Science Advances
AAAS

advances.sciencemag.org/cgi/content/full/6/24/eaaz0002/DC1

Supplementary Materials for

Three-dimensional superlattice engineering with block copolymer epitaxy

Jiaxing Ren, Tamar Segal-Peretz, Chun Zhou, Gordon S. W. Craig, Paul F. Nealey*

*Corresponding author. Email: nealey@uchicago.edu

Published 12 June 2020, *Sci. Adv.* **6**, eaaz0002 (2020)
DOI: 10.1126/sciadv.aaz0002

This PDF file includes:

Figs. S1 to S7

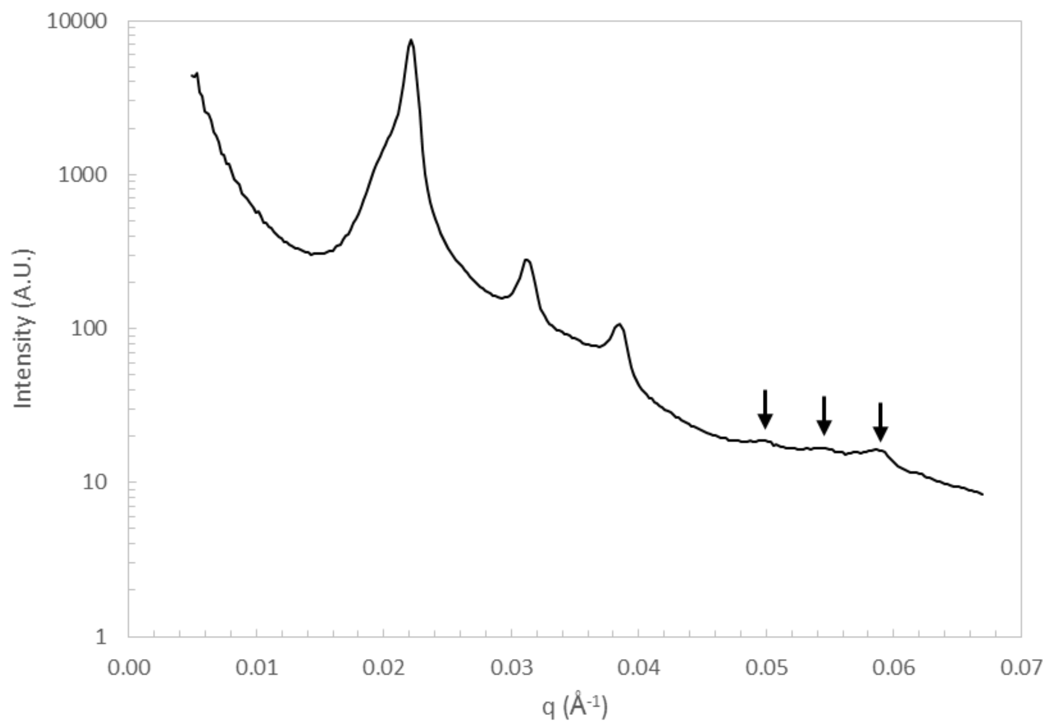


Fig. S1. SAXS pattern of bulk PS-*b*-PMMA after thermal annealing. The SAXS pattern shows at least 6 distinctive peaks, corresponding to the BCC lattice with lattice parameter $L_{\mathrm{BCC}} = \sqrt{2} \times 2\pi/0.0222\text{Å}^{-1} = 40.1$ nm.

