Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Macroscopically Ordered Hexagonal Arrays by Directed Self-Assembly of Block Copolymers with Minimal Topographic Patterns

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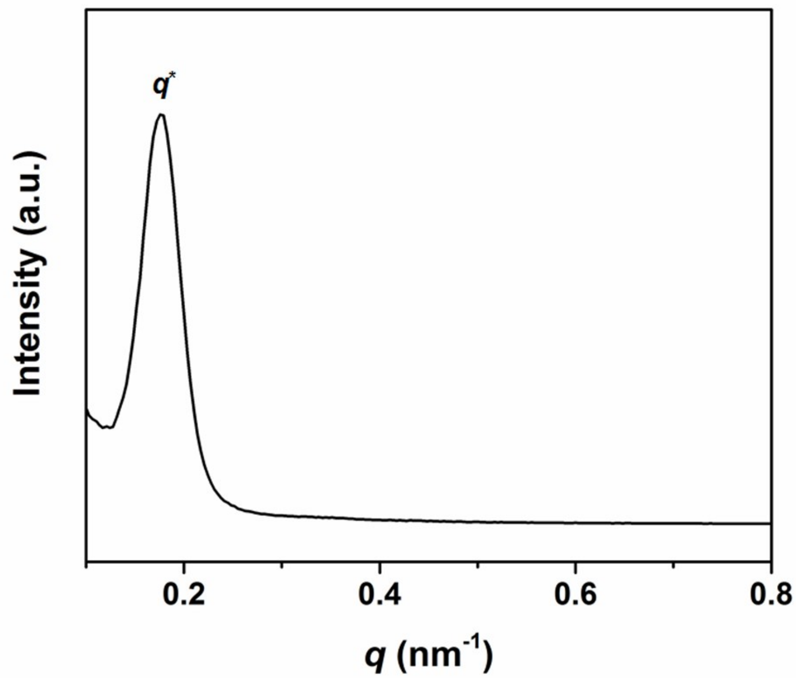

Figure S1. Small angle X-ray scattering (SAXS) profile of a PS-*b*-PEO (M_n = 32.0 kg mol^{-1} and M_n = 11.0 kg mol^{-1} for PS and PEO blocks, respectively). The first-order reflection was observed at q^* = 0.1757 nm^{-1} corresponding to the natural period ($L_0 = 2\pi/q^*$) of 35.8 nm. It is noted that the higher-order peaks of the first-order reflection were not observed.

