Fluorinated Organic−Inorganic Hybrid Mold as a New Stamp for Nanoimprint and Soft Lithography

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In this paper, we fabricated a fluorinated organic−inorganic hybrid mold using a nonhydrolytic sol−gel process which can produce a crack-free mold without leaving any trace of solvent. No special chemical treatment of a release layer is needed because the fluorinated hybrid mold has fluorine molecules in the backbone. The other advantages of the hybrid mold are thermal stability over 300 °C. The hybrid mold produced from UV nanoimprint lithography (UV−NIL) was used as a mold for the next UV−NIL and soft lithography without requiring use of an antisticking layer. Various nanometer scale patterns including sub-100 nm patterns could be obtained from the hybrid mold. Nanopatterning processes using this low-cost mold are useful because they preserve the expensive original master.

Nanoimprint lithography (NIL)[1] and soft lithography[2] are useful techniques because of their low cost and high throughput capability for the fabrication of submicrometer patterns which has potential applications in micro-optics,[3] magnetic memory devices,[4] bio sensors,[5] and photonic crystals.[6] To pattern sub-micrometer features, a delicate stamp is needed, which is usually a hard and stiff stamp made of silicon (Si) or silicon dioxide (SiO_2). These nanoscale stamps are generally fabricated by a high cost and low throughput process of electron beam lithography (EBL). Additionally, a chemical surface treatment of the stamp is needed to ensure a clean release after imprinting.

Recently, several polymer materials have been used as an alternative low cost stamp including poly(dimethylsiloxane) (PDMS),[2] polyurethane (PU),[7] and amorphous fluoropolymer[8] in most soft lithography techniques. However, a PDMS mold has some disadvantages for the fabrication of nanopatterns with high-density and sub-100 nm resolution because of a relatively low modulus (1.8 MPa).[9] To solve these problems, a modified hard PDMS (h-PDMS) with a high tensile modulus, which seems to replicate nanostructures well, has been used as a mold for nanopatterning by several groups.[9]

Other useful polymeric materials have been suggested for nanoimprinting with sub-100 nm resolution.[10,11] These polymer replica molds from quartz stamps are obviously useful because they can preserve the expensive original master. When general organic polymers are used for the mold, however, the antisticking treatment is needed and the coating of a release layer onto these polymers is difficult because it is usually coated onto Si or SiO_2. Recently, Wu et al. have used silicon containing a photocurable material to coat a release layer for the replication of a quartz stamp.[11] A fluoropolymer by Lee et al. is useful, but needs a high temperature and pressure in the mold fabrication process.[8] Recently, a useful photocurable fluoropolymer for the microfluidic device has been suggested to solve the swelling problem of PDMS chips to organic solvent.[12] Organic fluoropolymer is useful, but the mechanical properties are similar to that of PDMS.[12] Thus, it is necessary to find a new, cheaper stamp that does not require an antisticking treatment and that provides sufficient rigidity for nanopatterning.

In this work, we fabricated a fluorinated organic−inorganic hybrid mold as a new mold for for the next UV−NIL and soft lithography, which could be realized without an antisticking layer, using a nonhydrolytic sol−gel process. This hybrid mold has advantages not only in the organic flexibility of the polymer but also in the inorganic thermal stability from the inorganic glass network. There is no need for any special chemical treatment of a release

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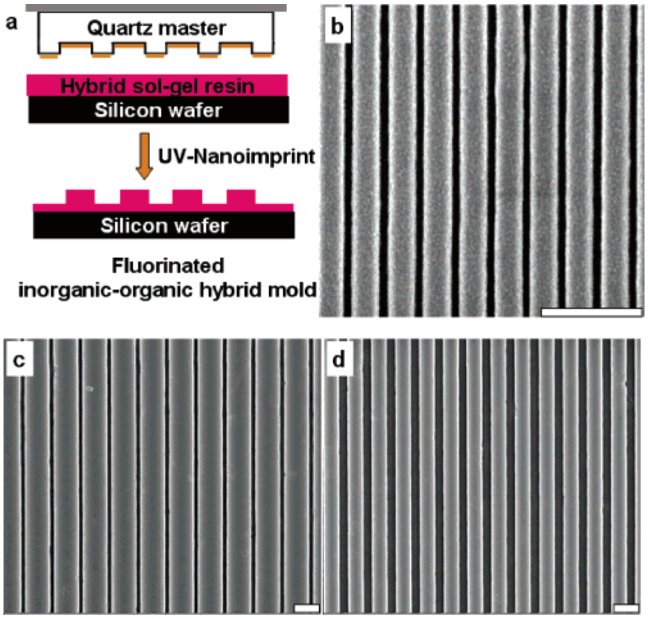