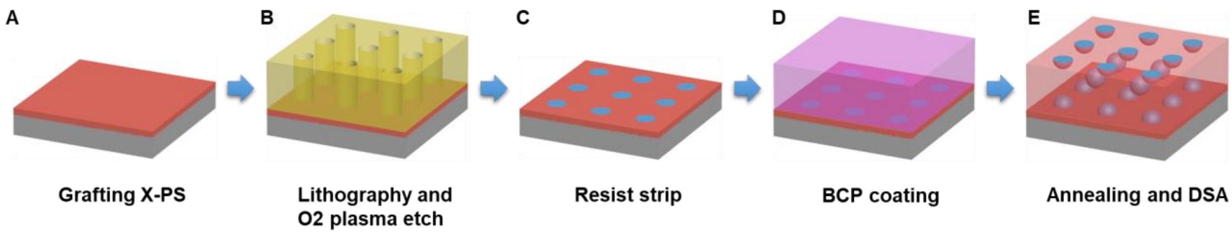


Fig. S2. Process flow for chemoepitaxy directed self-assembly of a sphere-forming block copolymer. (**A**) An 8-nm-thick cross-linkable polystyrene (X-PS) layer was coated and grafted onto the Si substrate. (**B**) A 40-nm-thick resist was coated and patterned with e-beam lithography. The film was then treated with O_2 plasma to modify the wetting behavior of the exposed area. (**C**) The resist was removed to reveal the chemical template. (**D**) The block copolymer (BCP) was spin coated to a desired thickness. (**E**) The BCP was annealed at 190 °C to assemble into the superlattices of spherical micelles.

