Fabrication of Multiscale Patterns via Serial Imprinting with the Hierarchical Molds

Jung Won Bang

School of Mechanical and Aerospace Engineering

Seoul National University

Korea

Abstract

Multiscale patterning process is a technique which can be achieved from both the micro- and nanoscale patterns. Recently, the multiscale patterns have been utilized across a variety of research fields. In particular, multiscale patterning technique, which could fabricate patterns on the same plane regardless of scale, shape, height and depth of patterns, is one of emerging issues in the research area with polymers. Existing patterning techniques were suitable for fabricating monoscale patterns, however, which have been limited to fabricate multiscale patterns on the same plane because of the essential utilization of the etching or developing process. Here, we present a new type of multiscale patterning technique via serial imprinting with hierarchical molds. The hierarchical molds, which were made of ultraviolet (UV)-curable polymer resins, were composed of microscale bottom part and micro/nanoscale top part. These structures enabled to fabricate multiscale patterns on specific area on the same plane by serial imprinting, which was possible because of enough height and width of these structures. In the method, multiscale patterns were generated on the same plane regardless of scale, shape, height and depth of patterns. In addition, the multiscale patterns simply generated on flat and complex surfaces by using the developed patterning technique.

Key Words: Multiscale patterning, Hierarchical structure, Imprinting

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imprinted patterns on the flat surface. The patterns were imprinted by the hierarchical molds based 150-μm dot patterns (width/space = 1:1).

Figure 4. Multiscale patterns fabricated by the third imprinting process on the flat surface. (a) Schematic illustration of the third imprinting process for fabricating the multiscale patterns. (b, e, h) Optical images of aligning process for the serial imprinting process. (c, d) Micro- and microscale patterns (15-μm box and 5-μm dot arrays). (f, g) Micro- and nanoscale patterns (5-μm dot and 300-nm line arrays). (i, j) Nano- and nanoscale patterns (800-nm dot and 300-nm line arrays).

Figure 5. Multiscale patterns fabricated by the serial imprinting process on the complex patterns. (a) Schematic illustration of multiscale pattering technique on the complex patterns. (b-f) SEM images of the first imprinted patterns by the complex patterned molds. (g-p) The multiscale patterns fabricated by two times imprinting process. (g, h) Optical images of aligning process for the serial imprinting. (h-k): (i) 5-μm dot, (j) 800-nm dot and (k) 300-nm line arrays fabricated on 200-μm line patterns (h). (m-p): (o) 800-nm dot and (p) 300-nm line arrays fabricated on microscale radial patterns (m, n).

Figure 6.	Multiscale line patterns composed with alternated nanoscale patterns. (a) Schematic illustration of the multiscale line patterns fabricated by serial imprinting with cross aligning process. (b) 3D graphic images of the multiscale line patterns. (c) Optical images of cross aligning process for fabricating alternate nanoscale patterns. (d-f) SEM images of multiscale line patterns imprinted alternate nanoscale patterns (800-nm dot, 300-nm line arrays) on 200-μm line patterns.

Nomenclature

γ	Surface tension
E	Young's modulus
h	Height of line pattern
a	Width of line pattern
w	Spacing between the adjacent lines

1. Introduction

With the advances of nanotechnology, patterning process have been extensively researched and developed over the past decades.[1-3] Recently, demands of multiscale patterning process have been increased across a variety of research fields including photovoltaics,[4-5] fuel cells,[6] display devices,[7-8] Biomimetics,[9-10] lab chips,[11] sensors,[12] aerosol lithography,[13-14] and transfer printing techniques.[15] In particular, multiscale patterning technique, which can fabricate patterns on the same plane regardless of scale, shape, height and depth of patterns, is one of emerging issues in the research fields with polymers.

In general, existing patterning techniques were potentially suitable to fabricate monoscale patterns, however, which have been limited to fabricate multiscale patterns on the same plane. For example, photo lithography, which is one of typical patterning techniques, included the essential utilization of developing and etching process. In this case, patterns fabricated by this technique could not help having some limitations in scale, shape, height and depth of them. If patterns were designed from microscale to nanoscale, these would have no choice but to be fabricated in monoscale, because of the essential utilization of the etching or developing process. [16] Also, electron-beam (e-beam) lithography was barely suitable to fabricate patterns on large and flexible substrate.[17] The ways of making hierarchical structures have been presented in soft lithography,[18-19] however, this methods was in no condition to fabricate multiscale patterns on the same level of plane.

