Supplementary Information for

Micro- and nano-patterns fabricated by embossed microscale stamp with trenched edges

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I. Capillary-force lithography without Au nanomembrane

As a control experiment, capillary-force lithography (CFL) was carried out on a non-Au nanomembrane-deposited thin Al layer (50 nm)-coated glass substrate. 1 M KOH-ink solution was loaded on a dot-array PDMS stamp (hexagonal close packing (*hcp*) lattice, ϕ: 4.5 μm, gap: 3 μm), and CFL was carried out with different molding times (5 min, 10 min, and 15 min). As shown in Figure S1, the molded $Al(OH)_3$ structures are characterized by atomic force microscopy (AFM). Unlike the results shown in Figure 2, the molded $Al(OH)_3$ structures show rough surfaces; moreover, ring-like structures are scarcely observed. Figure S1(a) shows a vague image of protruded dot patterns, from which it can be considered that the KOH ink can react more with the Al layer than the Au nanomembrane-deposited Al layer on the contact area of the PDMS stamp. In addition, ring-like patterns are not observed at the edges of the hole patterns shown in Figure S1(b) and (c). In the case of molding for 20 min, most of the Al layer on the substrate seems to have been etched away; thus, protruded patterns are hardly observed.

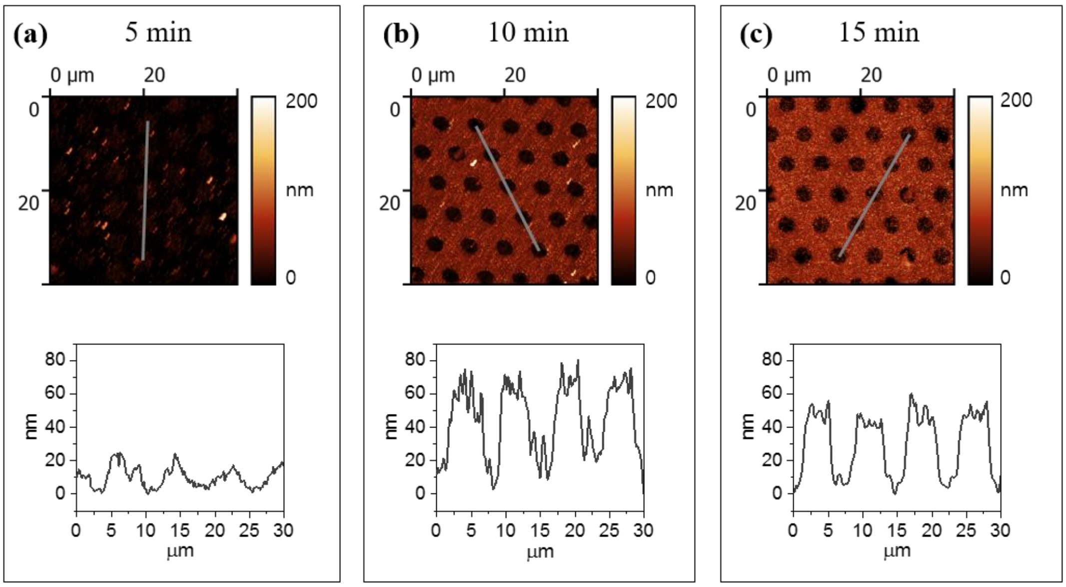


Figure S1 Topographic AFM images and cross-sectional line profiles (measured from the grey lines in the AFM images) of molded $Al(OH)_3$ structures carried out on 50-nm-thick Al layer-coated glass substrate with molding times of (a) 5 min, (b) 10 min, and (c) 15 min.