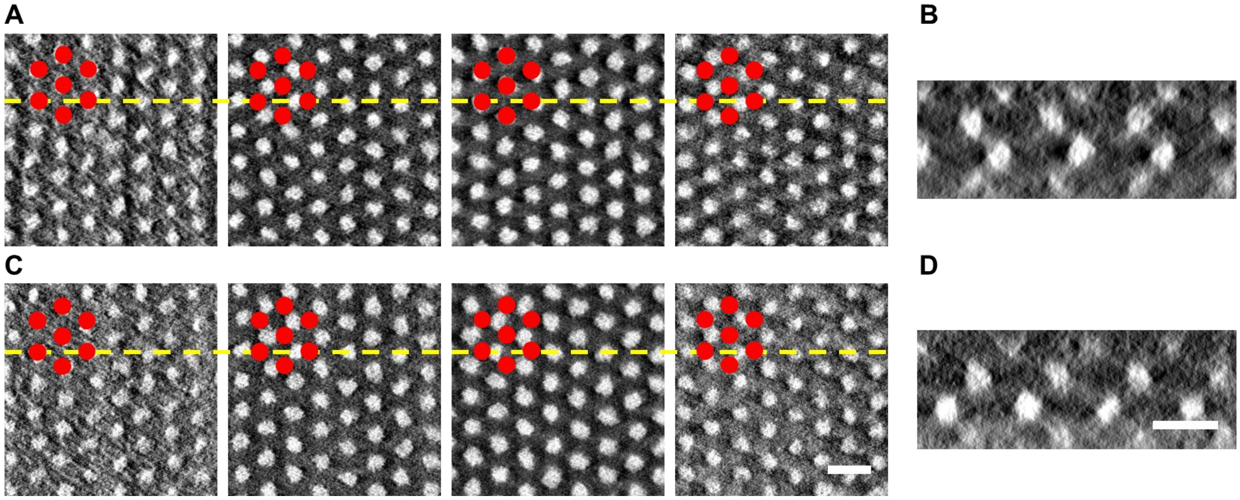
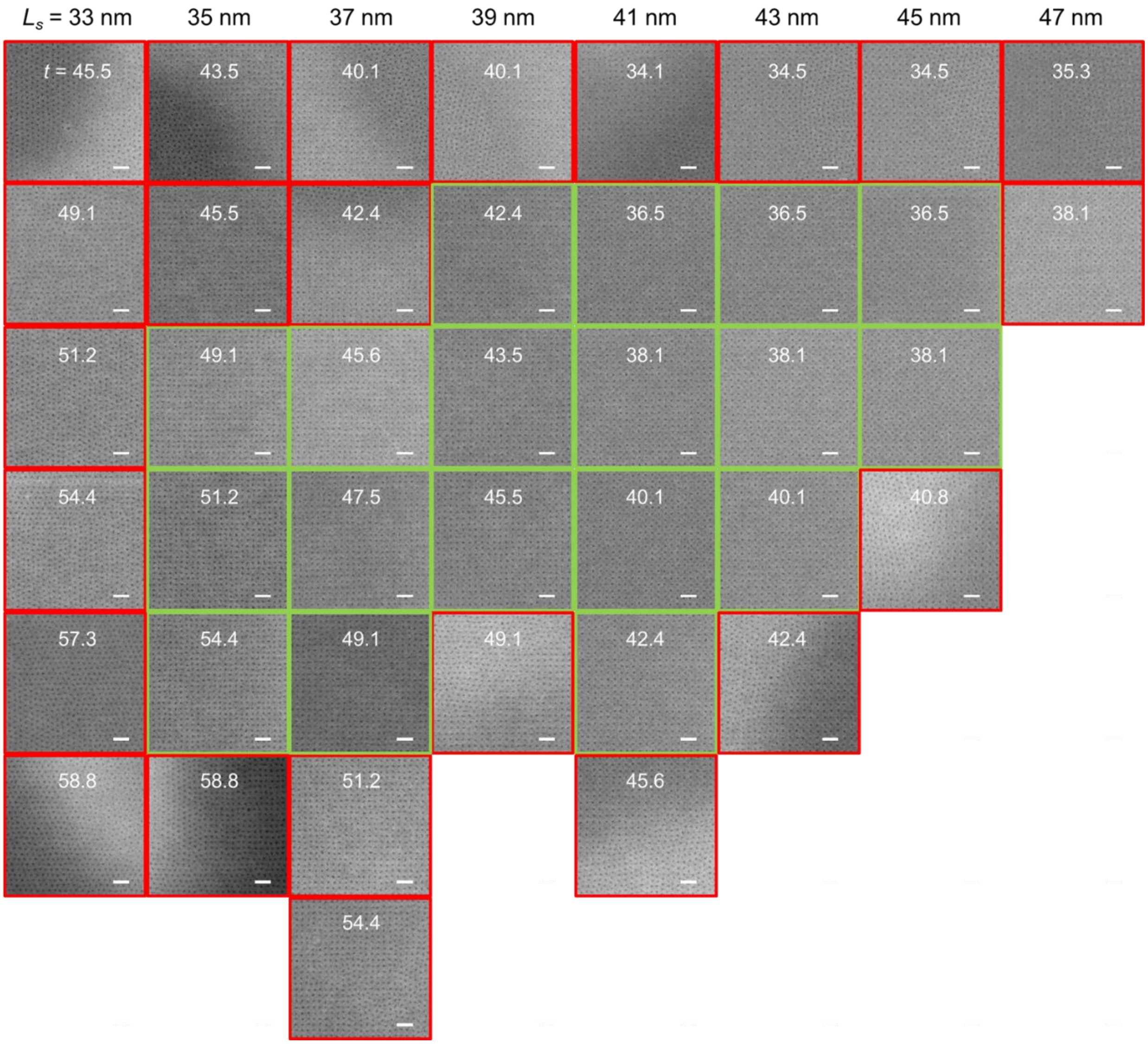


Fig. S3. Polytypism in the directed self-assembly of an HCP lattice. The template is a hexagonal pattern with a dot-to-dot distance of 36 nm. The film thickness is 120.2 nm, corresponding to 4 layers of spheres. (**A**) In-plane slices created from STEM tomography showing the 4 hexagonal layers from top to bottom. Red circles mark the sphere positions of the top layer. (**B**) Digitally sliced cross-section along the yellow dashed line in a showing the spheres arranged in an A-B-A-B pattern, suggesting HCP lattice. (**C** to **D**) STEM slices from a different location, where the spheres are arranged in an A-B-C-B pattern. Both lattice structures have the same free energy, giving rise to the polytypism observed here. Scale bars are 50 nm.