Here, we present multiscale patterning technique to fabricate patterns on the same plane regardless of scale, shape, height and depth of them. A key idea is the serial imprinting process with hierarchical molds. The process allowed for hierarchical molds to fabricate multiscale patterns sequentially on the specific area on the same plane. The serial imprinting processes, which were repeated several times on other parts in the same plane, resulted in multiscale patterns to substrate overall. Besides, the hierarchical molds, which composed of microstructural bottom base and micro/nanoscale top part, provided structural compliance for the serial imprinting process. In addition, the multiscale patterns could be fabricated not only on the flat surface but also on the complex patterns by the patterning technique.

2. Results and Discussion

Fabrication process of the hierarchical structures is illustrated in Figure 1a. As reported in previous studies,[20-21] the process required two-step capillary force lithography (CFL) with UV-curable polymer resins (e.g., PUA: polyurethane acrylate, PFPE: perfluoropolyether, Table 1). In the first step, microscale bottom part of hierarchical structures were fabricated from polydimethylsiloxane (PDMS) molds on a flexible poly(ethylene terephthalate) (PET) film. When covered with the PDMS molds patterned from designed silicon masters, the PFPE resin spontaneously filled up the voids by capillary force, and then was partially cured by oxygen inhibition effect. The inner part of these structures solidified, however, the interface part between PFPE resin and PDMS molds was incompletely cured due to the effect. It is already reported that the effect caused by oxygen, passed through the PDMS molds, would act as inhibitor against polymerization of the resin.[22] After fabrication of the partially cured structures that were bottom part of the hierarchical structures, these were monolithically integrated with micro-/nanoscale patterns from PUA molds via vacuum-assisted CFL in the second step of the process. The monolithic hierarchical structures fabricated via the two-step CFL are shown in Figure 1. As shown Figure 1b-m, the structures were composed with various shape (dot, box, line, and radial form) and length scale (from 150 to 500 μm for the bottom part and from 300 nm to 20 μm for the top part) on the macroscale PET film (1 cm^2). The multilevel structures have not only structural compliance but also could be rationally designed. These notable advantages of the structures would open up the potential to be tools in patterning process.

Figure 2 depicts a schematic illustration for the fabrication process of multiscale patterns via serial imprinting with the hierarchical molds. To fabricate patterns on the same plane regardless scale, shape, height and depth of them, three key factors were required. The first key factor is the serial imprinting process which could allow multiscale patterns to be fabricated on the flat and complex patterns. The serial process was required the specially designed molds for fabricating patterns on the specific area on the same plane, but prevalent molds (e.g., holey monoscale patterned molds) have been unsuitable to this process. The second key factor is the rationally designed molds which were hierarchical structures utilized as molds in this process. As mentioned above, structural rigidity and design freedom of the hierarchical molds were suitable by comparison with that of the prevalent molds in the repetitive process. Also, as shown in Figure 2a, the hierarchical molds could imprint on the specific area which was contacted with top part of them and substrate. The third key factor is delicate time control of UV exposure for curing UV-curable resins. In our experiment, the number of imprinting process was controlled by UV exposure time (Figure 2b). If the UV exposure time was longer or shorter than moderate range (10~30 sec in each steps), the fabricated patterns would not be built properly. It means that the time control of UV exposure is the dominant factor in order to achieve the serial process. In other words, the serial imprinting process was needed for fabrication of multiscale patterns, and also, the hierarchical molds and the time control of UV exposure were required for the serial process.

To fabricate multiscale patterns on the flat surface, a series of three imprinting processes are required and the technique is illustrated in detail in Figure 3a. The first imprinting process was operated with PUA 311RM resin on the PET film by the flat mold, and subsequently, the second imprinting was carried out on specific area which was contacted by the hierarchical mold which could have diverse patterns. As shown in Figure 3b-e, the patterns (20-μm box arrays, 5-μm dot arrays, 800-nm dot arrays, and 300-nm line arrays) were two-step imprinted on specific area by rationally designed hierarchical molds (Figure 2b-e). The third imprinting would be the repeated process with another patterned mold on the other specific area (the circled region in Figure 3b).