II. Cross-sectional SEM images of the molding time-dependent $Al(OH)_3$ micro-structures

Figure 2 in the manuscript represents the molding procedure of $Al(OH)_3$ micro-structures by CFL with a dot-array PDMS stamp. The molding time-dependent cross-sectional schematic images shown in Figure 2 are concluded with the cross-sectional line profiles of the AFM images of the molding time-dependent $Al(OH)_3$ micro-structures. In order to support the molding procedure of $Al(OH)_3$ micro-structures obtained from the cross-sectional line profiles of the AFM images, measurement of cross-sectional SEM images of the molding time-dependent $Al(OH)_3$ micro-structures are complementarily carried out. Figure S2 shows the secondary electrons (SE) and back-scattered electrons (BSE) mode cross-sectional SEM images of $Al(OH)_3$ micro-structures fabricated by molding times of 5 min, 20 min, and 25 min. Similar to the molding time-dependent cross-sectional schematic images, no-ring like structures are shown in the SEM images of 5 min of molding time and the ring-like structure array of $Al(OH)_3$ is clearly shown in the SEM images of 20 min of molding time. In addition, as molding time increases to 25 min, $Al(OH)_3$ keeps growing in the molding space (outside of contact area of the PDMS stamp) as show in the SEM images. The suggested molding procedure of $Al(OH)_3$ micro-structures is double-confirmed by the cross-sectional SEM images of the molding time-dependent $Al(OH)_3$ micro-structures; the $Al(OH)_3$ starts to solidify near the walls of the PDMS stamp, then continues to solidify at the center of the recessed space of the PDMS stamp.

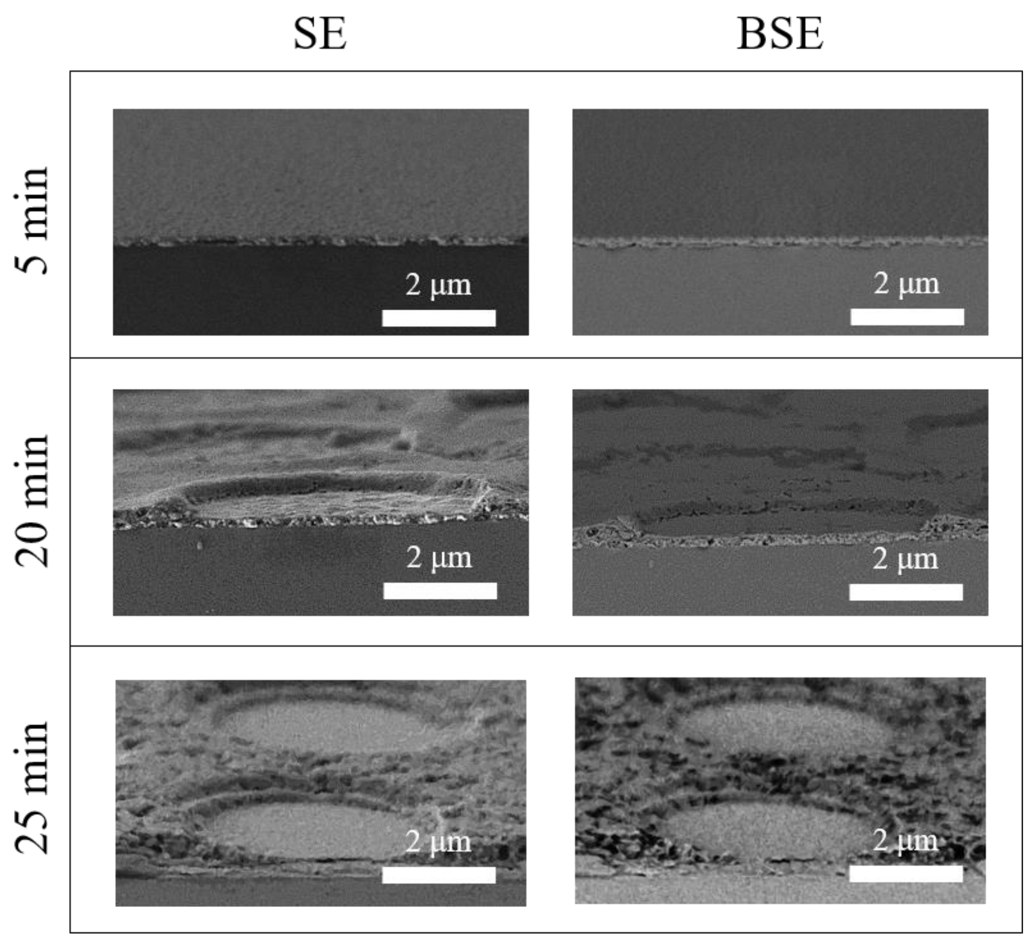


Figure S2 Cross-sectional SEM images (SE and BSE modes) of $Al(OH)_3$ micro-structures with the molding time of 5 min, 20 min, and 25 min.