A



Ls = 33 nm
35 nm
37 nm
39 nm
41 nm
43 nm
45 nm
47 nm
t = 45.5
43.5
40.1
40.1
34.1
34.5
34.5
35.3
49.1
45.5
42.4
42.4
36.5
36.5
36.5
38.1
51.2
49.1
45.6
43.5
38.1
38.1
38.1
54.4
51.2
47.5
45.5
40.1
40.1
40.8
57.3
54.4
49.1
49.1
42.4
42.4
58.8
58.8
51.2
45.6
54.4

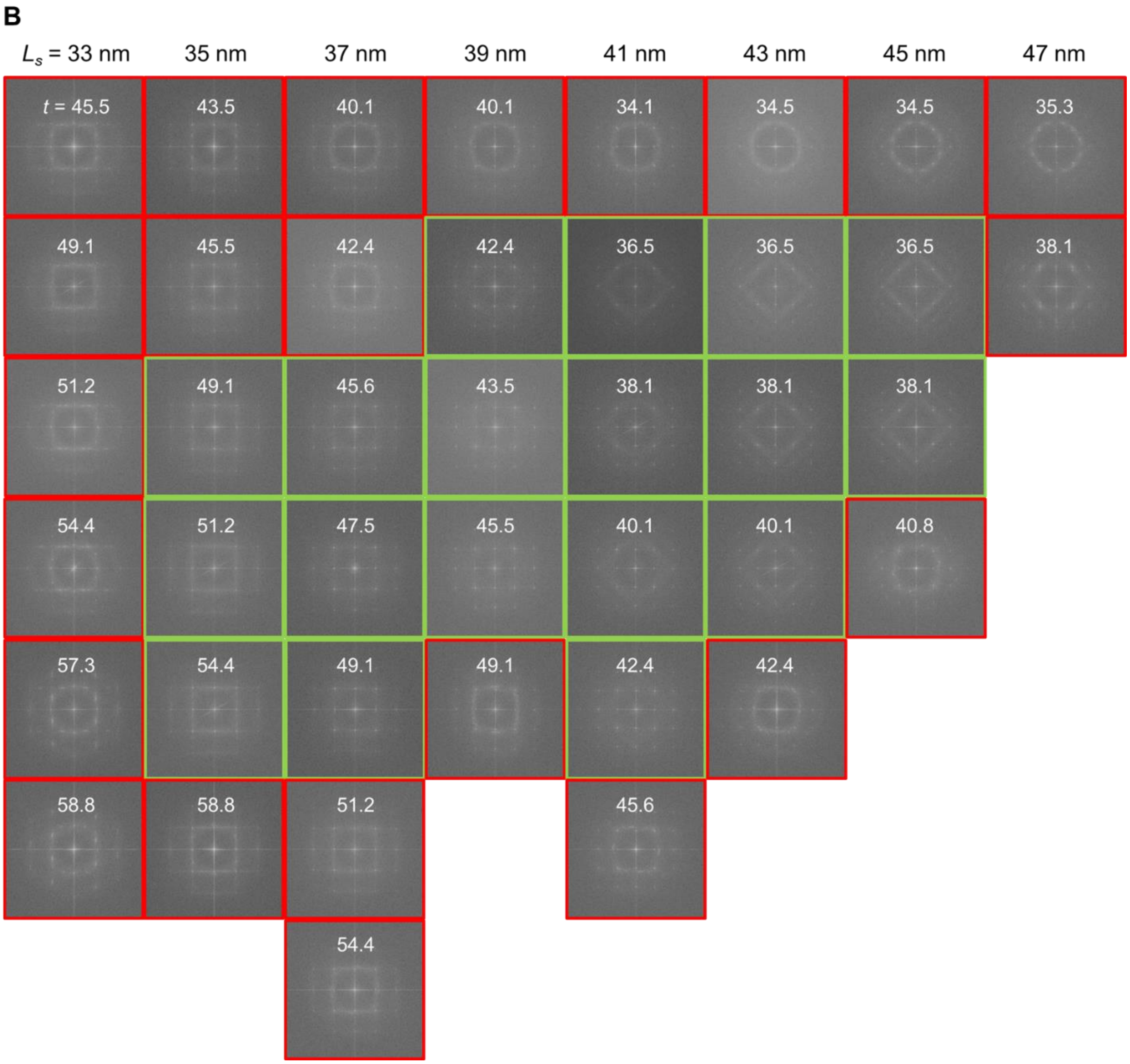


Fig. S4. Epitaxy window with different template pitch and film thickness. (**A**) Top-down SEM images of directed self-assembly with template pitch L_S from 33 to 47 nm and the film thickness t from 34.1 to 58.8 nm. Assemblies with perfect ordering are outlined in green, and assemblies with defects are outlined in red. Scale bars are 100 nm. (**B**) FFT images for the corresponding samples in (**A**). FFT calculations were performed on individual SEM images that cover a 2 × 3 μm^2 area.