Figure 4 displays the third imprinting process (Figure 4a) operated by aligning process (Figure 4b, e, h) and shows SEM images of multiscale patterns on the flat substrate. Figure 4b-d display microscale patterns included 15-μm box arrays, 5-μm dot arrays on 150-μm dot arrays on the same plane. Compared with the circled regions in Figure 3b and Figure 4c, it was demonstrated that the multiscale patterning technique operated via the three times serial imprinting process. Figure 4e-g display micro- and nanoscale combined patterns include 5-μm dot arrays and 300-nm line arrays. It is noteworthy that these multiscale patterns, which have the scale difference (about 20 times) between microscale patterns and nanoscale patterns, could be coexisted on the same plane by this technique. Also, serial imprinted nanoscale patterns include 800-nm dot arrays, 300-nm line arrays are shown in Figure 4h-j.

The Figure 5 demonstrates that the patterning technique would be able to fabricate various patterns with wide scale range (from 300 nm to 500 μm) on the flat surface as well as on the complex patterns. The first imprinting was operated for making complex patterns (Figure 5b-f) of PUA 311RM on the PET film, which were imprinted by inverse patterns from the bottom part of the PFPE hierarchical molds (Figure 2f-m). On this process, the first imprinted patterns were engraved sequentially via aligning process (Figure 5g, i) with usage of the digital microscope and XYZR moving stage. As shown in Figure 5g-p, the multiscale patterns were generated with micro-/nanoscale negative patterns (5-μm box arrays, 800-nm dot arrays, 300-nm line arrays) on the various shape (line, radial form) and microscale patterns (50~500 μm). According to the circled region in Figure 5, it is more apparent that the multiscale patterning technique could be carried out on the complex patterns.

In our experiment, we elaborated on the advantages of the serial imprinting process for the novel patterns. As shown in Figure 6, the multiscale patterning technique could be also achieved on the line patterns among the complex patterns. To fabricated unique line patterns (Figure 6b) imprinted alternate nanoscale patterns, the cross aligning process (Figure 6c) with rationally designed molds is a critical factor. The process enabled hierarchical molds based microscale line patterns to imprint multiscale patterns on the line patterns by turns. As shown in Figure 6a, microscale line arrays were formed on the PET film by the first imprinting, and then alternate nanoscale patterns were imprinted by the two times cross aligning process with the rationally designed molds. Figure 6d-f display that the unique line patterns were composed with alternately 800-nm dot arrays and 300-nm line arrays on 200-μm line arrays. It should be noted that the multiscale patterning technique with cross aligning process would open up possibilities for fabrication of patterns combined complex micro- and nanoscale patterns regardless shape, height and depth of them, and also, the noble patterns would be utilized to various research fields.

3. Conclusion

In this research, we have presented a fabrication technique for multiscale patterns by serial imprinting process with monolithic hierarchical molds which were made of UV-curable polymer resin via capillary force lithography. It turned out that the imprinting processes repeated several times on the specific areas on the same plane by hierarchical molds and delicate time control of UV exposure. Using this technique, rationally designed patterns are fabricated on the flat and complex patterned substrate, regardless of scale, shape, height and depth of them. The patterning technique would be useful in variety applications of research fields, especially in photovoltaics, fuel cells, display devices, Biomimetics, lab chips and sensors.

Experimental Section

Preparation of silicon, PDMS, PUA molds:

Silicon molds were designed by computer programs and fabricated by photo lithography. The master molds have negative impression patterns from 150 nm to 500 μm. PDMS molds were prepared on the silicon master molds. PDMS pre-polymer (Sylgard 184 silicon elastomer, Dow Corning) and its curing agent were mixed at a weight ratio of 10:1, and then thermally cured at 70℃ for 2 h in an oven. The PUA molds were also fabricated by the procedure reported earlier. [23]

Preparation of PEPE UV-curable Resin:

PFPE UV-curable resin was obtained by mixing with the PFPE-urethane methacrylate (MD700, Solvay Solexis, Italy) as the prepolymer and 2-hydro-2-methyl-1-1phenyl-1-propane (Darocur1173, Ciba Specialty Chemicals, Switzerland) as the photoinitiator at weight ration 97:3, and then thoroughly mixed for 24 h.

Fabrication of hierarchical molds of PFPE:

The monolithic hierarchical molds were fabricated by two-step CFL with PFPE UV-curable resin. In the first process, the bottom part of hierarchical molds was formed from resin covered patterned PDMS mold on a flexible PET film. When covered with the patterned PDMS molds, the liquid resin spontaneously filled up the voids by capillary force. On this process, generated structures were incompletely cured by oxygen inhibition effect. In the second step, the partial cured structures were monolithically integrated with micro-/nanoscale patterns via vacuum-assisted CFL with patterned PUA molds.