Figure 1. (a) Schematic of fabrication process for the fluorinated hybrid mold. (b−d) SEM images of nanostructures with 140 nm (40 nm spacing), 1 μm (170 nm spacing), and 600 nm (350 nm spacing) line widths, respectively. Scale bar of (b) is 500 nm. Scale bars of (c) and (d) are 1 μm.

layer because the hybrid mold has fluorine molecules in the backbone. The other advantages of the hybrid mold are thermal stability over 300 °C and easy surface energy control by changing the PFAS content.[13]

Fabrication of a Fluorinated Hybrid Mold

UV−NIL was used to fabricate the hybrid mold.[14] A quartz stamp 5 × 5 in.^{2}, an elementwise patterned stamp (EPS) for large-area pattering at atmospheric pressure and room temperature, was made using E-beam lithography and wet etching. Experimental details of the fabrication of the EPS stamp can be found in our previous report.[15] Each element was separated by channels with a depth of 1 μm and a width of 5 mm (see Figure S1 for details of stamp).

Figure 1a outlines the fabrication process of the fluorinated inorganic−organic hybrid mold. Our material has an intrinsic anti-releasing property, but it is still important to protect the expensive original master against contamination because some contamination would be induced from many repeat tests. Therefore, the surface of the quartz stamp was functionalized by a liquid-phase coating of trichloro(1H,1H,2H,2H-perfluorooctyl)silane (97%, Aldrich) for 10 min to form a self-assembled monolayer (SAM), which has a functional unit of $-CF_3$ as a releasing layer. The stamp was rinsed with ethanol and acetone after the fluorosilane SAM treatment. The fluorinated releasing layer lowers the surface energy of the stamp and assists in separation. The contact angle of the stamp after the SAM treatment was about 105°.

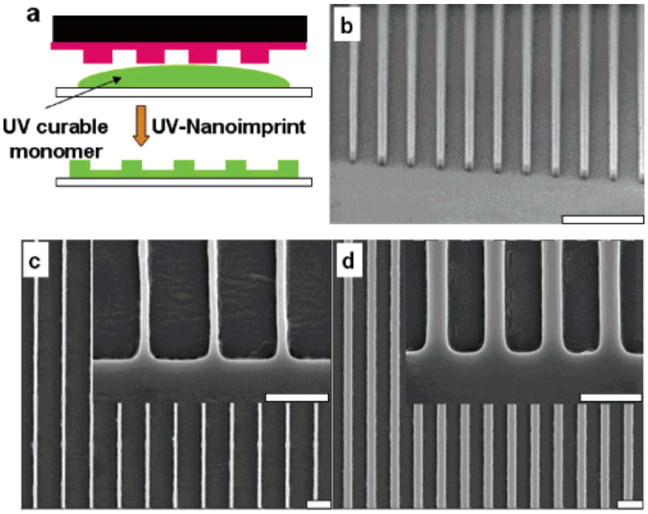

Figure 2. (a) Schematic of UV-nanoimprinting process using the hybrid mold. (b−d) SEM images of the nanostructures with 40 nm (140 nm spacing), 170 nm (1 μm pitch), and 350 nm (600 nm pitch) line widths replicated from patterns of the fluorinated hybrid mold of Figure 1b−d, respectively. Scale bar of (b) is 500 nm. Scale bars of (c) and (d) including those of insets are 1 μm.