III. Example of $Al(OH)_3$ template fabrication: dependence on dimension of the PDMS stamp for molding

Besides the ring-like $Al(OH)_3$ micro-structure and the replicated PDMS stamp shown in Figure 3(b) and (c), another *hcp* lattice dot-array PDMS (*hcp* lattice, ϕ: 4.5 μm, gap: 3 μm) was used to fabricate the $Al(OH)_3$ template [Figure S3(a)] and dot-array PDMS stamp with trenches around the contact area [Figure S3(b)]. As shown in Figure S3(a), the averaged values of the h_{Edge}, h_{Center}, Ring Height, and Ring Width of the fabricated ring-like $Al(OH)_3$ template are 335 nm, 204 nm, 131 nm, and 1 μm, respectively. Figure S3(b) shows that the replicated PDMS stamp has opposite dimensions to the ring array-shaped $Al(OH)_3$ template [Figure S3(a)]. In Figure S3(b), the trenches around the contact area of the replicated PDMS stamp show approximately 15 nm of depth and 800 nm of width.

Dependence of dimension of the molding PDMS stamp on structure of the $Al(OH)_3$ template can be evaluated by comparing the structural parameters obtained from Figure S3(a) and Figure 3(b). In Figure S4, the structural parameters of the $Al(OH)_3$ templates fabricated by the molding PDMS stamps with different dimension are summarized. As molding space of the PDMS increases, volume of fabricated $Al(OH)_3$ template in the molded space increases as denoted in Figure S4(b). While more volume of the $Al(OH)_3$ are molded in larger molding space of the PDMS, Ring height of the $Al(OH)_3$ template becomes lower in larger molding space of the PDMS. For Ring width, h_{Center}, and h_{Edge}, the values are similar in both Figure S3(a) and Figure 3(b). It can be considered that molding process of $Al(OH)_3$ template would be favorable in relatively larger space of the PDMS stamp (the volume of KOH solution loaded in the space becomes larger) and weaker capillary force working on the wall of the PDMS stamp of the larger molding space would lower Ring height of the $Al(OH)_3$ template.

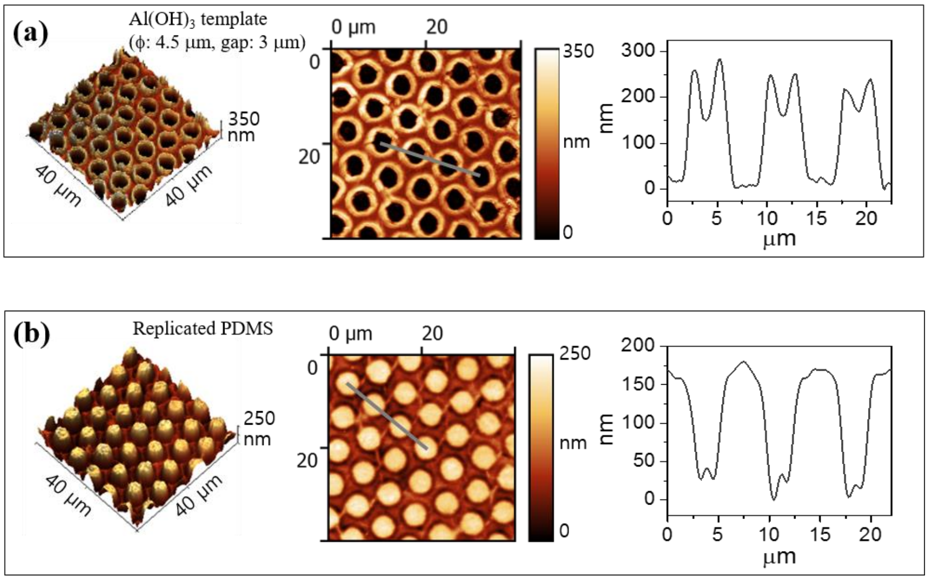
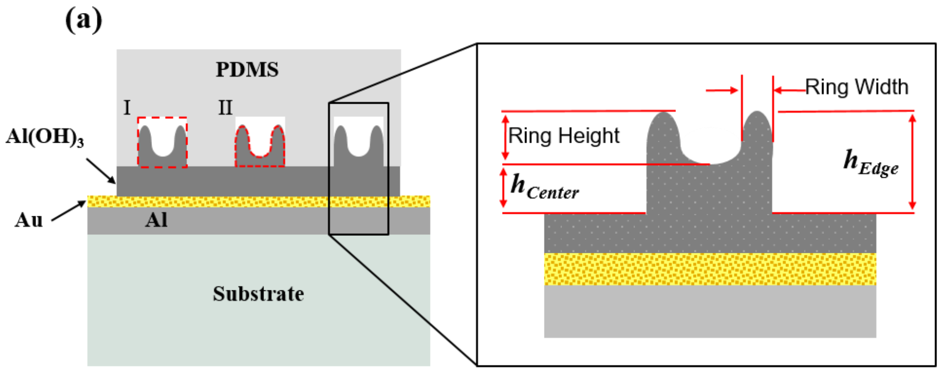