Multiscale patterning technique:

For the multiscale patterning technique, rationally designed hierarchical molds were utilized to serial imprint on the flat and complex patterns. The serial imprinting process allowed these molds to fabricate patterns on the specific area on the same plane, regardless scale, shape, height and depth of them. The process was operated with the digital microscope (Dino-Lite, Taiwan), XYZR stage (Science Town, Korea) and UV portable lamp (East-West Science, Korea).

Scanning electron microscopy (SEM):

SEM images were obtained using MERIN Compact/VP Compact en01 (Carl Zeiss, Germany) operating at accelerating voltages of 2~10 kV. The samples were coated with Pt to avoid charging effects.

Optical microscopy:

Optical images were obtained using AM4115T (Dino-Lite, Taiwan) operating at magnification of 20~220. The samples were aligned on XYZR stage (Science Town, Korea).

Table and Figures

Table 1. Surface and mechanical properties of UV-curable resins.

Material	Surface tension (γ_s) (mJm^{-2})	Elastic modulus (E) (MPa)
PUA 311RM (Polyurethane acrylate)	20-60	> 320
PFPE (Perfluoropolyether)	~ 12.7	~ 10.5

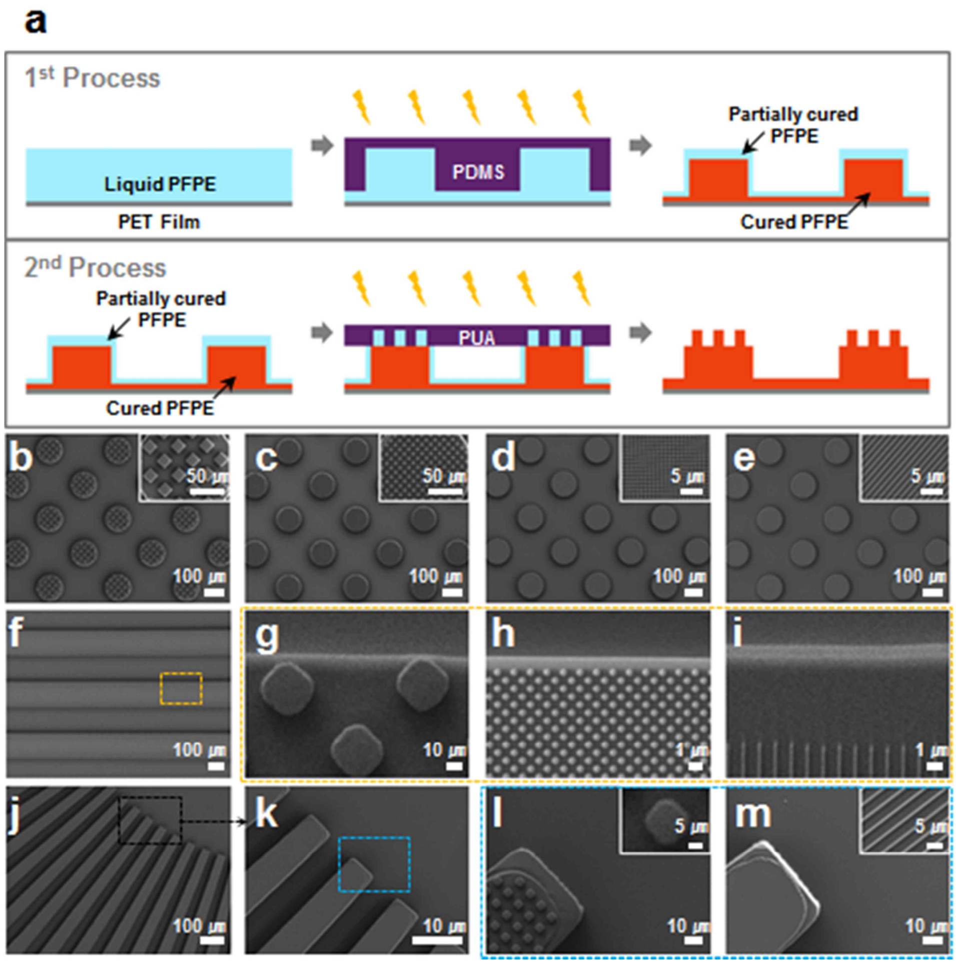


Figure 1. Monolithic hierarchical structures fabricated by two-step CFL. (a) Schematic illustrations of the two-step CFL. (b-m) SEM images of the hierarchical structures. (b-e): (b) 20-μm box, (c) 5-μm dot, (d) 800-nm dot, (e) 300-nm line arrays (top part) on 150-μm dot arrays (bottom part). (f-i): (g) 20-μm box, (h) 800-nm dot, (i) 300-nm line arrays (top part) on 200-μm line arrays (bottom part). (j-m): 20-μm box, 300-nm line arrays (top part) on microscale radial patterns (bottom part).

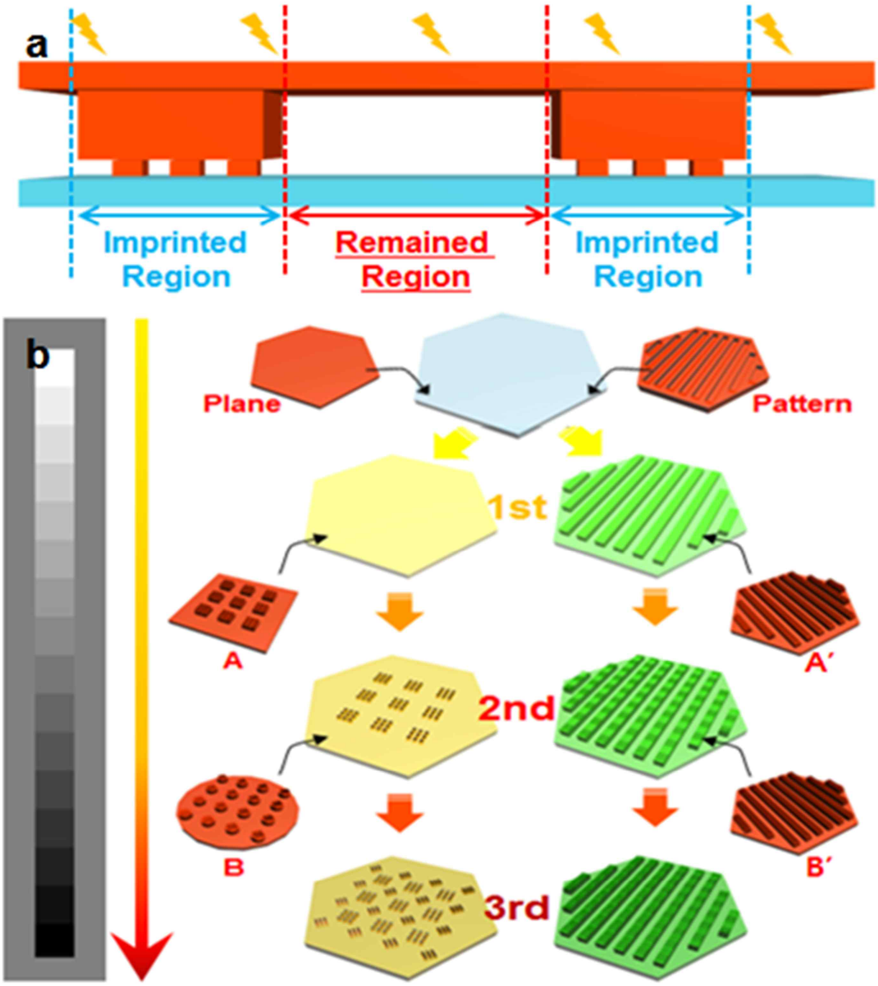


Figure 2. The serial imprinting process with the hierarchical molds for fabricating multiscale patterns. (a) The monolithic hierarchical structures utilized as molds in the serial imprinting process. (b) Schematic illustrations of the multiscale pattering techniques via serial imprinting with the hierarchical molds on the flat and complex patterns.

