3410 *Chem. Mater.* **2004,** *16,* 3410−3413

Two-Dimensional Polymer Nanopattern by Using Particle-Assisted Soft Lithography

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Received September 22, 2003
Revised Manuscript Received July 8, 2004

Structures with an ordered two-dimensional (2D) pattern have attracted great attention because they are applicable to microelectronic and optoelectronic devices,[1] displays, biochips and sensors,[2] and photonic band gap materials.[3] Recently, various polymeric structures have been made by using soft-lithographic pattern formations such as microcontact printing, replica molding, and embossing.[4−9]These lithographic techniques are very useful in pattern fabrication for microelectronic devices and biotechnology applications such as microelectrode arrays, well-defined polymer patterns, memory devices, and biosensors.[5] In particular, a patterned array of colloidal particles with feature dimensions comparable to the wavelength of light can be used as optical biosensors and biochips, as well as photonic devices. For example, a photonic crystal is an ordered structure whose dielectric constant (or refractive index) is periodically modulated on a scale comparable to the wavelength of light. Multiple interference of light waves scattered from the dielectric lattice leads to stop bands or complete photonic band gaps. Therefore, the patterned arrays with feature size comparable to the optical wavelength will exhibit a stop band and can be used as optical waveguides.

Advanced lithographic technologies such as E-beam, X-ray, and ion beam have been used to make nanoscale masters for soft lithography. However, they are limited in reducing the master size or feature scale as well as the cost and processing time. Alternative methods are based on the "bottom-up approach" using the self-assembly of amphiphilic molecules[10,11] or colloidal particles;[12] their advantages include simple control of the pattern size and low-cost parallel processes. In this work, we report a novel fabrication route to polymeric nanopatterns via colloidal particle-assisted soft lithography. The fabrication of well-ordered 2D periodic arrays of nanoparticles is important in applications of 2D photonic crystals, stamps for microcontact printing,[13] microlenses for projection photolithography,[14]and nanosphere lithography, which use colloidal arrays as lithographic masks to fabricate nanostructures.[15] Specifically, we fabricated designed 2D polymer nanopatterns by embossing and replica molding with colloidal stamps prepared from self-assembled particle arrays in patterned, soft poly(dimethylsiloxane) (PDMS) molds.

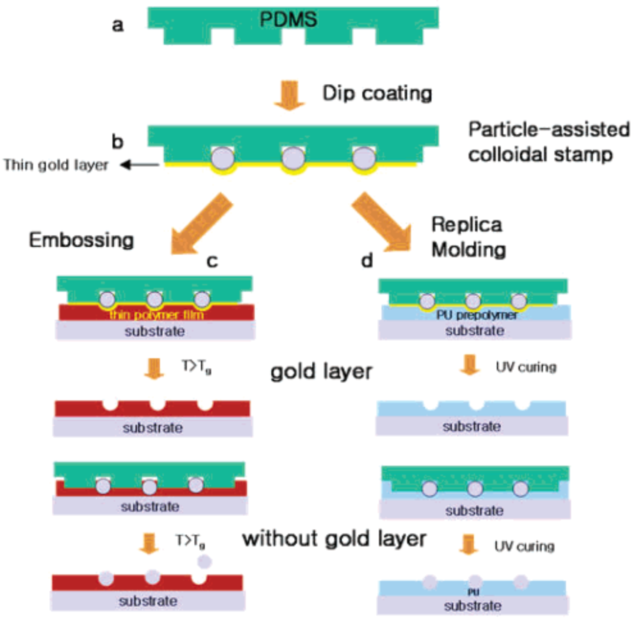

Figure 1. Schematic of the fabrication of patterned polymer. (a) Patterned PDMS mold. (b) Colloidal stamp on the patterned PDMS mold. (c) Polymer pattern by embossing. (d) Polymer pattern by replica molding.

Silicon and quartz masters that have line widths ranging from 350 nm to 1.6 μm were made by e-beam lithography. Patterned PDMS molds were prepared by a standard procedure of replica molding on the bas-relief master. Colloidal silica was synthesized by the Stöber method.[16] The average diameter of the prepared silica particles was 320 nm and the polydispersity was 0.5%. To fabricate a patterned colloidal stamp, a patterned PDMS mold was dip-coated with 0.02 wt % silica