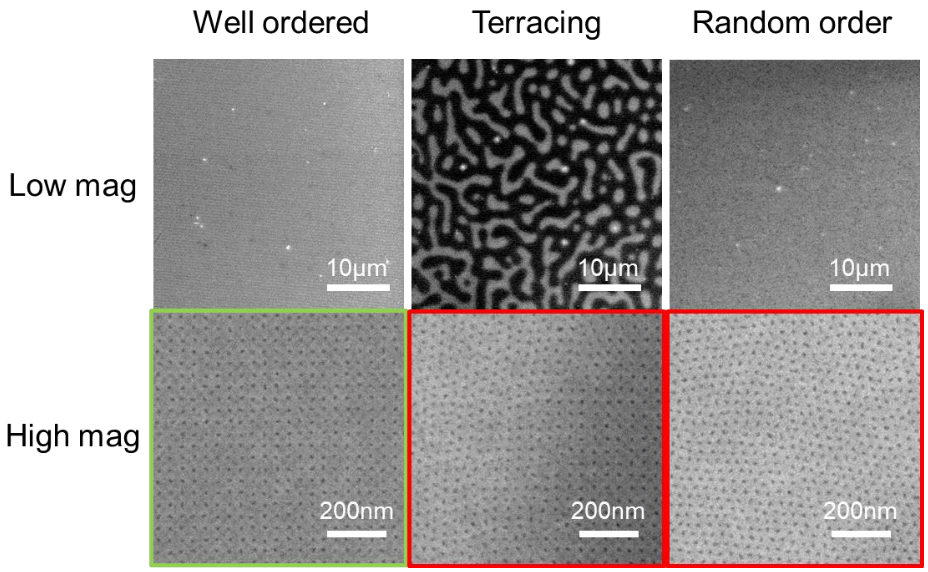
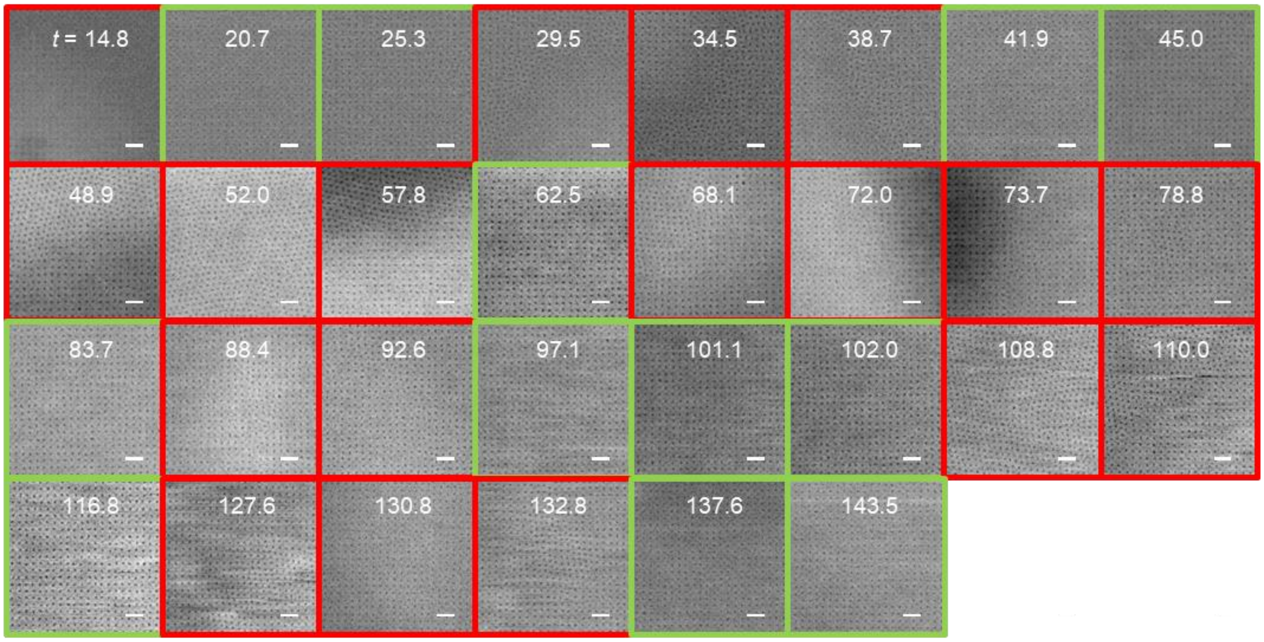
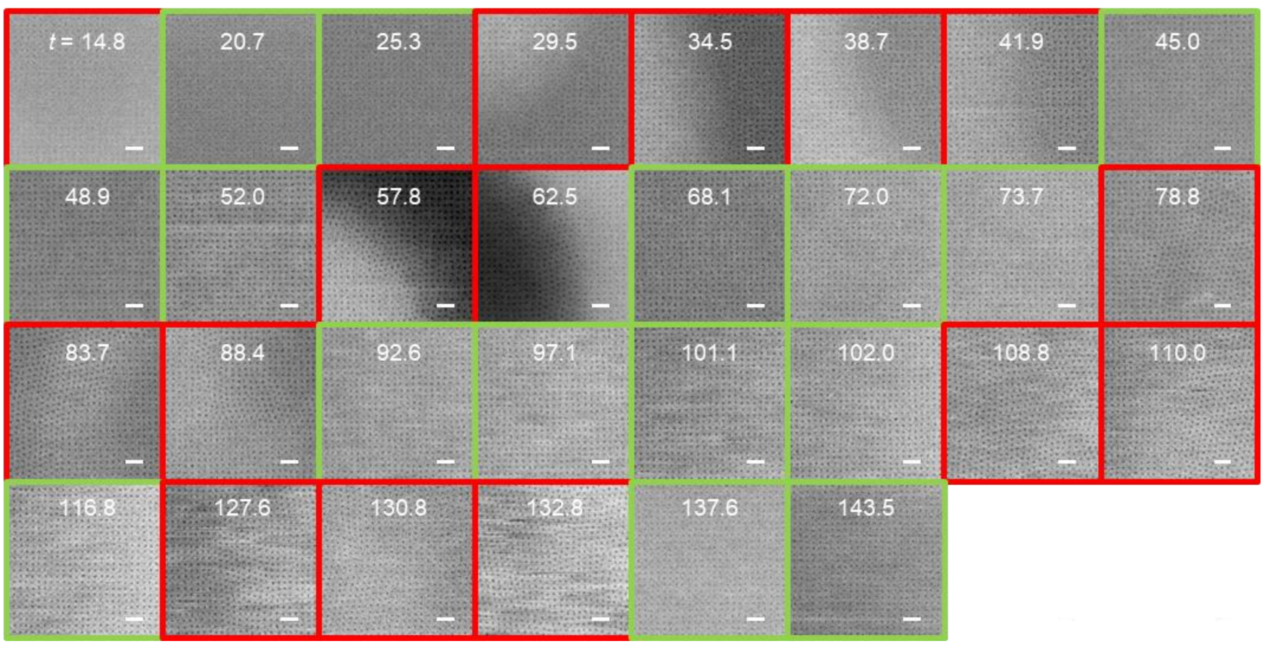


Fig. S5. Categorization and criteria for the quality of assembly. Three distinctive types of morphologies were observed: 1) well-ordered assembly; 2) terracing and hole-island formation; and 3) randomly ordered assembly. Samples are only categorized the as "well-ordered" (green) when no terracing was observed in the templated area (100×100 μm^2) at low magnification and no random ordering of the spheres was observed at high magnification.