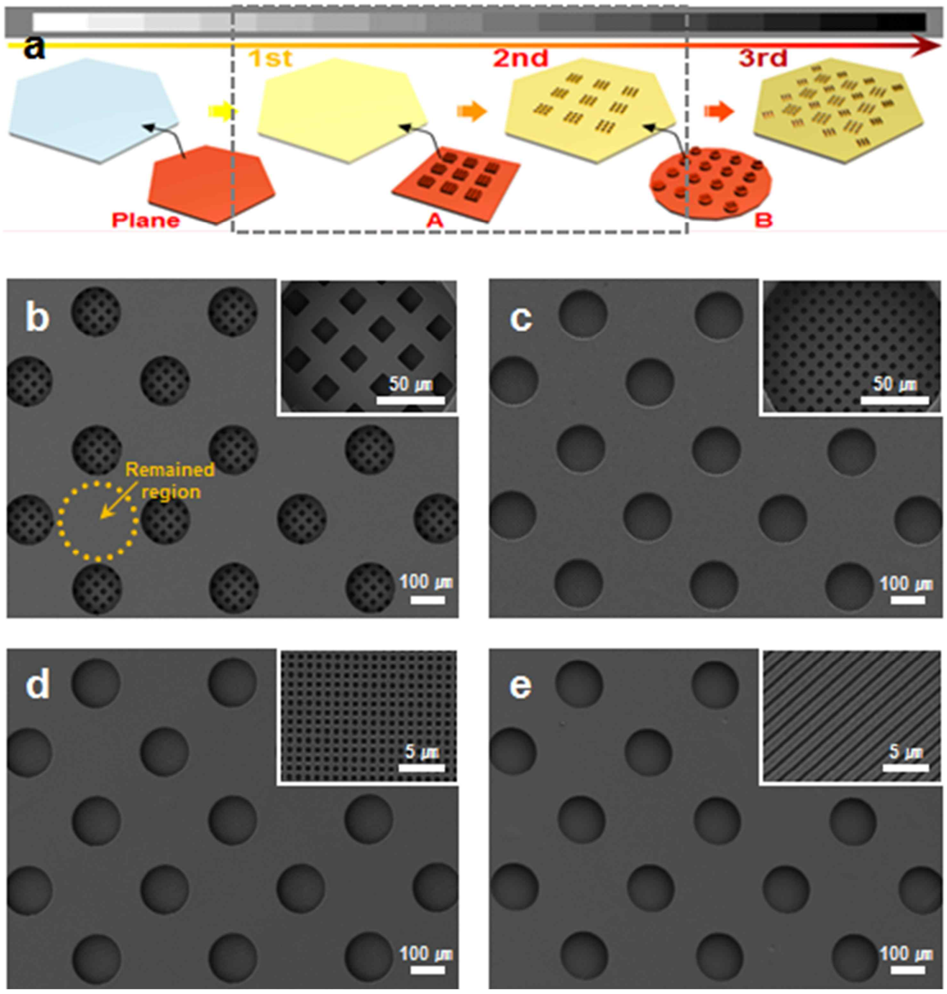
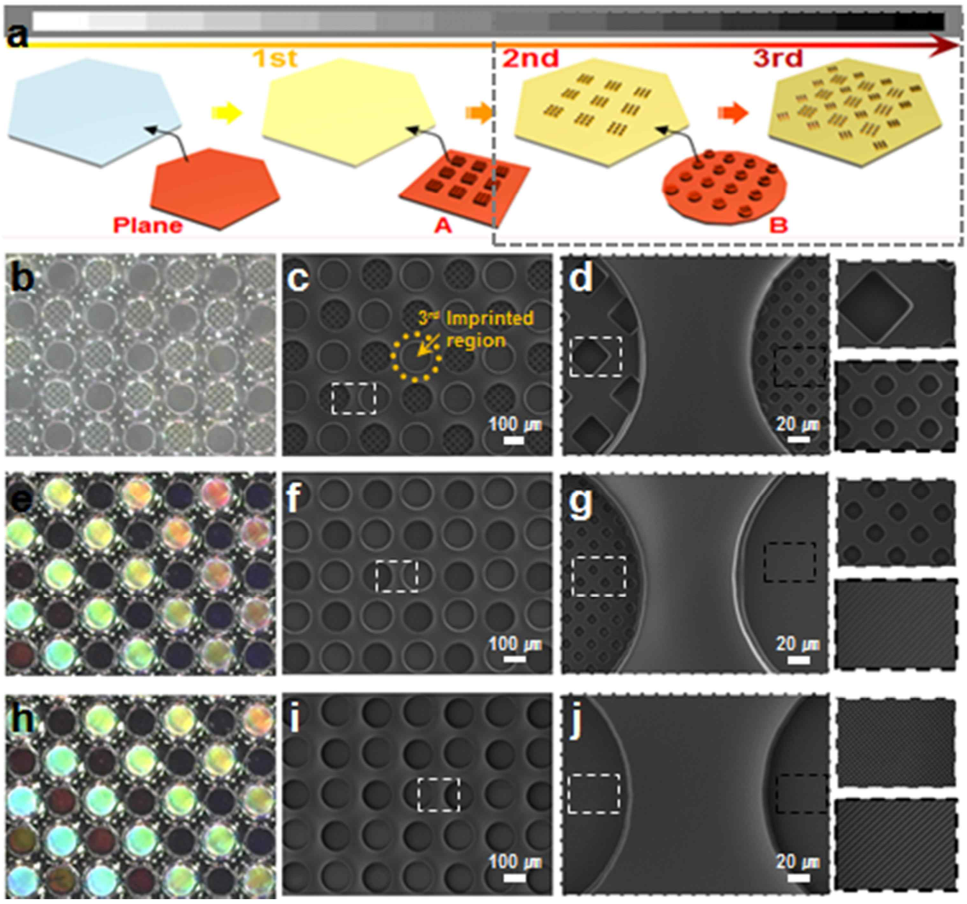


