ORIGINAL ARTICLE

Self-assembled porous templates allow pattern transfer to poly(dimethyl siloxane) sheets through surface wrinkling

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Euler buckling forms surface microwrinkles ranging in size from sub-micrometers to tens of micrometers as a result of the modulus difference between the surface of the material and the material itself. When the buckling occurs in the limited areas smaller than the wrinkle wavelength, the shape of the buckled surface deforms into concave dimples or convex lenses. The shape of the buckled surface can be controlled by changing the modulus of poly(dimethylsiloxane). Hierarchical patterning can also be achieved by using a photomask. This surface wrinkling process provides a novel way to nano- and micropattern soft substrates, including elastomers and gels.

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INTRODUCTION

Strong demand for the miniaturization of surface patterns has driven the development of novel fabrication technologies. Nanoimprint lithography makes it possible to realize a nanoscale surface pattern by stamping a patterned solid mold onto a melt of thermoplastic polymer or a photocurable resist.¹ Xia and Whitesides² have reported several processes for surface pattern transfer using poly(dimethylsiloxane) (PDMS) elastomer molds; this technique is called 'soft lithography'. By using PDMS molds, the surface patterns of the PDMS elastomer mold can be easily transferred to the surface of another substrate by using polymers,³ silicates⁴ and so on.⁵ In soft lithography, microcontact printing is one of the most well-known patterning processes that facilitate the formation of thiol patterns on a gold substrate.⁶ After etching of the bare gold surface, gold patterns can be formed. In this process, thiol ink has an important role in the pattern transfer process. We have also reported that surface patterns can be transferred onto polymer materials by using a PDMS elastomer swollen with solvent.⁷ Liquid solvent softens the polymer surface, and the PDMS mold engraves the patterns onto the surface of the polymer materials. Grzybowski *et al.*^{8–10} reported that metal nanostructures can be patterned by placed hydrogels containing an etching agent on a metal surface. These examples show that chemical reactions, degradation, swelling, adsorption and so on, which deform the surface structures of materials, can be used for patterning the surface of materials.

Euler buckling is one of the universal phenomena that occurs when a stiff skin layer is formed on a soft substrate.¹¹ Because of Euler buckling, surface wrinkling occurs on soft substrates. There are some reports, both theoretical and experimental, describing the formation of microwrinkles originating from Euler buckling. Whitesides *et al.*¹¹ reported the formation of microwrinkles when forming a metal layer on a patterned PDMS surface. Rogers *et al.*¹² showed the buckling of GaAs ribbons and its application for electronics. Stafford *et al.*¹³ showed that microwrinkles formed when grafting polymer brushes onto PDMS surfaces. Many other studies have reported the formation of microwrinkles and their applications.^{14–19} It has been reported that periodic microwrinkles are formed when the surface of the PDMS elastomer is oxidized by O₂ plasma or UV-O₃ treatments owing to the difference in Young's elastic modulus between the oxidized surface layers and bulk PDMS.²⁰ The periodicity of the microwrinkles can be controlled by changing the thickness and elastic modulus of the oxidized skin layer and PDMS, respectively. Kim *et al.*⁴ have reported that instead of microwrinkle formation, a convex microlens can be formed on a stretched PDMS sheet by introducing UV-O₃ through a porous mask following release of the stretching force. Chan and Crosby²¹ showed the confinement effect on the surface wrinkling of PDMS from introducing UV-O₃ through a mask with various pore sizes. They also show that the surface wrinkles disappeared when the size of the oxidized area was smaller than the persistent length of buckling.²² We also observed the same confinement effect on the

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surface wrinkles of the metal dots formed on a shrinkable polymer substrate.^{23–27} The persistent length (ζ) of one-dimensional buckling is calculated by the following equation:

$$\zeta = \lambda_0 \left(\frac{1}{2\epsilon^{1/2}} + 2\eta^{1/3} \right) \quad (1)$$

Here, λ_0 is the buckling wavelength of a semi-infinite surface, ϵ is the strain of the local region, and η is the moduli-mismatch ratio. The length scale ζ is a critical parameter in determining the morphology of the buckling structures. Typically, the ζ of an oxidized layer on a PDMS surface is approximately 50 μm . For dimensions D much greater than the persistence length, the wrinkles persist radially inward to ζ . Beyond this length, they interact with adjacent wrinkles. However, if the pore size of the mask (D) $< \zeta$, the surface pattern can be transferred to the PDMS surface by UV- O_3 exposure, and two types of buckled structures are observed: the microlens pattern and the dimple pattern.²²

In this paper, we show a novel surface patterning method based on the buckling of PDMS elastomers. A porous template was prepared by using self-organized honeycomb films or colloidal crystals. After transferring the template onto PDMS films with different elastic moduli, the porous patterns were transferred onto the PDMS surface as dimples or lenses via the introduction of UV- O_3 onto the PDMS surface through the template pores. Hierarchical patterning of the dimple structure was also shown. The surface patterns and the surface modulus are discussed based on the results of atomic force microscopy (AFM) measurements.