A fluorinated methacrylic organic−inorganic hybrid material (hybrimer) was used as a precursor. The fluorinated hybrimer was composed of 3-(trimethoxysilyl)propyl methacrylate (MPTMS, Aldrich) as a organo alkoxysilane, diphenylsilanediol (DPSD, TCI) as a main precursor including hydroxyl group for hydrolysis reaction, (heptadecafluorodecyl)trimethoxysilane (PFAS, Toshiba) as a fluorine modifier, and Irgacure369 (Ciba Geygy) as a photoinitiator. The content of PFAS was fixed at 20 mol percent. The viscosity of the hybrimer can be controlled from 20 to 220 mPa·s by the content of monomer and thermal heating.[15] To fabricate the fluorinated organic−inorganic hybrid mold, the fluorinated precursor (hybrimer) was spin-coated at 2000 rpm for 60 s on the silicon wafer which had been cleaned in a piranha etch and O_2 plasma. The hybrid mold was fabricated using UV-nanoimprint on the hydrophilic 4 in. silicon wafer (Figure 1a). The imprinting conditions are as follows: a UV (365 nm) exposure dose of 14.4 mW/cm^2, vacuum pressure of 1000 mbar, and a compression time of 60 s. Finally, the hybrid mold was thermally baked at 150 °C for 2 h to remove solvents in the precursor. In this work, the crack-free hybrid mold was obtained easily because this is a nonhydrolytic sol−gel process. The nonhydrolytic sol−gel process, in contrast to the conventional hydrolytic sol−gel process, facilitates the fabrication of the crack-free mold without leaving any trace of solvent and without abrupt volume shrinkage.[13] A crack-free hybrid mold without abrupt volume shrinkage can be fabricated because the nonhydrolytic sol−gel process does not need additional water compared with general water adding sol−gel process[17] because the precursor has hydroxyl groups in itself which can react with the alkoxysilane groups of the organo alkoxysilane and does not leave any trace of a solvent such as water.[13]

The fluorinated hybrid mold with large area accuracy prepared from the patterned master, with ditches of various feature sizes, was successfully fabricated as shown in the Figure 1. Figure 1b−d shows that nanostructures with 140 nm (40 nm spacing), 1 μm (170 nm spacing), and 600 nm (350 nm spacing) line widths were successfully replicated from the master, respectively. Ultimate tensile strength of the hybrid mold is 13 MPa, Young's modulus

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is 115 MPa, and volume shrinkage is 2.5−2.7% after the final thermal curing at 150 °C. This measured volume shrinkage is slightly smaller than that of the general Sylgard PDMS (3%). These results show that the hybrid mold is flexible and exhibits polymer-like mechanical behavior. There are no bending effects until a 1 mm bending radius is reached (Supporting Information). General tensile strengths of glasses and thermoplastics are 100−120 and 5−50 MPa, respectively. Fluorine content of the fluorinated hybrid film is constant through the thickness because every oligomer of fluorinated hybrid material has fluorine molecules (see XPS data in the Supporting Information).

The fluorinated hybrid mold is hydrophobic and has a low surface energy because it contains fluorine molecules in the PFAS. Also, the hybrid mold has an anti-swelling property to organic solvent (see the Supporting Information). Therefore, there is no need to do any special chemical treatment of a fluoroalkylsilane release layer. It is meaningful and useful to abbreviate the step of releasing layer treatment in the imprinting or pattern replication process because it is a tiresome and harmful process. Water contact angles of the original quartz and hybrid molds are 50° and 105°, respectively (Figure S2). The surface energy of hybrid mold was about 15 mN/m. Other advantages of the hybrid mold are thermal stability over 300 °C (see the TGA data in the Supporting Information) and easy refractive index control from 1.40 to 1.45 by changing the PFAS content. It is anticipated that these materials will be useful in flexible waveguide and optical devices that require thermal stability.

UV−Nanoimprint with the Fluorinated Hybrid Mold

The fluorinated hybrid mold was used without any treatment as a stamp for UV-nanoimprint. A schematic of the imprint process is shown in Figure 2a. UV-curable resin (PAK01) with a low-viscosity (7 mPa·s) was patterned on the hydrophilic transparent glass using commercial UV-imprinting equipment (EVG620). PAK01 is composed of tri(propylene glycol) diacrylate, 2,2-dimethoxy-2-phenylacetophenon as a photoinitiator, and several additives. Imprint conditions are exactly the same as those used in the fabrication of the hybrid mold, except thermal post baking. The SEM images in Figure 2b−d show that nanostructures were successfully imprinted without mold determination after release from patterns of the hybrid mold with 140 nm line (40 nm spacing), 1 μm line width (170 nm spacing), and 600 nm line width (350 nm spacing) of Figure 1b−d, respectively.