Figure S3 3-D and 2-D topological AFM images and cross-sectional line profile: (a) $Al(OH)_3$ template fabricated by CFL with a *hcp* dot-array PDMS stamp, of which the diameter is 4.5 μm and the gap is 3 μm, and (b) replicated PDMS stamp by (a). The cross-sectional line profiles were measured from the grey lines in the 2-D topological AFM images.



(b)

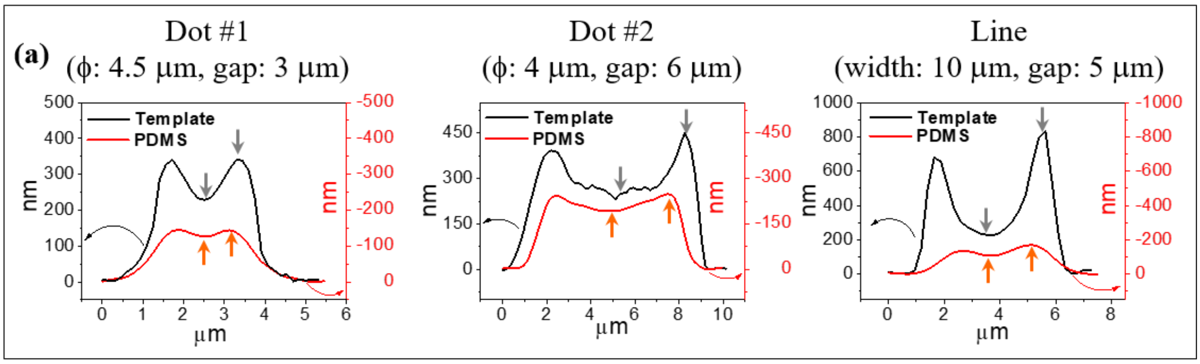
Parameter [Unit]	[I]Molding space of PDMS [a.u.]	[II]Molded volume of $Al(OH)_3$ [a.u.]	h_{Center} [nm]	h_{Edge} [nm]	Ring width [μm]	Ring height [μm]
Figure S3(a) (ϕ: 4.5 μm, gap: 3 μm)	1	1 ± 0.06	204.8 ± 53.8	345.8 ± 23.5	1.05 ± 0.10	0.15 ± 0.05
Figure 3(b) (ϕ: 2 μm, gap: 6 μm)	1.30	1.40 ± 0.09	217.5 ± 17.1	323.8 ± 10.6	1.06 ± 0.11	0.13 ± 0.02

Figure S4 (a) Scheme of fabrication of the $Al(OH)_3$ template with the structural parameters. (b) Table of the structural parameters of the $Al(OH)_3$ templates obtained from the PDMS stamps of two different dimensions. [I]Molding space of PDMS and [II]Molding volume of $Al(OH)_3$ are denoted as the red-dashed closed figures in Figure S4(a).