MATERIALS AND METHODS

Preparation of porous templates:

Honeycomb-patterned polymer films were prepared by a simple casting process under humid conditions.²⁸ An amphiphilic copolymer (**1**) was synthesized according to the procedure outlined in the literature Chart 1.²⁹ Polystyrene (PS) and **1** were dissolved in chloroform to form a 10 mg ml⁻¹ solution. The solution was cast onto a glass substrate, and the solvent was evaporated by applying a flow of humid air (relative humidity > 90%) with a velocity of 100 l min⁻¹. After complete evaporation of the solvent, the surface structure was observed by using an optical microscope or a scanning electron microscope (SEM).

Colloidal crystal films were prepared by coating an aqueous dispersion of PS latex (diameter = 500 nm, Duke Scientific, Waltham, MA, USA) by using a handmade apparatus described in the literature.³⁰ Typically, the two glass slides were placed parallel with a 500 μm gap, and then, the aqueous dispersion of PS latex was used to fill in the gap between the glass slides. One glass slide moved steadily at a velocity of 10 $\mu\text{m s}^{-1}$, and the colloidal crystal films were continuously formed from the meniscus of the aqueous dispersion formed at the edge of the glass slide. After complete evaporation of water, fcc-type colloidal crystal films were prepared. The surface structure of the film was observed by using an SEM.

Experimental Details

Preparation of PDMS sheets: PDMS elastomer sheets having various moduli were prepared from Sylgard 184 (Dow Corning, Midland, MI, USA). The

Chart 1 Chemical structure of polymer 1 ($m/n = 4$)

prepolymer of PDMS and the Pt catalyst were mixed and cast on a glass dish ($\phi = 90$ mm). After degassing in vacuo for 1 h, the PDMS elastomer sheets were prepared by heating the samples at 70, 120 and 200 °C for 2 h. The mixing ratio between the PDMS prepolymer and the catalyst was changed from ten-to-one to forty-to-one.

Surface wrinkling. A schematic illustration of surface wrinkling is shown in Figure 1a. The PDMS elastomer sheet was washed with benzene or chloroform, and then dried at room temperature. The PDMS elastomer sheet was cut using a surgery knife and removed from the glass dish with tweezers. The PS honeycomb films were treated with UV- O_3 to make the film brittle by using a UV- O_3 cleaner (OC-250615-D + A, IWASAKI, Tokyo, Japan) equipped with six 25 W lamps.³¹ The PDMS elastomer sheet was placed on the porous template upside down and pressed. Only the surface porous structure was transferred onto the PDMS elastomer after removing the PDMS elastomer from the template surface. The UV- O_3 treatment was performed for 3–10 min. After the UV- O_3 treatment, the porous template was removed with adhesive tape.

The same surface wrinkling process was performed by using colloidal crystal templates. After the formation of colloidal crystals, a PDMS sheet whose ϵ was 0.18 MPa was placed on the colloidal crystal and pressed.

Hierarchical patterning was performed by placing a photomask (Edmund Scientific, New York, NY, USA) on the template-loaded PDMS sheet. After the same surface wrinkling procedures, the surface pattern was formed after removing the template.

Analysis. The surface structures of prepared samples were observed by using a digital optical microscope (VHX-1000, Keyence, Tokyo, Japan), a field emission-type scanning electron microscope (FE-SEM, S-5200, Hitachi, Tokyo, Japan), an atomic force microscope (AFM, SPI400, Seiko Instruments, Chiba, Japan), and a laser scanning microscope (LSM, LEXT OLS4000, Olympus, Tokyo, Japan). Young's elastic modulus of the prepared PDMS elastomer sheets was measured by a drawing experiment.¹⁵ The edges of a PDMS specimen were fixed on the clamps of a drawing stage and a load cell (SPZ, IMADA, Toyohashi, Japan), and then the sample was stretched and the applied force and strain of the sample were measured. The PDMS elastic modulus ϵ is extracted from the mono-axial strain–stress equation $\sigma_{zz} = \epsilon \bullet E$, where σ_{zz} is the axial true stress applied to the PDMS and E is the axial strain of the PDMS. We have dF/S_z , where dF is the axial resultant force applied to the PDMS and S_z is the cross section of the PDMS specimen; $E = \delta l_0/l_0$, where l_0 is the initial length of the specimen and δl_0 is the stretch for the current axial resultant force. Thus, Young's modulus ϵ of PDMS is obtained from the following equation:

$$\epsilon = \frac{dF_z}{S_z} \cdot \frac{l_0}{\delta l_0} \quad (2)$$

The modulus of PDMS elastomer sheets before/after UV- O_3 treatment was measured by using an AFM.³² By using a procedure based on a combination of Johnson–Kendall–Robert contact mechanics and a ‘two-point method’ together with AFM force volume measurements, maps of the elastic modulus of the PDMS surface were obtained. Force volume (FV) experiments were performed using a commercial AFM system (Multimode series with a NanoScope V controller) under ambient conditions. In the FV-mode, force curves were collected over randomly selected surface areas at a resolution of 64 × 64 pixels. The cantilevers used were OMCL-TR800PSA-1 (Olympus), whose nominal spring constant is 0.57 N m⁻¹. The actual spring constant was measured by the thermal tune method with a value of the spring constant of 0.53 N m⁻¹. The calibrated deflection sensitivity with a hard metal surface was used in the analyses.

RESULTS AND DISCUSSION

Surface pattern transfer of honeycomb structures onto a PDMS surface

Figure 1b shows a typical SEM image of honeycomb films. A hexagonally arranged microporous structure was clearly observed. The pore size of the honeycomb film used in this experiment was 14 μm , which is smaller than the ζ of PDMS microwrinkles. The inset

Figure 1 Schematic illustration of the surface wrinkling process (a), an scanning electron microscope (SEM) image of a honeycomb film of Polystyrene (b), an SEM image of a porous template on a poly(dimethylsiloxane) (PDMS) sheet (c), and atomic force microscopy images of a concave dimple array (d) and a convex lens array (e).

image in Figure 1b shows a cross-sectional SEM image of the honeycomb film. It has a double-layered structure supported by pillars at the apexes of the honeycomb hexagons. After pressing onto the PDMS surface, the center portion of the pillar, which is mechanically the weakest portion of the pillar, was broken. Figure 1c shows an SEM image of the porous template on the PDMS sheet. The hexagonally arranged porous template was clearly observed. Figure 1d shows an AFM image of the dimple array structure prepared by a 15-min UV-O₃ treatment through the honeycomb template onto the PDMS sheet whose ϵ was 1.18 MPa. Concave-shaped dimples are clearly observed. In contrast, the convex-shaped lenses were observed on the PDMS surface whose ϵ was 0.18 MPa (Figure 1e).

These structural differences were caused by the ϵ difference of PDMS. Figure 2 shows plots of the respective depths and heights of dimples and lenses formed on PDMS sheets having various ϵ . When ϵ is high enough, concave-shaped dimples were formed on the surface (Figure 2a). The depth of the dimple increased with decreasing ϵ until c.a. 0.5 MPa. When the ϵ decreased, the shape of the UV-O₃-exposed region changed from concave dimples to convex lenses (Figure 2b). The height of the lenses also increased with decreasing ϵ . As reported in the literature, the surface structure transition from dimple to lens was observed under strong confinement ($D < \zeta$).^{23–26} According to the equation (1), the ζ of buckling increases with decreasing ϵ of PDMS. Thus, the oxidized layer on the soft PDMS substrate is under a stronger confinement field than that of the hard PDMS substrate. Because of the oxidation, the volume of the oxidized layer gradually increased, as a result, the curvature of the surface was inverted. Thus, this strong confinement makes the oxidized surface protrude.