A


t = 14.8
20.7
25.3
29.5
34.5
38.7
41.9
45.0
48.9
52.0
57.8
62.5
68.1
72.0
73.7
78.8
83.7
88.4
92.6
97.1
101.1
102.0
108.8
110.0
116.8
127.6
130.8
132.8
137.6
143.5

B


t = 14.8
20.7
25.3
29.5
34.5
38.7
41.9
45.0
48.9
52.0
57.8
62.5
68.1
72.0
73.7
78.8
83.7
88.4
92.6
97.1
101.1
102.0
108.8
110.0
116.8
127.6
130.8
132.8
137.6
143.5

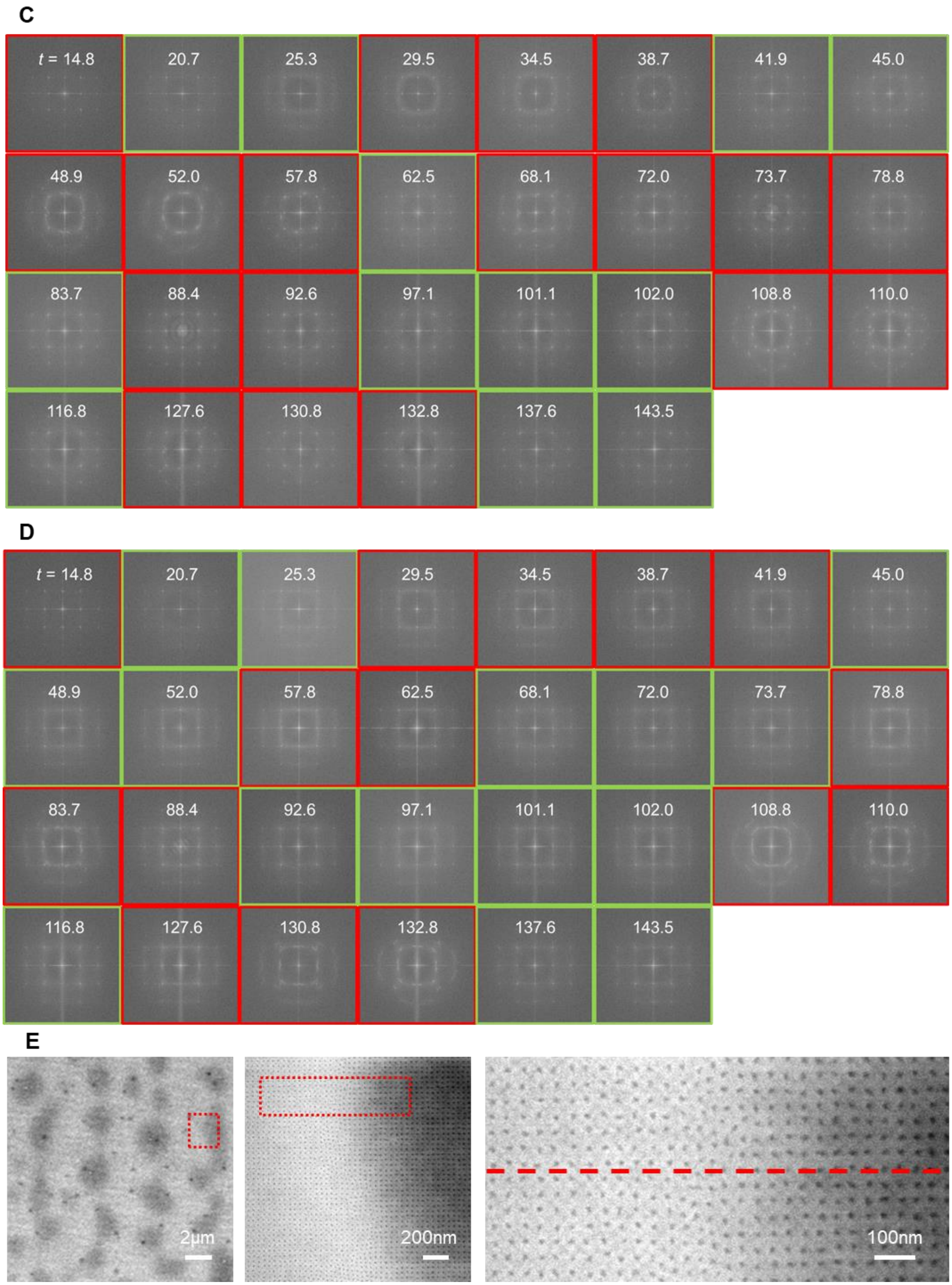


Fig. S6. Directed self-assembly on BCC (100) and FCC (100) templates with different film thicknesses. (**A** to **B**) Progression of directed self-assembly with increasing film thickness on BCC (100) and FCC (100) templates respectively. Assemblies with perfect ordering are outlined in green, and assemblies with defects are outlined in red. Scale bars are 100 nm. (**C** to **D**) FFT images