IV. Fill-in factor of the replicated PDMS stamps in the $Al(OH)_3$ templates

The cross-sectional line profiles of the $Al(OH)_3$ templates and replicated PDMS stamps are compared, as displayed in Figure S5(a). The line profiles of the replicated PDMS stamps have been inverted in the y-axis for convenient comparison. The fill-in factor of the replicated PDMS stamp in the $Al(OH)_3$ template is determined as the following equation: $\text{Fill–in factor [\%]} = h_{PDMS}/h_{Template} \times 100$, where h_{PDMS} and $h_{Template}$ are the height of the replicated PDMS stamps and the $Al(OH)_3$ template, respectively. h_{PDMS} and $h_{Template}$ can be measured with the cross-sectional line profiles shown in Figure S5(a); the gray and orange colored arrows in Figure S5(a) denote where the values are measured. Owing to a difference at the center and edge of the cross-sectional line profiles between the templates and PDMS stamps, the fill-in factor has been calculated distinguishably at the center and edge with h_{PDMS} and $h_{Template}$ measured at the center and edge of the templates and PDMS stamps. As shown in Figure S5, the PDMS stamps are not fully filled into the $Al(OH)_3$ templates; this seems because the PDMS materials are not fully filled into the recessed space of the $Al(OH)_3$ templates during the replication process. In particular, the fill-in factor at the edge is lower than that at the center; the PDMS materials are less filled into the narrower recessed space of the $Al(OH)_3$ template.

A reason of the imperfect fill-in factors of the replicated PDMS stamps is due to insufficient modulus of the resin materials (Sylgard 184) of the PDMS stamp.[1] It was reported that hard PDMS (*h*-PDMS) materials is required for the resin of PDMS stamp to form submicron features.[2] Moreover, it is known that the minimum feature size of PDMS stamp is about 500 nm when only typical resin materials (Sylgard 184) are used for PDMS stamp fabrication.[3,4] Because our replicated PDMS stamps were fabricated without adding *h*-PDMS materials, the imperfect fill-in factors were obtained.



(b)

Fill-in-factor	Dot #1	Dot #2	Line
@ Center	55.1 ± 0.9 %	81.2 ± 2.4 %	47.0 ± 0.4 %
@ Edge	42.2 ± 0.6 %	57.2 ± 1.7 %	20.7 ± 0.6 %

Figure S5 (a) Overlapped cross-sectional line profiles of the $Al(OH)_3$ templates and replicated PDMS stamps. The gray and orange colored arrows denote where the $h_{Template}$ and h_{PDMS} are measured, respectively. (b) Fill-in factor of the stamps into the template.

1. C. Y. Hui, A. Jagota, Y. Y. Lin and E. J. Kramer, *Langmuir*, 2002, **18**, 1394-1407.
2. T. W. Odom, J. C. Love, D. B. Wolfe, K. E. Paul and G. M. Whitesides, *Langmuir*, 2002, **18**, 5314-5320.
3. Y. N. Xia, J. A. Rogers, K. E. Paul, G. M. Whitesides, *Chem. Rev.* 1999, **99**, 1823-1848.
4. Y. N. Xia, G. M. Whitesides, *Angew. Chem. Int. Ed.* 1998, **37**, 551-575

V. Edge-transfer lithography with replicated PDMS stamp by ring-shaped $Al(OH)_3$ template

Sub-micron Au patterns were fabricated by the edge-transfer lithography (ETL) process carried out with the replicated PDMS stamps shown in Figure S3(b). Figure S6 shows the Au patterns obtained by the ETL process carried out for 5 min [Figure S6(a)] and 10 min [Figure S6(b)]. Similar to the sub-micron Au patterns obtained by the ETL process carried out with the replicated line PDMS stamp [Figure 4(a)IV], Au ring patterns of 550 nm in width were obtained, as shown in Figure S6(b).