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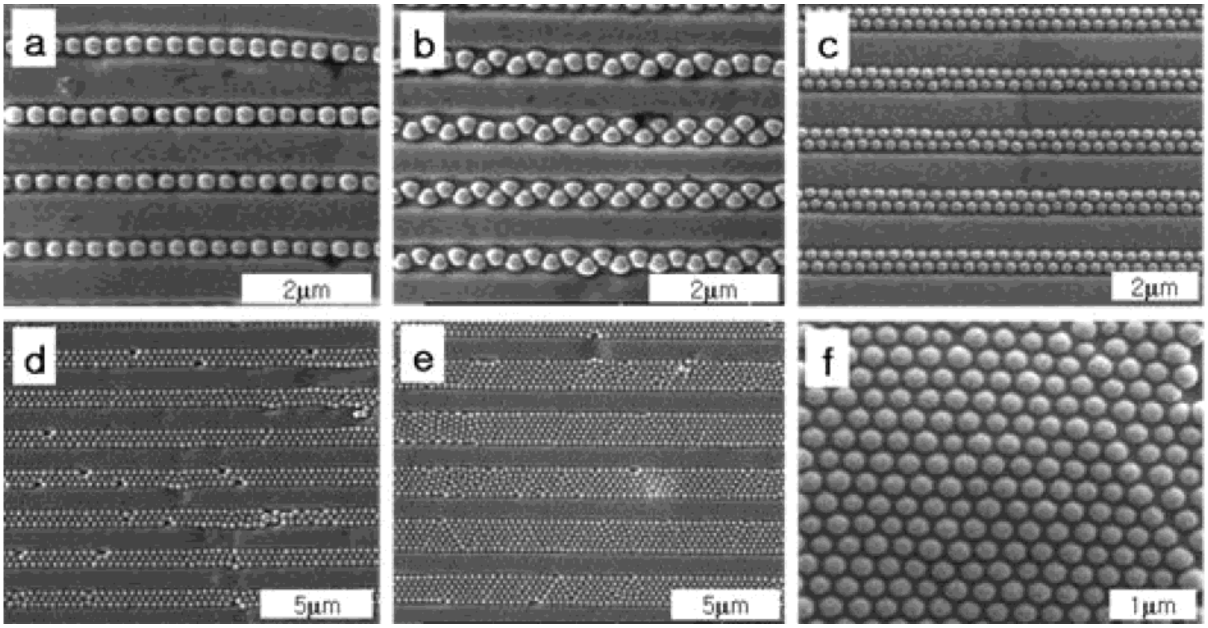

Figure 2. Colloidal stamps with self-organized particle arrays in the soft, patterned PDMS molds with different ditch sizes: (a, b) 300 nm; (c) 600 nm; (d) 800 nm; (e) 1.6 μm. The lower right image (f) was for the unpatterned colloidal PDMS stamp.

suspension at a speed of 0.2 μm/s. The speed was slow enough to allow the silica particles to arrange themselves into the ordered structure.

For the embossing of the PS layer, a solution comprising 10 wt % of polystyrene (PS) (Aldrich, $M_w = 45.7$ kg/mol) dissolved in toluene was spin-coated onto the clean-washed wafer at 3000 rpm for 1 min. The patterned colloidal stamp was loaded onto the PS-coated substrate and annealed at 160 °C for 10 h in a vacuum oven under 1.96 kPa.

Polyurethane (PU) (NOA 61, Norland Products Inc.) was used as a prepolymer for the replica molding. The liquid PU prepolymer was dropped onto a wafer substrate, and then the patterned colloidal stamp was softly placed onto the liquid prepolymer. The prepolymer filled the cavity by capillary force and was then cured with UV light (ELC-500, Electro-Lite Corp.) for 10 min. The morphology was observed by SEM (Philips-XL20SFEG).

The experimental schemes are illustrated in Figure 1. To fabricate colloidal stamps (step b of Figure 1), patterned PDMS molds (step a of Figure 1) with ditches of various feature sizes were prepared from patterned quartz masters (see Figure S1 of the Supporting Information). Figure 2 shows the SEM images of the various colloidal stamps prepared in this work with self-assembled particle arrays on the patterned soft PDMS mold. During dip-coating, the silica particles were preferentially deposited on the recesses of the patterned relief structures and assembled into colloidal crystals of which the structures were determined by the geometric confinement provided by the PDMS pattern.[17] The SEM image of Figure 2f shows a colloidal stamp formed with a silica bead monolayer on the unpatterned region. In the subsequent molding process, a 20-nm-thick gold layer was deposited by using a commercial gold sputter (Technics: Hummer V) at a rate of 0.11 nm/s onto the colloidal stamp to reduce adhesion between the colloidal particles and the polymeric replicating medium. Any adhesion layer was not used between the silica colloids and the gold layer in our experiment and the silica master was recoated after each replication. Recently, thin metal layers in the replica molding have been applied to fabricate and replicate successfully positive and negative patterns.[18]