As shown in Figure 2, the depths and heights of the respective dimples and lenses were increased with increasing UV-O₃ treatment

Figure 2 Relationship between the elastic modulus of poly(dimethylsiloxane) sheets and the height or depth of the concave dimples and convex lenses. The depths and heights of the dimples and lenses after 3 min (■), 5 min (●), 10 min (◆), and 15 min (▲) of UV-O₃ treatment.

time. Supplementary Figure S1 For example, the depths of dimples formed on a 1.8 MPa PDMS sheet decreased from 143 to 102 nm with increasing UV-O₃ treatment time from 5 to 15 min. The amplitude of the deformation depends on the difference of ϵ between the oxidized

Figure 3 Elastic modulus mapping of poly(dimethylsiloxane) surfaces after 5 min (a), 10 min (b) and 15 min (c) of UV-O₃ treatment measured by using an atomic force microscopy.

layer and the bulk PDMS. The modulus distribution on the PDMS surface was measured by FV AFM measurements. The surface modulus can be calculated from the pull-out force between an AFM cantilever and the PDMS surface. By using this method, the effect of the UV-O₃ exposure time on the surface modulus was observed. Figures 3a–c show two-dimensional modulus distributions at the surface of the PDMS sheets, which had a ϵ of 1.8 MPa after the formation of dimples by UV-O₃ treatment for 5–15 min. The modulus measured on the dimples increased with increasing UV-O₃ exposure time. In contrast, the other portion of the PDMS surface did not show any significant modulus changes compared with their original modulus. Because of the difference in the surface modulus and the bulk modulus, the depth of the dimple increased with increasing UV-O₃ exposure time.

Hierarchical patterning of honeycomb structures onto PDMS sheets

Hierarchical patterning of the concave-shaped dimple array structure was fabricated by exposing UV-O₃ through a photomask onto a PDMS sheet covered with a porous template (Figure 4a). Because O₃ molecules were generated by irradiation with UV light of atmospheric O₂ molecules in the UV-O₃ chamber, the generation of O₃ was prevented at the PDMS surface covered with the photomask. Figure 4b shows a photograph of hierarchically patterned PDMS sheets whose ϵ was 1.4 MPa after a 15-min UV-O₃ treatment. The patterns of the photomask were clearly observed. Figures 4c and d show an optical micrograph and an LSMS image of patterned PDMS surfaces, respectively. A clear boundary between the concave-shaped dimples and the nondimpled surface was observed. From these results, hierarchical patterning via a combination of the porous template and the photomask was demonstrated by using surface wrinkling. The convex-shaped lenses are also hierarchically patterned by using a photomask when the ϵ of the PDMS sheet was 0.18 MPa.

Pattern transferring of colloidal crystals

The resolution limit of the lithographic technique is an important factor for practical applications. To examine the nanoscale pattern transfer using the surface wrinkling, colloidal crystals of 500 nm PS particles were used as templates. Figure 5a shows a schematic illustration of the sample preparation procedure. Colloidal crystals of 500 nm PS colloidal particles were prepared and placed on a PDMS sheet ($\epsilon = 0.18$ MPa). After UV-O₃ treatment, the surface pattern was observed by using an AFM. Figure 5b shows prepared surface patterns on the PDMS sheet. Hexagonally arranged dimples were formed. In this case, the UV-O₃ was introduced through the gap between the colloidal crystals, and then, the hexagonal rims rose up spontaneously. Finally, the hexagonally arranged dimples were clearly observed. The

Figure 4 Schematic illustration of the hierarchical patterning process of surface wrinkling (a), a photograph (b), an optical micrograph (c) and a laser scanning microscope image (d) of a hierarchically patterned poly(dimethylsiloxane) (PDMS) sheet.

width of the rim was c.a. 100 nm, which was smaller than the wavelength of the UV light ($\lambda = 197$ nm) used to generate O₃ molecules from the O₂ molecules in the chamber. Because the buckling caused formation of a surface-oxidized layer via reactive O₃ molecules, the resolution of the pattern transfer does not depend on the wavelength of the light. This result indicates that this surface wrinkling process can transfer a pattern that is smaller than the diffraction limit of the light.

CONCLUSION

In this paper, we show a novel pattern transfer process using Euler buckling. By using the buckling process, concave-shaped dimples or convex-shaped lenses were formed on PDMS sheets, depending on

Figure 5 Schematic illustration of the surface wrinkling process using colloidal crystals (a), an scanning electron microscope image of the colloidal crystal (b), and an atomic force microscopy image of surface patterns formed on a poly(dimethylsiloxane) (PDMS) sheet (c).

the elastic modulus of the PDMS sheets. Hierarchical patterning of the PDMS surface could be achieved by using photomasks. The resolution of this process can exceed the diffraction limit of the UV light used in this experiment. This ‘surface wrinkling’ process can be used as a novel fabrication technique for patterning soft and brittle materials without any expensive equipment. By using this process, surface patterns can be created on various soft materials, including rubbers, gels and stretched polymer films. These patterned materials may be applicable for various photonic, electronic and biotechnological applications.

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