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Miniaturization of Surface Patterns by Combination of Contact Etching Lithography and Multi-step Shrinking of Stretched Polymer Films

By Hiroshi YABU[1,*] *and Masatsugu* SHIMOMURA[2]

We demonstrate here a novel pattern transferring method named "Contact Etching Lithography" onto stretched polymer films by using a solvent-swollen polydimethylsiloxane (PDMS) molds as a template. Furthermore, the transferred patterns can be miniaturized by thermal shrinking of the patterned stretched polymer film.

KEY WORDS: Stretched Polymer Films / Contact Etching Lithography / Pattern Miniaturization /

Strong demand for miniaturiztion of surface patterns enforces to develop new lithographic technologies in the fields of electronics and photonics. Recent development of microfabrication technologies as represented by photolithography provides highly integrated nano-scale silicon devises. The conventional photo-lithography managed to meet the needs for pattern miniaturiztion with improving its light source, resolution of the masks, and cleanlinesss of the fabrication conditions. However, it requires multi-step fabrication processes, expensive instruments and so on. Whitesides *et al.* have reported the "soft-lithography"[1] including micro-contact printing (μCP),[2] which uses a silicone rubber stamp and a thiol ink to copy the micro-structures onto gold substrates, as a novel fabrication method of micro-pattens without elaborate multi-step processes. Nanoimprint lithography is also applied to fabricate micro and nanopatterns by molding the patterned template on the surface of polymer materials[3] or cross-linked resins.[4] Soft-lithography and nanoimprint lithography are basically fabricated by photolithography, thus, the size of these templates was also limited by the photolithography itself. As long as using photolithography, the diffraction limit of the light source rules the fabrication size. Thus, novel pattern fabrication technologies and miniaturiztion methodologies are required.

On the other hand, bottom-up type microfabrication technologies based on building up the molecular level materials to form larger scale devises are emerging including colloidal crystals,[5] micro-phase separation of block-copolymers,[6] and so on. We have reported that hexagonally arranged microporous polymer films can be prepared by casting polymer solution under humid condition as a bottom-up self-organization system.[7] Water droplets condensed on the casting solution surface, these water droplets are packed by capillary force, and the hexagonally arranged microporous film can be formed by using these packed water droplets as templates after complete evaporation of solvent. By using this microporous film as template, the inverted image of the microporous film from polydimethylsiloxane (PDMS) was fabricated, and it worked as a micro lens array.[8] This process can be applicable to prepare polyacrylamide (PAm) hydrogel micro lens arrays (see supporting information, S-1). We found that, the surface pattern was easily transferred onto the polyvinylalcohole (PVA) film by simple pressing process when the PAm hydrogel mold was placed on a surface of PVA film. Scince the PAm hydrogel mold contains much amount of water, the water molecules were seeped from the hydrogel mold during pressing, and then, the surfacce of the PVA film was swollen and dissolved by seeped water. After releasing the PAm hydrogel mold, the surface pattern was transferred to the PVA film. This result implies that the surface patterns of cross-linked polymer mold containing solvent or etchant can be transferred onto the surface of materials, which can be damaged by the solvent and the etchant. The pattern transferring process named "Contact Etching Lithography (CEL)" can be considered as a novel pattern formation technique of the materials surface by simple contact of cross-linked polymer mold cotaining solvent or etchant of materials.

Shrinking patterns by using shrinkable materials is possible way to miniaturize the surface patterns. By combining the patterning process and shrinking process, the surface patterns should be miniaturized. There are some materials that can be shrunk by external stimuli. Gels and other cross-linked materials containing solvents can shrink after deswelling by immersing in their poor solvents or evaporation of solvents. Stretched polymer film is another candidate of the miniturization of the surface pattern. The stretched polymer film shrinks after heating over glass transition temperature (T_g). Polymer molecules were stretched and aligned with stretching their film, the entropic relaxasion of aligned polymer molecules shrinkes the film by elevating the temperature. If these materials are patterned, the size of the surface patterns will be miniaturized by simple deswelling or heat treatment. However, patterning stretched polymer film is basically difficult because of their low thermal and chemical stabilities. Here, we show the simple pattern transffering by CEL process onto stretched polymer film and miniaturiztion of surface patterns by simple treatment.