Figure 3. The second imprinting process for fabricating multiscale patterns on the flat surface. (a) Schematic illustration of the multiscale patterning techniques via serial imprinting with the hierarchical molds on the flat surface. (b-e) SEM images of the second imprinted patterns on the flat surface. The patterns were imprinted by the hierarchical molds based 150-μm dot patterns (width/space = 1:1).



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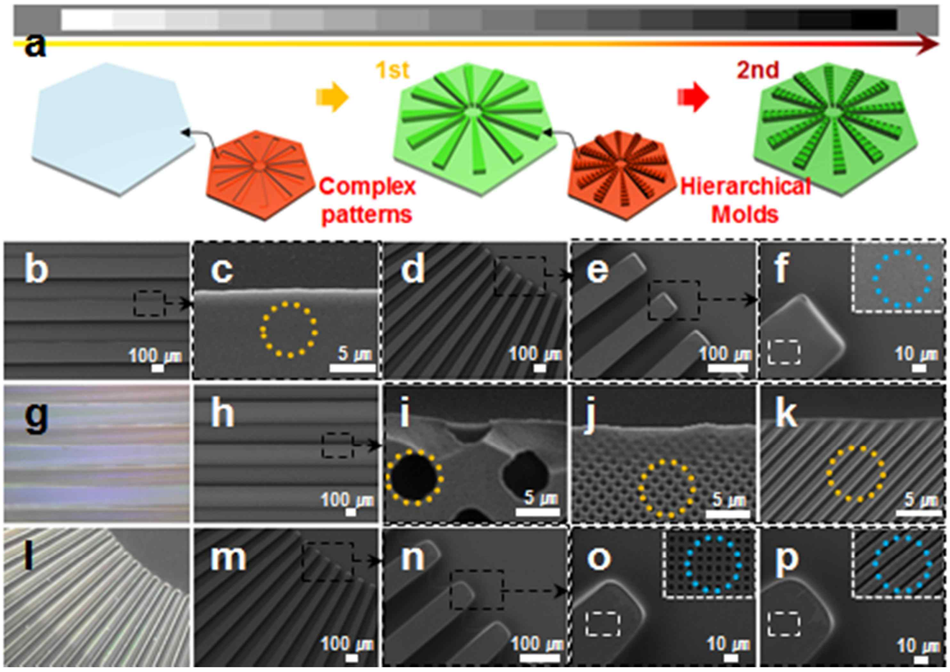