Fabrication of Hard PDMS Molds with the Fluorinated Hybrid Mold

Flexible PDMS molds have attracted great attention because they are useful in microcontact printing, micromolding, and bio-microfluidics. Hard PDMS (h-PDMS) patterns were produced using the fluorinated hybrid mold as a replication test of nanopatterns because the fabrication of conventional soft PDMS with high-density nanometer-scale resolution was difficult because the mold collapsed due to low elastic modulus (tensile modulus of 1.8 MPa).[9,10] For the fabrication of h-PDMS (tensile modulus of 8.2 MPa), various nanometer scale patterns could be obtained from the fluorinated hybrid mold (Figure 3b−d). To fabricate the hard PDMS mold, we mixed 6.8 g of a vinyl PDMS prepolymer (vinylmethylsiloxane-dimethylsiloxane; VDT-731, Gelest), 36 μL of a Pt catalyst (platinumdivinyltetramethyldisiloxane; SIP6831.1, Gelest), and one drop of a modulator (tetramethyltetravinylcyclotetrasiloxane; 87927, Fluka), and degassed for 1−2 min. We then gently stirred 2 g of hydrosilane prepolymer (methylhydrosiloxane; HMS-301, Gelest) into this mixture. Immediately, we poured the mixture of h-PDMS on the hybrid mold without any special treatment and cured for 1 h at 60 °C.[9,10] For the fabrication of the composite mold, a liquid prepolymer of PDMS (Sylgard 184 A:B) from Dow Corning was mixed at the ratio of 1:10, degassed for 1−2 min, poured onto the thin film of h-PDMS, and subsequently cured for 1 h at 80 °C.

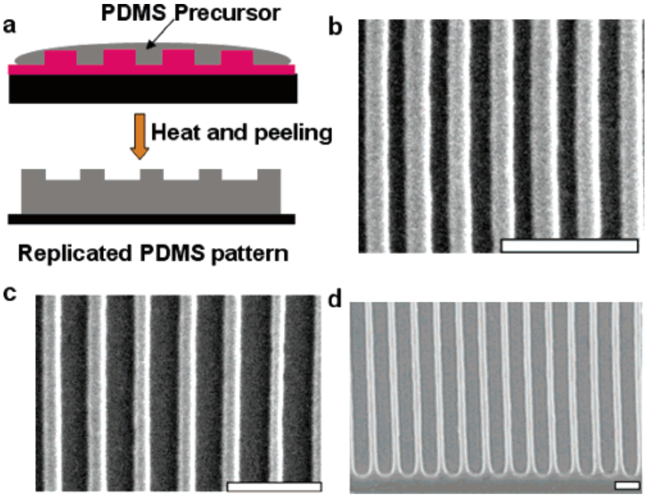

Figure 3. (a) Schematic for the fabrication of PDMS patterns using the hybrid mold. (b−d) SEM images of h-PDMS with various size patterns: (b) 80 nm line (60 nm spacing); (c) 100 nm line (150 nm spacing); (d) 170 nm line (380 nm spacing). Scale bar is 500 nm.

Submicrometer dense patterns with various line widths could be also successfully replicated using h-PDMS from the florinated hybrid mold as shown in Figure 3. Some cracks were observed in h-PDMS patterns because of brittleness caused by low (approximately 7%) elongation at break.[9]

In conclusion, we fabricated the fluorinated organic−inorganic hybrid mold with high modulus of 115 MPa by using a nonhydrolytic sol−gel process which can produce a crack-free mold without leaving any trace of solvent. There is no need for any special chemical treatment of a release layer because the fluorinated hybrid mold has fluorine molecules in the backbone. The hybrid mold produced from UV nanoimprint lithography (UV−NIL) was used as a mold for the next UV−NIL and soft lithography without an antisticking layer. Various nanometer scale patterns including sub-100 nm patterns using an acrylate polymer and h-PDMS could be obtained from the fluorinated hybrid mold. Using this low-cost mold for nanopatterning processes is useful because it preserves the expensive original master.

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Supporting Information Available: Detailed synthesis method of resin and additional mechanical and chemical data about the hybrid stamps. This material is available free of charge via the Internet at http://pubs.acs.org.

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