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[1] Institute of Multidiciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan
[2] Advanced Institute for Materials Research, WPI, Tohoku University, 2-1-1 Katahira, Sendai 980-8577, Japan
[*] To whom correspondence should be addressed (Tel: +81-22-217-5825, Fax: +81-22-217-5824, E-mail: yabu@tagen.tohoku.ac.jp).

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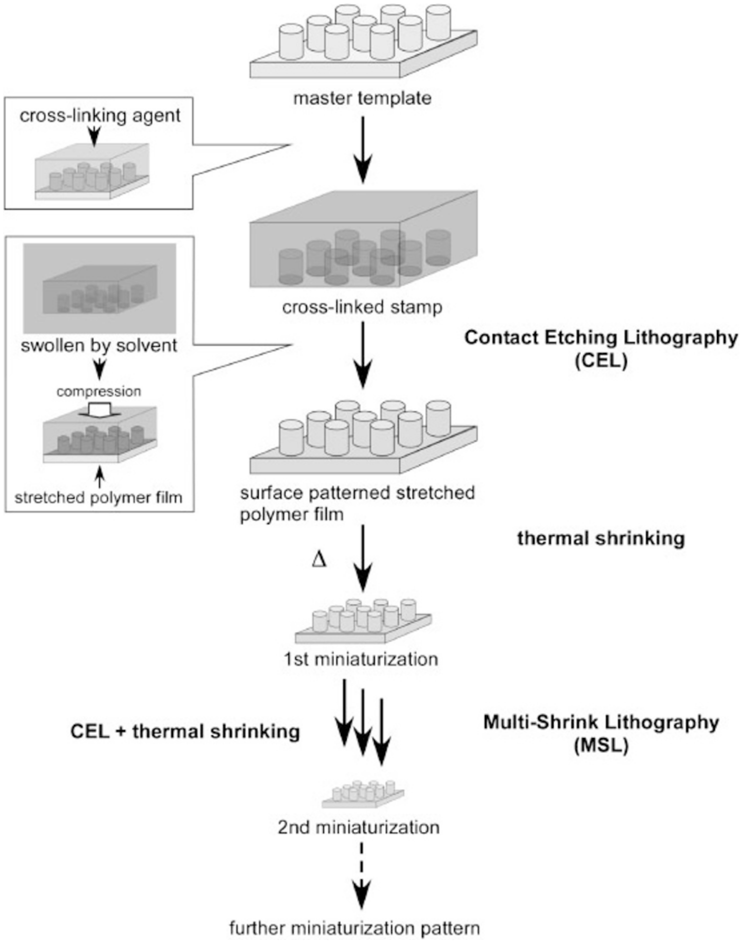

Figure 1. Schematic illustration of CEL process and MSL process.

EXPERIMENTAL

The schematic illustration of throughout experimental process is shown in Figure 1.

Preparation of Closs-linked Polymer Mold

Polystyrene (PSt) nanopillar sheets having several size pillars tetragonally arrenged on the surface of the sheet were kindly provided by Hitachi Co. Ltd., Japan and used as a template sheet. PDMS prepolymer and catalyst (Sylpot 184, Dow Corning, USA.) were mixed (mixing weight ratio was ten-to-one). The prepolymer with catalyst was cast onto the template sheet placed on a glass dish, and then, the sample was degassed *in vacuo*, and then, annealed at 200 °C for 2 h under normal pressure in an electric oven. The sample was immersed in chloroform or benzene to remove the polymer template for 2 h after cooling to the room temperature.

CEL Process

The 1.5 times biaxial- and uniaxial-stretched polymer films (APL8008T) was kindly provided by Mitsui Chemical Company, Japan. A PDMS mold was immersed in benzene for 1 min, and then, the swollen PDMS mold was placed on the stretched polymer film. After immersion in benzene, the PDMS mold was swollen *ca.* 5%. The PDMS mold was pressed by using a pressing instrument driven by stepping motor (see supporting information, S-2). The pressing pressure and the pressing temperature were 3∼5 MPa/cm^2 and room temperature (25 °C), respectively. After pressing for 2 min, the mold was removed from the surface of the stretched polymer film. After drying at room temperature, the surface patterns of the stretched polymer film were observed by using an optical microscope (BH-2, Olympus, Japan), a scanning electron microscope (SEM, S-3500N and S-5200, Hitachi, Japan), and an atmic force microscope (AFM, SPA400, SII, Japan).