for the corresponding samples in (**A** to **B**). FFT calculations were performed on individual SEM images that cover a 2 × 3 μm^2 area. (**E**) Hole-island structures formed on BCC (100) templates at a film thickness of 72.0 nm. The red dashed line shows that the spheres in the hole are offset from the spheres in the island by $0.5L_{BCC}$, suggesting that the hole and islands are offset by 1 layer of spheres in thickness.

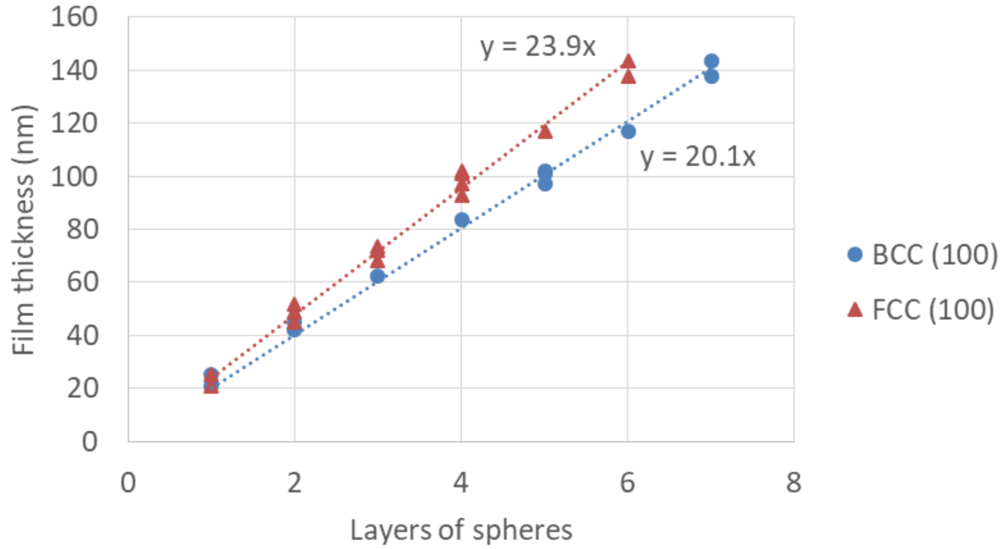


Fig. S7. Film thickness with perfect assembly vs. the number of layers for the directed self-assembly of BCC (100) and FCC (100). Fitting the data with linear regression showed that the distance between each layer of spheres was 20.1 and 23.9 nm for the BCC (100) and FCC (100) orientations, respectively.