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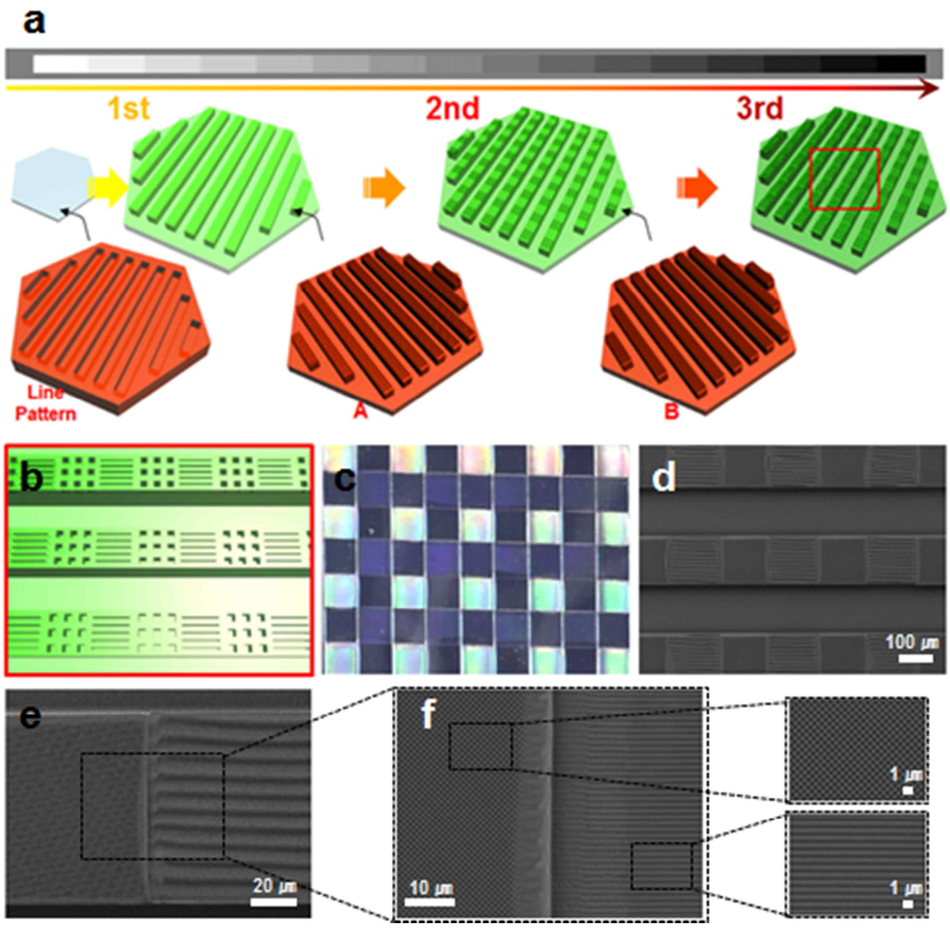

Figure 6. Multiscale line patterns composed with alternated nanoscale patterns. (a) Schematic illustration of the multiscale line patterns fabricated by serial imprinting with cross aligning process. (b) 3D graphic images of the multiscale line patterns. (c) Optical images of cross aligning process for fabricating alternate nanoscale patterns. (d-f) SEM images of multiscale line patterns imprinted alternate nanoscale patterns (800-nm dot, 300-nm line arrays) on 200-μm line patterns.

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계층 구조물의 순차적 각인공정을 통한 멀티스케일 패턴 제작

서울대학교 공과대학 대학원

기계항공공학부

방 정 원

요 약

멀티스케일 패터닝 공정은 마이크로스케일과 나노스케일의 패턴을 함께 제작할 수 있는 기법으로 다양한 연구 분야에서 활용된다. 그러나 동일 평면상에서 패턴의 스케일, 모양, 높이와 깊이에 제약 없이 패턴을 제작하는 것은 패터닝 연구 분야에서 아직 풀지 못한 과제이기도 하다. 기존의 공정들은 단일 스케일의 패턴을 성형하는 것에는 적합하지만, 현상 또는 에칭과정 때문에 동일 평면상에서 멀티스케일 패턴을 제작하기에는 제한적이다. 본 논문에서는 계층 몰드를 이용한 순차적 각인공정을 통해서 멀티스케일 패턴을 제작하는 기법을 제시한다. 자외선 경화 고분자 물질로 제작된 계층 몰드는 마이크로스케일 하단부와 마이크로/나노스케일의 상단부로 구성된다. 충분한 높이와 너비를 갖는 이러한 계층 몰드는 순차적인 각인공정을 통해서 동일 평면상에서 특정 부분만을 멀티스케일 패턴으로 성형할 수 있게 한다. 이러한 기법으로 우리는 동일 평면상에서 스케일, 모양, 높이와 깊이에 제약 없는 멀티스케일 패턴을 구현하였다. 특히, 이 기법을 통해서 평면상에서뿐만 아니라 복잡한 패턴 위에서도 제약 없는 멀티스케일 패턴들을 구현할 수 있는 점에서 이 기법을 제시한 것에 의의가 있다.

주 요 어: 멀티스케일 패터닝 공정, 계층 구조, 임프린팅 공정

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