Figure 3 shows the effect of the thin gold layer predeposited to prevent polymer infiltration. When a gold layer was used, various negative PU nanopatterns were successfully fabricated by replica molding with the colloidal stamps; these patterns are shown in parts of a, b, and c of Figure 3. The successful pattern transfer was achieved obviously because the infiltration of PU prepolymer at the interstices between the colloidal particles was suppressed and the prepolymer had just been molded upon the layered colloidal particles. Similarly to the silica beads, the negative patterns in Figure 3a−c have pores ranging in width from 300 to 310 nm; the patterns also have a depth of 60 nm, which is shallower than the patterns in the silica hemisphere. The gold layer prevents colloids from transferring to the polymer mold by two mechanisms. The first proposed mechanism is that the polyurethane preferentially wets the gold over the silica colloid. The second mechanism is that gold transfers to the polymer mold and acts as a release layer. To examine the difference in wettability, we measured the contact angles of PU prepolymer onto a silica surface and Au film. As shown in Figure S7 of the Supporting Information, the contact angle (10.3°) of PU prepolymer on the gold film is smaller than that (20.1°) on the silica surface. Therefore, this difference in contact angle is not large enough for the polymer to wet only the gold, and the second mechanism plays a dominant role in preventing silica colloids from transferring to the polymer. To see the effect of Au film as a release layer, gold transfer to the polymeric replicating medium was observed by using an optical microscope.

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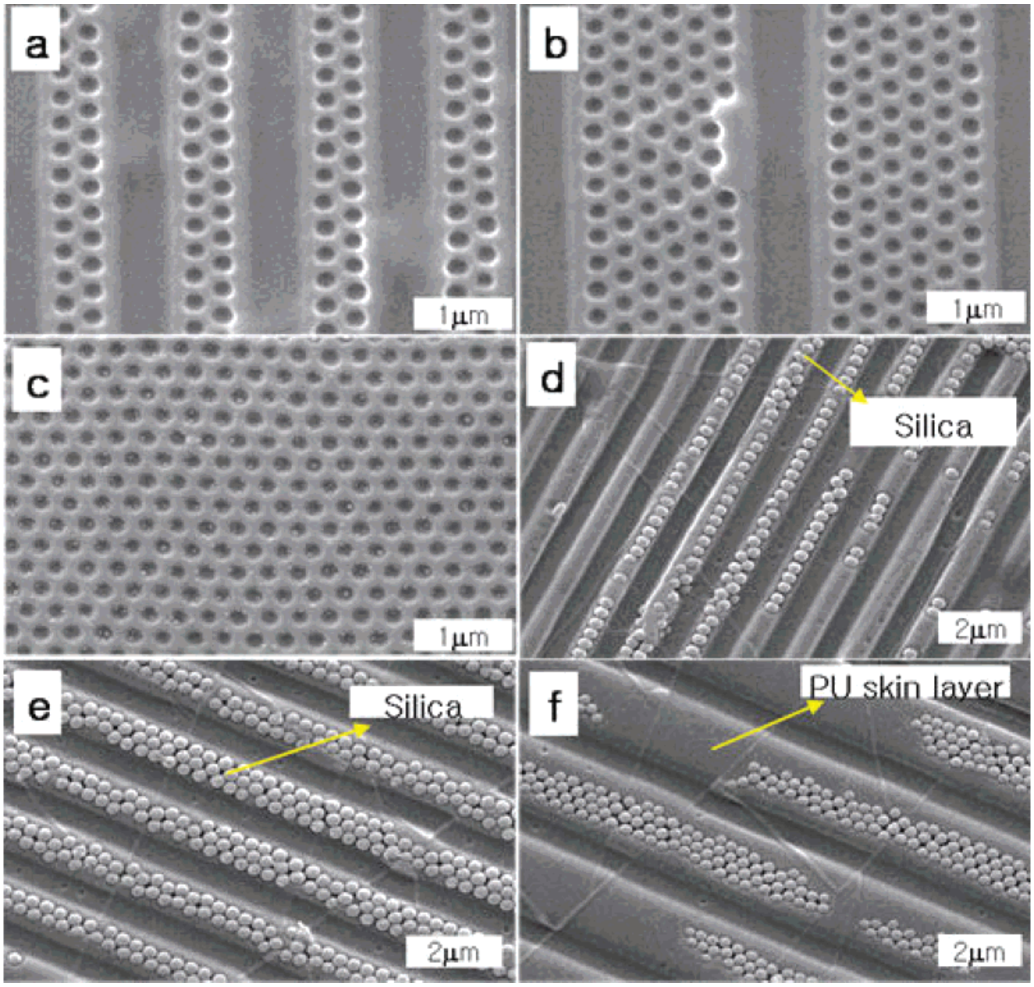

Figure 3. Patterned polyurethane (PU) films by replica molding. (a−c) SEM images of patterned PU films when a gold layer is used. Figures 3a−c were replicated from Figure 2c,e,f, respectively. (d−f) SEM images of silica−PS composite films when a gold layer is not used. Figures 3d−f were replicated from Figure 2c−e, respectively.

