000) and polystyrene (PS, 10 wt %, MW ~100 000) were purchased from Aldrich.

**Fabrication of Polymer Mold.** Figure 1 shows the schematic for fabricating a polymer mold using a photocurable prepolymer, NOA 63. We poured the prepolymer on the master, in this case SiO<sub>2</sub>/Si wafer, and cured it under UV light ( $\lambda = 365$  nm), using a UV lamp (Philips, TL 8W) as a light source. To peel off the polymer mold from the master, the surface of the master was treated with the vapors of the silane agent, (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-1-trichlorosilane, prior to casting the prepolymer. To avoid breaking and damaging of the master, a PDMS frame was used as a support. Precuring for 20 min was followed by postcuring for 12 h. Before postcuring, the polymer mold was peeled off the master on a hot plate at a temperature of approximately 70 °C, since the



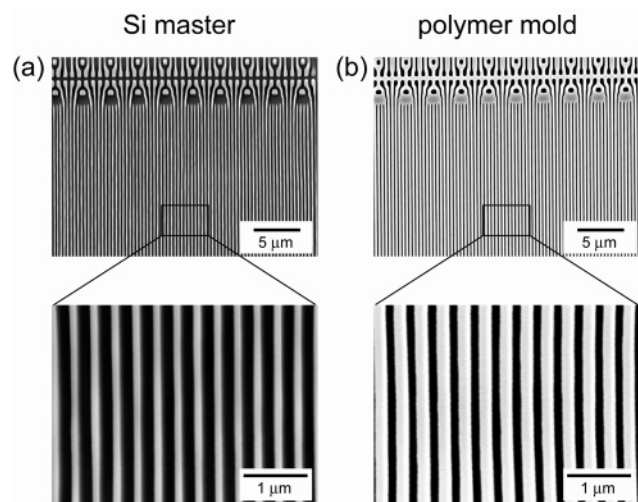
**Figure 2.** Schematic illustrations for transferring nanopatterns from NOA 63 based polymer mold onto a thin polystyrene (PS) film.

strong adhesion between polymer mold and master is dramatically decreased upon heating to 70 °C.

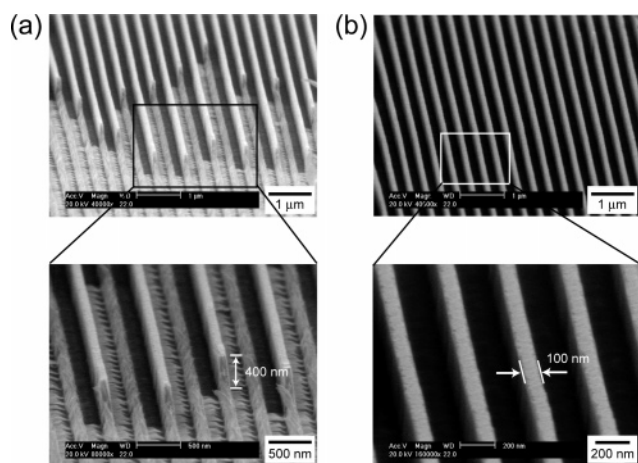
**Fabrication of Polymer Replica Film.** Figure 2 shows a schematic illustration for producing polymer replica film via a polymer spin-transfer printing process<sup>8</sup> utilizing the fabricated NOA 63 based polymer mold. First, the substrate, in this case Si wafer, was briefly exposed to O<sub>2</sub> plasma (0.5 Torr, 60 W, 2 min) using simple plasma equipment to create a negatively charged surface, and then dipped into an aqueous solution of 20 mM PDAC for 20 min. After surface treatment of the substrate, it was rinsed thoroughly with deionized water and then dried with N<sub>2</sub> gas. Next, the polymer mold was dipped into a fluorosilane agent, (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-1-trichlorosilane, for 1–2 min and then washed with anhydrous toluene for 20 s to reduce the adhesion of polymer mold with polymer film.

