1. Introduction

Micro/nano-fabrication plays an important role in optical devices, such as light-emitting diodes (LEDs),[1, 2] displays with micro-lens array[3, 4] and solar cells with a moth-eye structure.[5–7] Conventionally, the fabrication processes for these devices have been developed for planar bulk substrates.[1–9] Recently, patterning methods for self-standing curved films have attracted considerable attention because of their potential to be applied for human body implantable devices and flexible devices as well as optical devices.[10–14] Thus, to realize these devices, patterning methods for self-standing curved films are required. There have been numerous reports on methods for patterning curved bulk substrates.[15–17] However, the size of the patterning area is limited in these methods because it requires the complex three-dimensional (3D) stage control and precise focusing of lithography system.[17, 18] In addition, conventional patterning systems, such as X-ray lithography and direct laser beam process, are time consuming.[17]

Among these technologies, soft ultraviolet (UV) imprint lithography, which uses polydimethylsiloxane (PDMS)-based elastic molds, is a simple method for large-area patterning curved surfaces.[19] This method exploits the advantages of PDMS molds, such as their superior flexibility, which offers formability and uniform patterning.[17, 19, 20] Moreover, PDMS exhibits high releasability between the mold and the resist layer because of low surface free energy (~16 mJ/m²).[17, 19–22] Meanwhile, several studies have been reported on patterning curved bulk materials, although patterning a self-standing curved resin film has not been reported thus far.[15–17]

In this study, we proposed a novel fabrication method for a self-standing curved film with pillar-shaped hole patterns using large-area spherical soft UV imprint lithography. The concept of the fabrication process is illustrated in Fig. 1, which highlights the two key points of this method. Firstly, spherical soft UV imprint lithography enables patterning large-area curved surfaces. Secondly, simply by sandwiching a UV-curable resin between two hydrophobic PDMS molds, a thin curved film with pillar-shaped hole patterns is formed. The PDMS molds for the UV imprint were prepared using a 3D printer system, which can form fine structures over a large area. The proposed fabrication
process is considered effective for patterning the uniform spherical or curved surfaces of thin films.

2. Experimental

2.1 Fabrication of PDMS molds

The design of the patterned and convex PDMS molds is summarized in Fig. 2. The PDMS molds were prepared with a diameter of 70 mm, curvature radius of 40 mm, and height of 21.8 mm. The patterned mold was printed with pillars, each with a diameter of 500 μm and a height of 500 μm. All pillars were concentrically positioned perpendicular to the curved surfaces with intervals of 700 μm. The detailed fabrication process for the PDMS molds is shown in Fig. 3. The mold with the pillars was prepared as the initial mother mold, since pillar hole pattern is difficult to fabricate due to the resin deformation caused by the heat of 3D printer process. Firstly, mother molds were prepared using a high resolution 3D printer system (AGILISTA-3000, Keyence Co., Ltd.) to pattern the pillar-shaped holes uniformly over a diameter of 61 mm. Complex 3D structures can be easily produced by 3D printers, which print thin layers of photosensitive materials layer by layer by curing the materials with a UV light to form a solid structure. [23] The model material was rigid acrylic resin (AR-M1, Keyence Co., Ltd.), and the support material was water-soluble acrylic resin (AR-S1, Keyence Co., Ltd.) Next, to create an inverted mold from the mother mold, a mixture of PDMS and a curing agent (10:1 w/w, SILPOT 184, Dow Corning Toray Co., Ltd.) was poured into the mother mold and cured at 70°C. After peeling off the inverted mold, a daughter PDMS mold was replicated from the inverted mold under the same conditions. Finally, the inverted mold was peeled off from the daughter PDMS mold. The 3D-printed mother molds were replaced with PDMS to enable the transmission of UV light during the subsequent imprinting process.