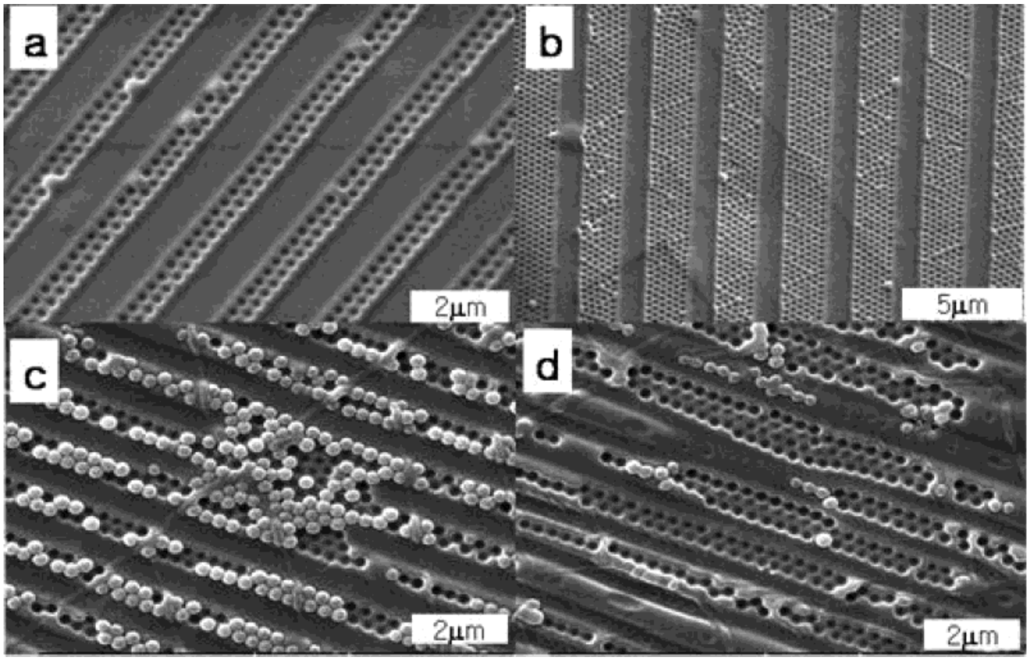

Figure 4. Patterned polystyrene (PS) films by embossing. (a and b) SEM images of patterned PS films when a gold layer is used. Figure 4a,b were replicated from Figure 2c,e, respectively. (c and d) SEM images of PS films when a gold layer is not used. Figure 4c,d were replicated from Figure 2c,d, respectively.

As shown in Figure S8 of the Supporting Information, most of the gold particles were transferred to the replicating medium because the adhesion between gold and the polymer surface is large compared to that between gold and silica. This adhesion phenomenon was also consistent with the difference in wettability and enhanced the mechanical stability of the colloidal array.

When the gold layer is not used, the PU prepolymer is expected to infiltrate the interstices between the silica spheres and deteriorate the structure of the molded PU pattern. To see this phenomenon, SEM images were taken of the replica-molded PU when the gold layer was not used; the images are reproduced in parts d, e, and f of Figure 3. As expected, the PU prepolymer infiltrated at the interstices between the silica spheres and it grasped all the particles from the PDMS stamp. The lift-off of the PDMS colloidal stamp consequently left silica beads behind on the molded PU pattern, and a composite structure of PU and silica beads was fabricated by replica molding without the gold layer. The negatively patterned PS films of parts a and b in Figure 4 were fabricated by embossing with the aid of a gold layer that suppressed the polymer infiltration as in the replica molding. When the gold layer was not used, however, the pattern transfer in the embossing with the colloidal stamp was incomplete, as noted from parts c and d of Figure 4.

In conclusion, we successfully used embossing, as well as replica molding, to fabricate polymer nanopatterns with various sub-micrometer features. We prepared a PDMS colloidal mold using a stamp patterned by soft lithography with a self-organized monolayer of colloidal particles. Our results suggest that polymer infiltration should be suppressed by depositing a metal layer such as gold in the embossing and replica molding process to successfully fabricate designed patterns. The present method is very attractive and cost-effective for the fabrication of designed patterns. The fidelity of replication was maintained after several replication cycles and concentration of defects did not change severely; see AFM and SEM images in the Supporting Information for the fidelity of replication**.**

Acknowledgment. This work was supported by the Center for Nanoscale Mechatronics and Manufacturing of the 21st Century Frontier Research Program (M102KN010001-02K1401-00212) and the National R&D Project for Nano Science and Technology. The authors also acknowledge partial support from the Brain Korea 21 program, CUPS-ERC, and the IMT-2000 Projects.

Supporting Information Available: AFM and SEM images for the fidelity of replication and experimental evidence on the role of the predeposited gold film. This material is available free of charge via the Internet at http://pubs.acs.org.

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