Thermal Annealing of Stretched Polymer Films with Surface Patterns

The stretched polymer film with surface patterns was placed on a glass substrate, the sample was heated at 90 °C for 5 min on a hot stage (RINKAM600, Japan hitech, Japan). After heating, the sample was coold to room temperature, and then, the surface structure was observed same as the film before thermal treatment.

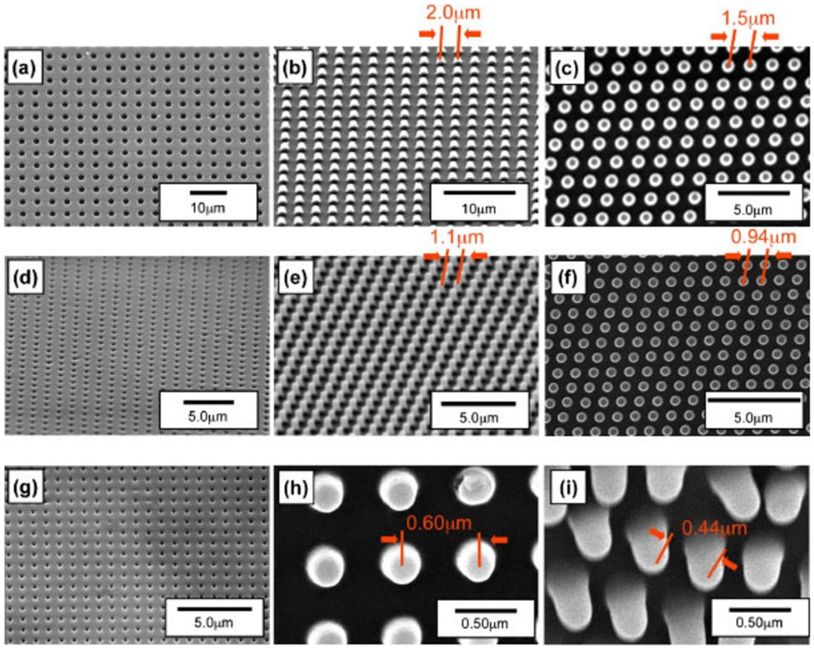

Figure 2. SEM images of the surface structures of PDMS molds (a), (d), (g), transferred structures onto stretched polymer films (b), (e), (h), and surface patterns after heat treatment (c), (f), (i).

MSL Process

The 2.0 μm diameter pillar with 2.0 μm spacing formed on a PSt film was used as template, the PDMS mold was prepared by above mentioned method. By using CEL process, the surface patterns were transferred onto 2.0 times uniaxial-sretched APL8008T film. After thermal treatment, PDMS mold was prepared according to the above-mentioned method by using the shrunk polymer film with surface patterns as template. By using this mold, the CEL process onto the same stretched polymer film and thermal treatment were performed. After heating the sample at 90 °C the surface patterns were observed.

RESULTS AND DISCUSSION

CEL Process and Shrinking the Stretched Polymer Films by Heat Treatment

Figure 2 shows SEM images of the surface patterns of PDMS molds (a), (d), (g) and transferred pattern onto the stretched polymer films by CEL process (b), (e), (h), respectively. PDMS molds have rectangular-arranged holes of 1.0 μm, 0.50 μm, and 0.25 μm diameters with same spacing, respectively. Thus, the center-to-center distances between holes of PDMS molds are 2.0 μm, 1.0 μm, and 0.50 μm, respectively. The depths of the holes were 1.0 μm reflecting the template polymer pillar heights. The negative images of the PDMS molds were successively formed on the surface of the 1.5 times biaxially stretched polymer film. The center-to-center distances of pillar structure prepared on the stretched polymer films are 2.0 μm, 1.1 μm, and 0.60 μm, respectively. The heights of the transferred pillars are 0.98 μm, 0.80 μm, and 0.52 μm, respectively. During pressing the PDMS mold, the dissolved polymer molecules are sacked by capillary force. However, there is air trapped in the pores of PDMS mold. Thus, the heights of the pillar are lower than that of the template polymer sheet.