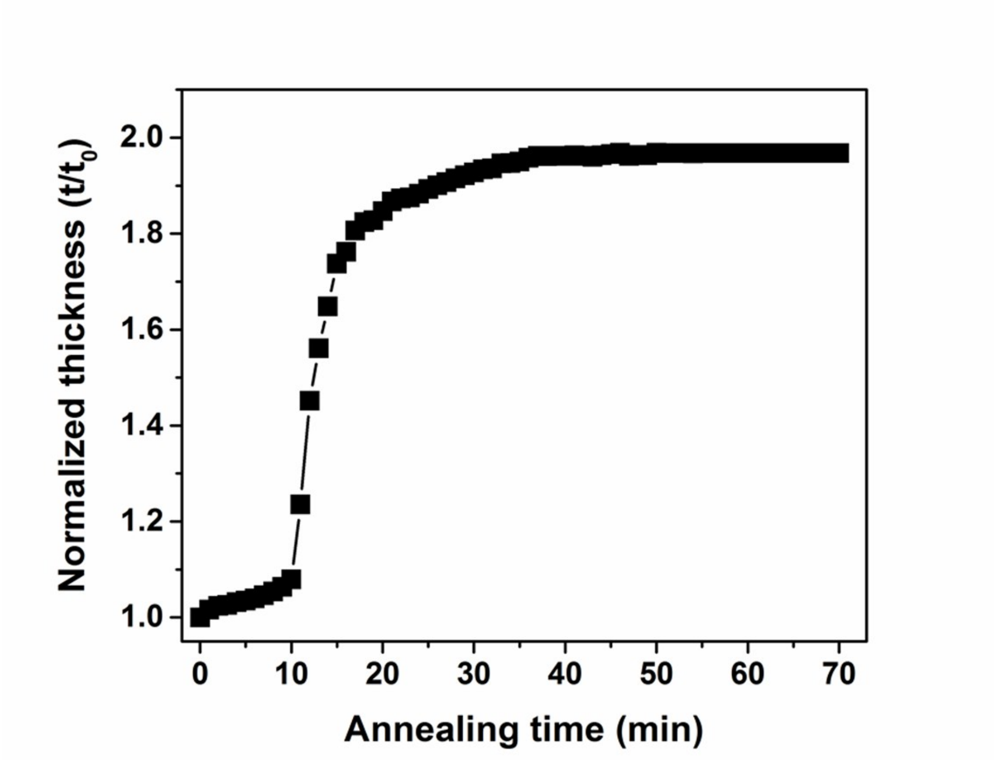

Figure S2. Swelling behavior of PS-*b*-PEO thin films on a flat silicon substrate, where the swollen film thickness (t) is divided by the initial film thickness (t_0). The films were initially pre-swollen in water vapor for 10 min to avoid dewetting, followed by exposing to tetrahydrofuran (THF) and water vapors for 60 min.

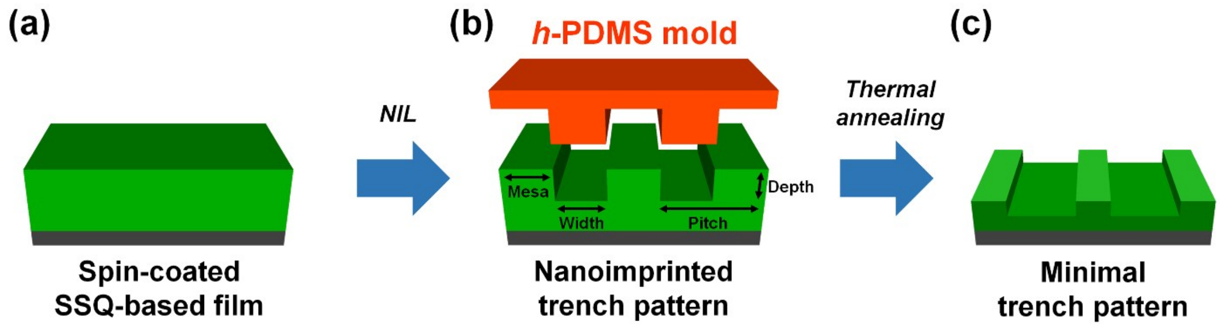

Figure S3. To fabricate a minimal trench pattern, we used size reduction lithography, which is based on nanoimprint lithography (NIL) and thermal annealing.[1] (a) In the first step, a silsesquioxane (SSQ)-based film was prepared by spin-coating onto a flat silicon substrate. (b) Next, a *h*-PDMS mold consisting of grating lines with the pitch of 132 nm, the line width of 70 nm, and the height of 50 nm was used to nanoimprint the SSQ-based film. Then, the nanoimprinted trench pattern with the pitch of 132 nm, the mesa width of 64 nm, and the trench depth of 50 nm was annealed at 500 °C in air for 2 h to reduce the pattern dimensions, in particular the trench depth. It is noted that this thermal annealing process changes the surface property from hydrophobic (nanoimprinted trench pattern) to hydrophilic (minimal trench pattern) due to the formation of silicon oxide structures. (c) As a result, we obtained the minimal trench pattern with the pitch of 132 nm, the mesa width of 26 nm, the trench width of 106 nm, and the trench depth of 11 nm. Table S1 summarizes the results of the pattern dimension reduction. The reduction in pattern dimensions after thermal annealing is related to the elimination of organic molecules in the SSQ-based film and densification of the SSQ material. The reduction in the trench depth (78.0%) was larger than the mesa width reduction (59.4%), which can be attributed to the lateral confinement of the mesas to the substrate.[1]