We spin-coated a thin polymer film on the patterned surface of the polymer mold with PS solution (10 wt %, toluene solvent) at 3000 rpm for 40 s; the thickness depended on the conditions of spin-coating. The coated polymer mold was allowed to remain undisturbed for approximately 30–60 min to remove residual solvent in the polymer film. The surface of the resulting polymer film was briefly exposed to O<sub>2</sub> plasma (0.5 Torr, 60 W, 10 s) to give a negative charge on top of the cast polymer film. The assembly of polymer film and polymer mold was pressed lightly onto a substrate, positively charged with PDAC, on a hot plate controlled at a temperature of ~75 °C for their binding via electrostatic interaction. The polymer mold was then peeled off the substrate while hot. Due to relatively weak adhesion between the polymer film and polymer mold compared to the electrostatic interaction between the polymer film and substrate, the polymer film was easily transferred onto the substrate when peeled off. The fluorosilane reagent is tightly bonded with NOA 63 polymer mold, so when the polymer solution is spin-coated and detached, the fluorosilane reagent does not come off.

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**Figure 3.** Scanning electron microscopy (SEM) images of nanostructures patterned on (a) Si master and (b) NOA 63 based polymer mold.

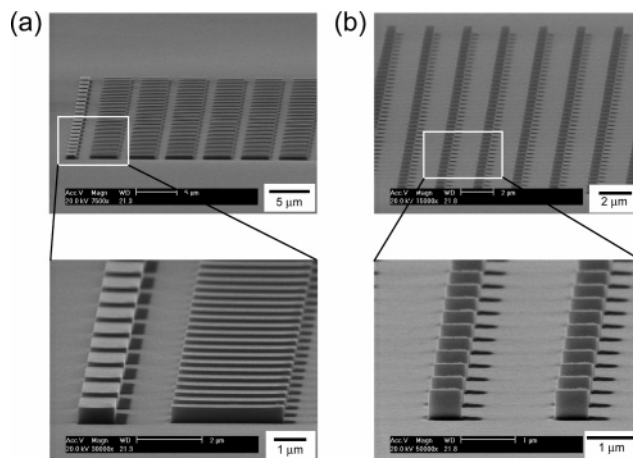


**Figure 4.** SEM images of nanostructures patterned on PS thin films when the surface of NOA 63 based polymer mold was (a) not fluorinated and (b) fluorinated with (tridecafluoro-1,1,2,2-tetrahydrooctyl)-1-1-trichlorosilane.

## Results and Discussion

**UV Curing Polymer Mold.** Figure 3 shows the scanning electron microscopy (SEM) images of nanostructures patterned on the Si master (Figure 3a) and transferred nanostructures on the NOA 63 based polymer mold (Figure 3b). Comparison of the patterns on the Si master and polymer mold revealed that highly complex and dense nanostructures were successfully transferred from the master onto the NOA 63 based polymer mold. Parts of the patterned nanostructures on the polymer mold possessed shapes of nanochannels, and the widths of the resulting nanochannels and the spacing between them were 100 and 250 nm, respectively. Nanoscale channels were patterned with high regularity at precisely determined nanoscale intervals, strongly indicating that nanostructures could be patterned with high feature density and precision using this technique.

**Effect of Surface Treatment of Polymer Mold.** Figure 4 demonstrates the effects of surface modification via fluorination. SEM images were taken to observe the surfaces of patterned nanostructures. When the surface of the polymer mold was not treated with silane agent in the process of polymer film coating (Figure 4a), nanopatterns transferred



**Figure 5.** SEM images of (a) high feature density nanostructures and (b) high aspect ratio nanostructures patterned on PS films using NOA 63 based polymer molds.