2.2 Fabrication of hole-patterned self-standing curved film

The fabrication process of the patterned self-standing curved film is shown in Fig. 4. First, UV curable resin (PAK-01, Toyo Gosei Co., Ltd.) was poured into the patterned PDMS mold. The amount of the resin was optimized to obtain a 500-μm-thick thin film. Then, a convex mold was set into the patterned mold with or without an additional weight (1.5 kg). After waiting for 5 min to fill the resin, UV light (λ = 365 nm) was irradiated at 2.4 J/cm² from the back side of the patterned PDMS mold under the ambient atmosphere to pre-cure the resin. Subsequently, the additional weight was removed, and the resist was completely cured by irradiation with UV light at 3.0 J/cm².
from the front side. Finally, the patterned resist film was peeled off from both of the molds.

3. Results and Discussion

3.1 Fabrication results of the PDMS molds

Figure 5 shows images of the patterned mother and replicated PDMS molds. The pillar pattern of the mother mold was transferred onto the PDMS mold. The pillars of the mother mold were formed only on the center part due to resolution limitation of the 3D printer system. Thus, we evaluated at the center part of the molds to confirm the proposed concept. The pillars were 511 μm (+2%) in diameter at the top, 809 μm (+62%) in diameter at the bottom, and 528 μm (+6%) in height, as shown in Fig. 6 (a). The bottom diameter of the pillar pattern was different from the designed diameter (500 μm) due to the resolution limitations of the 3D printer system, although the height and top diameter of the pillars were accurately formed, with an error of less than 6%. Meanwhile, on the center part of the PDMS replicated mold, the pillars were 513 μm in diameter at the top, 832 μm in diameter at the bottom, and 532 μm in height, as shown in Fig. 6 (b). These results show that the patterned PDMS mold successfully replicated the mother mold.

3.2 Fabrication results of the hole-patterned self-standing curved film

Figure 7 shows an image of the entire self-standing curved film with pillar-shaped hole patterns fabricated using the proposed spherical soft UV imprint lithography method, which successfully fabricated the thin curved film with a curvature radius of 40 mm. The low surface free energy of the PDMS molds enables demolding the thin resin film without any significant cracks.[17, 19–22]

Optical microscope images of the pillar-shaped hole patterns on the curved film without and with an additional weight are presented in Fig. 8 and 9. Without an additional
weight, the top and bottom diameter of the pillar-shaped holes were 808 μm and 512 μm, respectively, and 822 μm and 512 μm with an additional weight, respectively. The heights of the hole pattern without and with the additional weight were 529 μm and 509 μm, respectively. As shown in these figures, the pillar-shaped hole pattern was successfully transferred from the patterned PDMS mold over a diameter of about 14 mm with an error of less than 5% under both conditions. These results indicate that the elasticity of the PDMS molds provides an advantage for patterning on a uniform curved surface while accurately maintaining the hole pattern. Notably, the hole pattern without an additional weight exhibited a residual layer of 271 μm below the holes. Meanwhile, the hole pattern with an additional weight had no residual layer, and the pillars passed through the film.

In conventional imprint lithography, which generally uses a hydrophobic mold and a hydrophilic substrate, a residual layer remains.[19, 24, 25] In contrast, in the proposed method, the resin was sandwiched between a hydrophobic patterned PDMS mold and a hydrophobic convex PDMS mold. Thus, it is assumed that the resin between the patterned and convex molds was repelled when optimal forces were applied. This suggests the possibility of a zero-residual-layer imprint with other conventional imprinting methods as well as with the proposed soft UV imprinting method.

4. Conclusion

In this study, we proposed a novel method to fabricate a self-standing curved film with pillar-shaped hole patterns using large-area spherical soft UV imprint lithography. This study can be summarized as follow:

(1) A PDMS mold was fabricated from a 3D-printed mold to prepare a pillar pattern over a large area with a curvature radius of 40 mm.

(2) A self-standing curved film with pillar-shaped hole patterns was successfully fabricated by exploiting the elasticity and low surface free energy of the PDMS molds.

(3) A zero-residual-layer imprint was achieved by adding a weight of 1.5 kg on top of the mold maintaining the accuracy of the hole pattern.

Furthermore, evaluations of the wide range uniformity of the pillar pattern are undergoing study. In conclusion, we expect that in the near future, the proposed fabrication will be applied to pattern large area uniformly curved surfaces for functional devices such as artificial compound eyes. Moreover, we believe that the proposed method could be applied to not only microscale but also nanoscale imprint lithography.

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