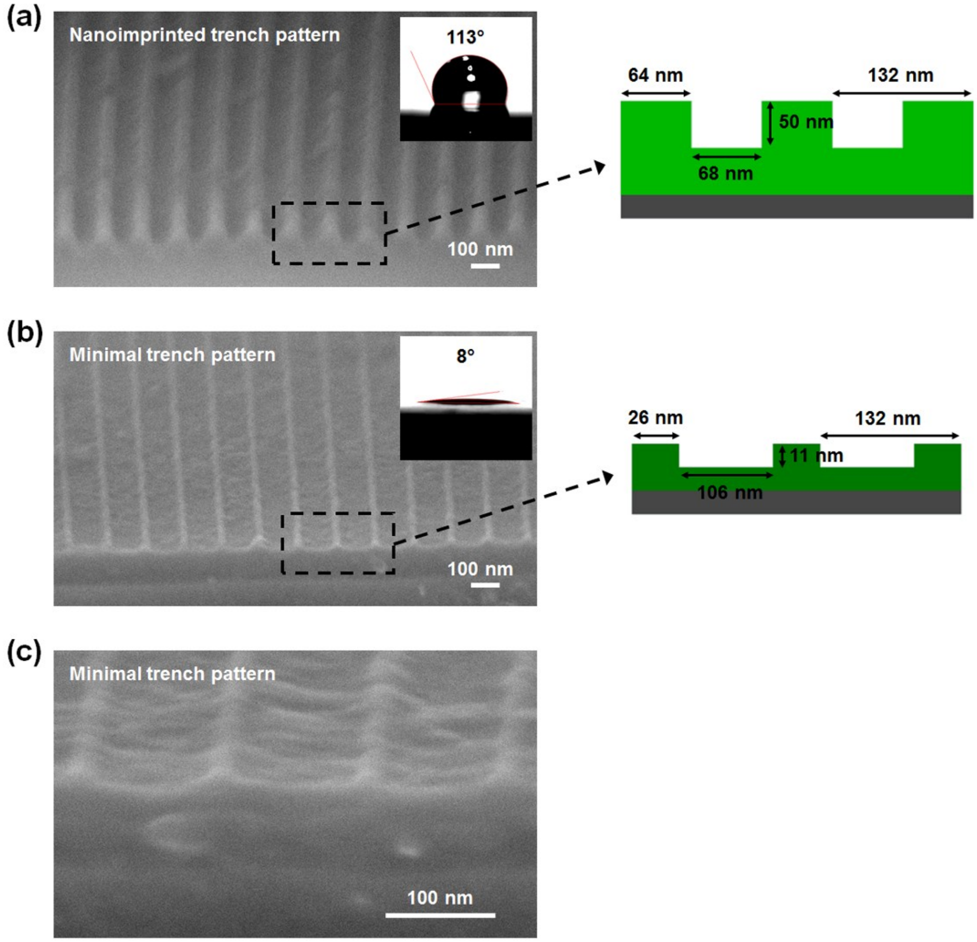

Figure S4. Cross-sectional (80° tilted) scanning electron microscopy (SEM) images of patterned trench surfaces. (a) Nanoimprinted trench pattern with the pitch of 132 nm, the mesa width of 64 nm, the trench width of 68 nm, and the trench depth of 50 nm. The inset shows the water contact angle of 113°. Since the nanoimprinted trench pattern is mainly composed of the SSQ material, the surface is hydrophobic. (b) Minimal trench pattern with the pitch of 132 nm, the mesa width of 26 nm, the trench width of 106 nm, and the trench depth of 11 nm. The inset shows the water contact angle of 8°, indicating a hydrophilic surface. Through thermal annealing, the surface property was changed from hydrophobic (113°) to hydrophilic (8°). Since the SSQ-based material (nanoimprinted trench pattern) was converted to silicon oxide structures (minimal trench pattern) by eliminating organic molecules, the surface of the minimal trench pattern became hydrophilic. (c) The magnified image of the minimal trench pattern shows that the surface at the base of the trench is rough, but this roughness could not be measured by SFM due to artifacts arising from the shape of the tip. Since the mesa width of the nanoimprinted trench pattern cannot be readily reduced due to the lateral confinement during thermal annealing, any internal stresses in this pattern are relieved by roughening the bottom surface of the trench.