After heating at 90 °C for 3 min, the film shrunk to the original unstretched state. After this heat treatment, the center-to-center distances of surface patterns decreased to 1.5 μm, 0.94 μm, and 0.44 μm, respectively (Figure 2(c), (f), (i)). The surface patterns were reduced to 30% of original patterns since the 1.5 times biaxially stretched films were used. When the pattern size comes to smaller scale (like as shown in Figure 2(i)), the shape of pillars lose their edge, and the some pillars vended due to the van der Waals force of them. Figure 3

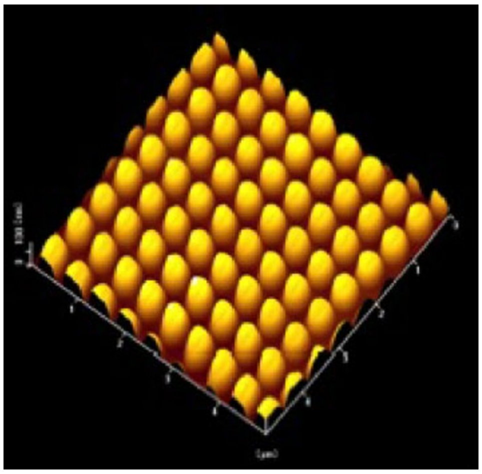

Figure 3. A typical AFM image of surface patterns of stretched polymer film after shrink.

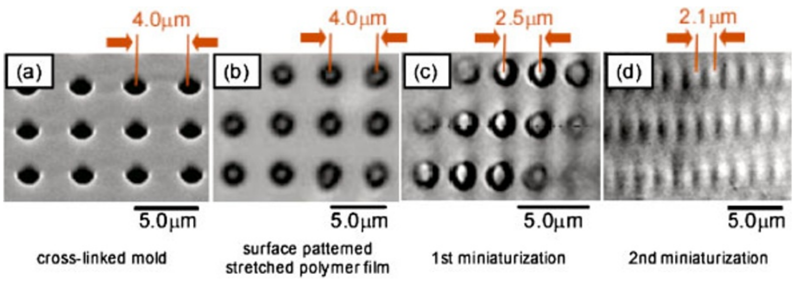

Figure 4. A SEM image of the PDMS mold (a), optical micrographs of transferred pattern (b), after 1st shrinking (c), and after 2nd shrinking (d), respectively.

shows a typical AFM image of the surface structures after shrink. The pillars have cone shapes due to the different shrinkages between top and bottom of pillars.

MSL Process

By using once miniaturized pattern as the 2nd template, the surface pattern will be miniaturized further. Figure 4 shows the result of the 2nd cycle processes. In this experiment, the 1.5 times uniaxially-stretched films were used. Figure 4(a) and 4(b) shows the SEM image and optical micrograph of cross-linked stamp and the transferred pattern onto the stretched polymer film, respectively. The pattern was successively transferred onto the surface of stretched polymer film. After shrinkage, the surface pattern was shrunk in one direction, the center-to-center distance of the pillar were miniaturized 4.0 μm to 2.5 μm (Figure 3(c), shrinkage ∼ 30%). Moreover, the top shape of the pillar was deformed from circle to ellipsoidal after shrink since the film shrunk uniaxially. By using this film as the 2nd template, the CEL process and heat treatment were performed for further miniaturization. As the result, the center-to-center distance of the pillar was miniaturized from 2.5 μm to 2.2 μm (Figure 4(d)). This result indicates that the pattern size can be miniaturized beyond the original size and shrinkage of the stretched polymer film by using this cycle of shrinking processes. From AFM measurement, the height of the pillars after 2nd miniaturization decreased from 1 μm to *ca.* 70 nm due to imperfection of filling the template pores and shrinkage of pillars. This problem should be improved to future applications.

CONCLUSION

We demonstrated the novel fabrication method of micro-patterns onto thermally and chemically weak stretched polymer films by using cross-linked polymer molds (the CEL process). The swollen mold softens only the surface of stretched polymer film, and surface patterns were easily transferred onto the stretched polymer film without any damage. After thermal shrinkage, the surface pattern was miniaturized. Furthermore, when these processes were performed repeatedly, the surface patterns miniaturized further. These processes can be a good candidate for micro patterning without using any expensive instruments and multiple processes. These processes can be applicable to fabricate micro-patterns not only hydrophobic polymer films but also to hydrophilic polymer films, inorganic materials and so on. In this experiment, we used a PDMS mold as a cross-linked stamp. The polymer gels including hydro-gels and organo-gels and other cross-linked materials can be used as templates, too.

Electronic Supporting Information Available: Figures S1 and S2. These materials are available *via* the Internet at http://www.spsj.or.jp/c5/pj/pj.html.

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