onto the polymer film partially collapsed after the polymer mold was peeled off and the surface of residual polymer layer was also very rough. However, when the surface of the polymer mold was treated with the fluorosilane agent, collapsing of the nanostructures was prevented and resulting nanopatterns were preserved while the polymer mold was released from the polymer film (Figure 4b). Nanostructures with high aspect ratio, whose heights and widths were 400 and 100 nm, respectively, were neatly transferred with high feature densities on a small area. Fluorination of polymer mold facilitated easy release of coated polymer film from the polymer mold. This allows the fabrication and replication of highly stable and precise nanostructures with high aspect ratio and accurate topographical features. Unlike PDMS, NOA 63 does not swell in water or in other solvents such as methanol, toluene, and trichloroethylene, which makes NOA 63 a suitable polymer, capable of tolerating swelling even when it is directly dipped into the silane agent. Because of this high stability in organic solvents, NOA 63 based polymer mold is considered to be a promising material suitable for direct contact with silane solution for surface treatment.

**Patterning of Nanostructure on Polymer Film.** Figure 5 shows SEM images of high density (Figure 5a) and high aspect ratio (Figure 5b) nanostructures and nanochannels patterned on PS film on Si master employing NOA 63 based polymer mold. As shown in Figure 5a, dense nanostructures having various patterns were successfully transferred onto thin polystyrene film. Forty identical high aspect ratio nanostructures were accurately patterned in one row, and a total of six rows were organized with high regularity and fidelity without any defect on an area smaller than  $30 \mu\text{m} \times 20 \mu\text{m}$  (Figure 5a). Also, repeated patterns of nanostructures with high aspect ratio were successfully fabricated with high feature densities, as shown in Figure 5b. The figures (Figures 4 and 5) of transferred nanostructures display the successful transfer of the nanopatterns in a polymer mold with high aspect ratio depth and step height.

Polymer mold requires rigidity to prevent the collapse of nanostructure, and at the same time, it should be sufficiently soft to release the cast polymer film. Taking these into account, NOA 63 is a highly suitable material to be employed as a template for manufacturing polymer molds because it



exhibits three distinct advantages when compared to the typical PDMS mold used in soft lithography. First, NOA 63 based polymer mold is rigid at room temperature. It has a modulus of elasticity of approximately 1655 MPa, which is more than 1000-fold higher than that of PDMS (1.5 MPa) at room temperature. Due to this property, firm and concrete nanostructures could be obtained to function as physical barriers for biomolecule immobilization. Although NOA 63 based mold is hard and therefore brittle at room temperature, the adhesion property between NOA 63 based polymer mold and Si master can easily be modified by controlling temperature and curing conditions. It becomes soft upon reaching a temperature of 70 °C, and the release of the mold containing high aspect ratio nanostructures from the master is facilitated without breaking or damaging the nanopatterns. Second, NOA 63 based polymer mold is highly resistant to swelling in various organic solvents such as methanol, toluene, and trichloroethylene. This high resistance in organic solvents becomes significantly important in the process of surface treatment when replicating nanopatterns onto various substrates using this polymer mold as a stamp. Third, the curing time is a lot shorter than that of PDMS at room temperature. Apart from these, NOA 63 has low fluorescence and excellent transmission from 360 to 1200 nm after curing, extending its potential application for developing nanosized optical devices. Because of these unique characteristics, NOA 63 based polymer mold is suited for transferring nanostructures onto a substrate with outstanding accuracy, and by

adopting these important features, we could transfer dense nanostructures onto NOA 63 based polymer molds and pattern various nanostructures and nanochannels with great simplicity.

### Conclusion

A new commercial material feasible for transferring high aspect ratio nanopatterns is introduced as a tool for constructing polymer molds featuring nanopatterns. Also, a simple and efficient technique using a new polymer mold and surface treatments with fluorosilane is established for the easy release of cast polymer film from the polymer mold. By combining these, high aspect ratio nanostructures with precise topographic features could be attained and easily transferred onto a Si substrate. We showed pattern transfer down to 100 nm nanostructures, which may be easily extended to transfer of smaller size with high density. A polymer mold made with NOA 63 and surface treatment technique using fluorosilane, introduced in this study, not only display a substantial potential for fabricating various nanostructures but also offer promising technology for developing nanofluidic, optical, electronic, and biological devices.

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