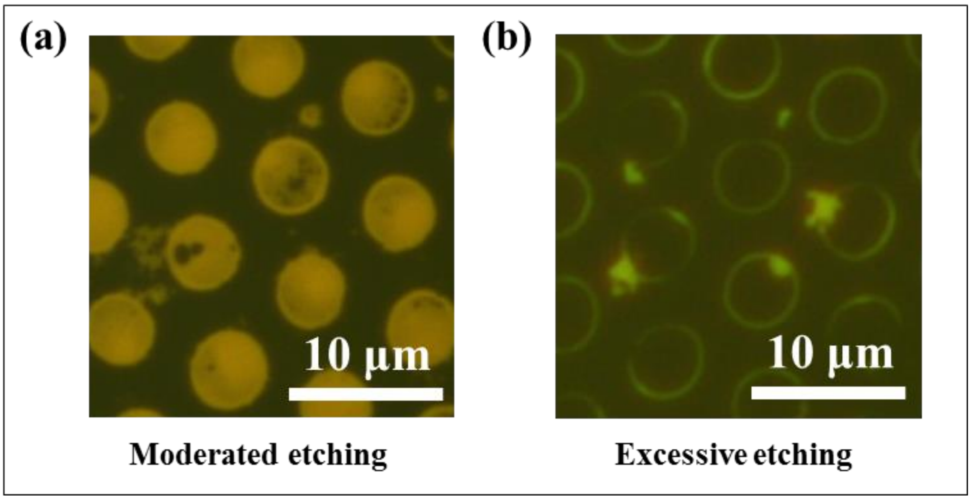


Figure S6 Optical microscopic images of Au patterns obtained by the ETL process with etching times of (a) 5 min and (b) 10 min. The ETL carried out with replicated PDMS stamps by the $Al(OH)_3$ micro-structure template fabricated by the CFL process with a dot-array PDMS stamp (*hcp* lattice, ϕ: 4.5 μm, gap: 3 μm).

VI. Edge-transfer lithography with a normal line PDMS stamp (without trenches)

As a control experiment, the ETL process was carried out with a conventional line PDMS stamp without trenches around the contact area. The ETL process was conducted with the same substrate and ink solution used in Figure 4; a thermally evaporated Au film (30 nm) with a Ti buffer layer (5 nm) on silicon substrate and 10 mM ethanolic 16-mercaptohexadecanoic acid (MHA) solution were used as the substrate and ink. Au patterns were obtained with etching times of 10 and 20 min, as shown in Figure S7(a) and (b), respectively. Figure S7(b) shows that the Au line patterns seem to be over-etched; however, sub-micron-wide Au bi-line patterns are not shown at the edge of the micron-wide Au line patterns. It can be concluded that the line PDMS stamp with trenches around the contact area is more suitable for the ETL process for sub-micron patterning than a normal line PDMS stamp.

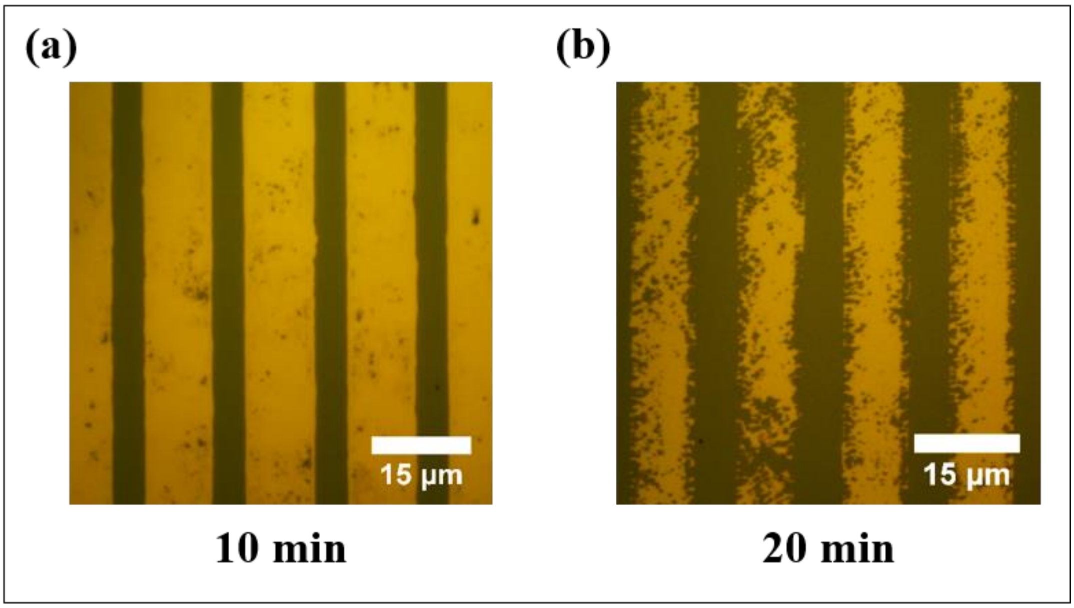


Figure S7 Optical microscopic images of Au patterns obtained by the ETL process carried out by a normal line PDMS stamp (width: 10 μm, gap: 5 μm, no trenches around the contact area) with etching times of (a) 10 min and (b) 20 min.