Table S1. Summary of the results of the pattern dimension reduction after thermal annealing

Dimension	Nanoimprinted trench pattern (before thermal annealing)	Minimal trench pattern (after thermal annealing)
Trench pitch (nm)	132	132 (3.7[a])
Mesa width (nm)	64	26
Trench width (nm)	68	106 (3.0[b])
Trench depth (nm)	50	11 (0.3[c])

[a]Commensurability between the trench pitch and L_0.

[b]Commensurability between the trench width and L_0.

[c]Commensurability between the trench depth and L_0.

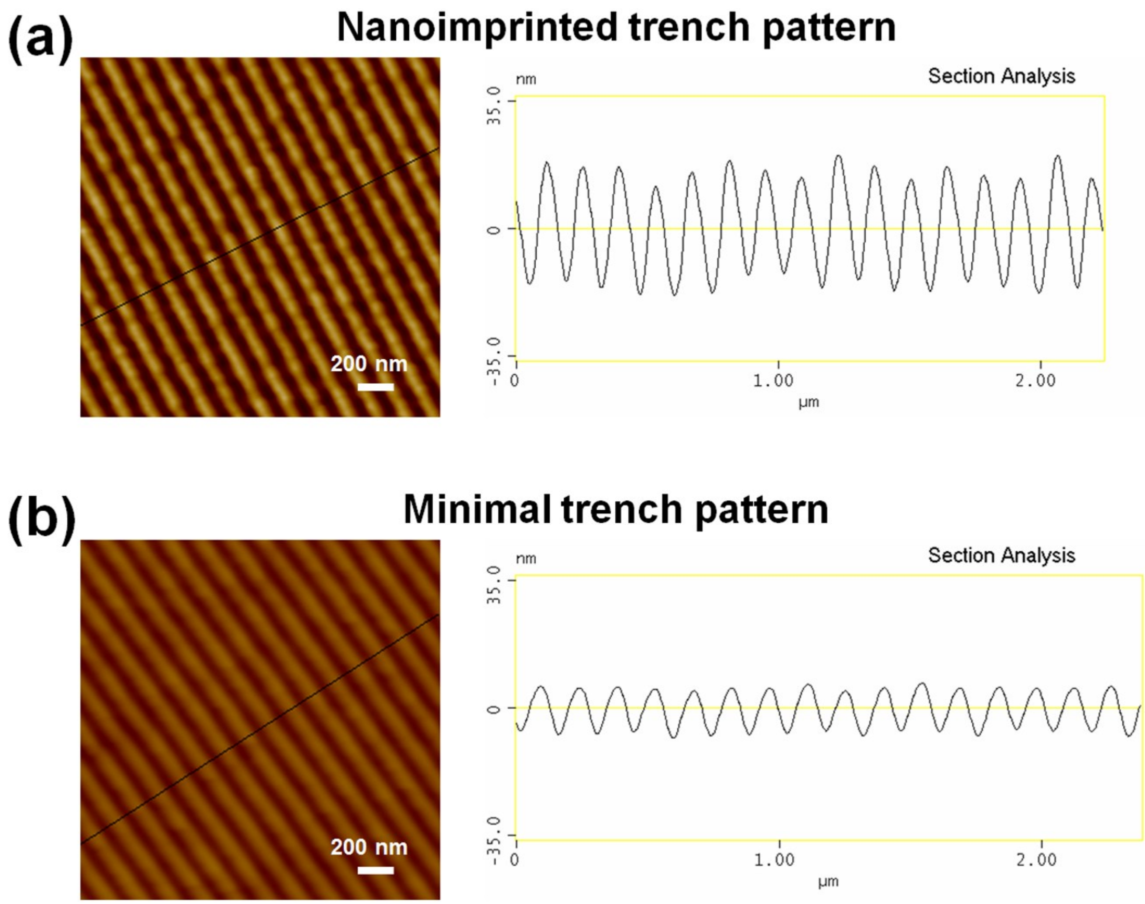

Figure S5. Scanning force microscopy (SFM) height images and height profiles of patterned trench surfaces. (a) Nanoimprinted trench pattern. (b) Minimal trench pattern.

REFERENCES

1. H.-H. Park, W. L. Law, X. Zhang, S.-Y. Hwang, S. H. Jung, H.-B. Shin, H. K. Kang, H.-H. Park, R. H. Hill and C. K. Ko, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2507-2514.