A hybrid chemo-/grapho- epitaxial alignment strategy for defect reduction in sub-10 nm directed self-assembly of silicon-containing block copolymers: Supporting Information

*Gregory Blachut[1], Stephen M. Sirard[2], Michael J. Maher[3], Yusuke Asano[3], Yasunobu Someya[3], Austin P. Lane[1], William J. Durand[1], Christopher M. Bates[4,5], Andrew M. Dinhobl[1], Roel Gronheid[6], Diane Hymes[2], Christopher J. Ellison[1,3], C. Grant Willson[1,3]**

[1]McKetta Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, United States

[2]Lam Research Corporation, 4400 Cushing Parkway, Fremont, California 94538, United States

[3]Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, United States

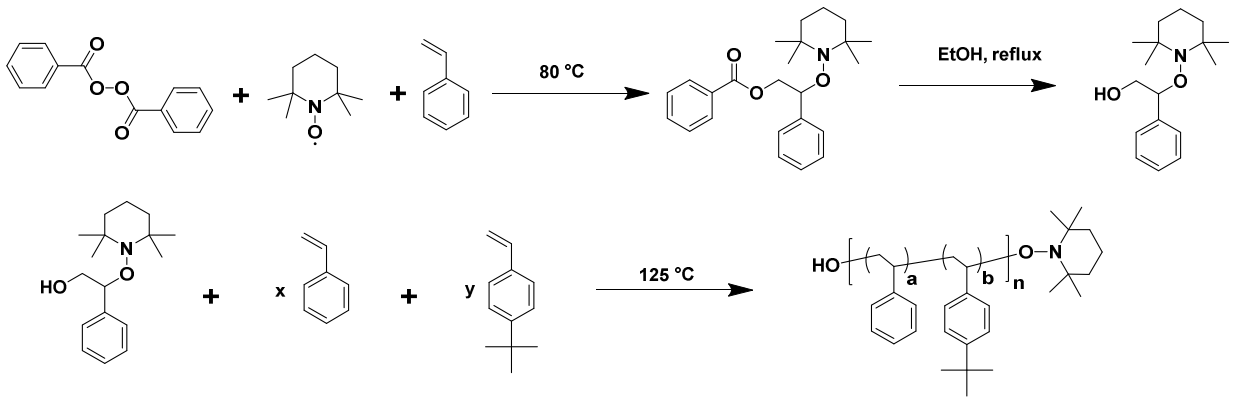
[4]Materials Department and [5]Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106.

[6]imec, Kapeldreef 75, 3001 Heverlee, Belgium

*to whom correspondence should be addressed: willson@che.utexas.edu

Supporting Information

Reaction schemes



Scheme S1. Synthesis of NMP hydroxyl initiator and corresponding brushes.

Supporting data

Table S.1 Summary of characterization data for 20 nm PMOST-*b*-PTMSS[A]

L_0[B]	$M_{n,PMOST}$[C]	$Đ_{PMOST}$[D]	$M_{n,BCP}$[C]	$Đ_{BCP}$[D]	f_{PMOST}[E]
19.6 nm	14.4 kg/mol	1.01	27.4 kg/mol	1.05	0.47

[A] Previously published in and adapted from Durand, et al. *J Poly Sci*. 2015. pg 344-352.
[B] Periodicity, determined by SAXS
[C] Molecular weight of both PMOST homopolymer aliquot and BCP, determined by MALDI
[D] Dispersity index of both PMOST homopolymer aliquot and BCP, determined by GPC
[E] Volume fraction of PMOST block, determined by ^{1}H-NMR and room temperature density measurements of homopolymers

Table S.2: Summary of optimized processing conditions (used to make Figure 2)

Process step	XPS chemo-	XPMOST chemo-	Hybrid
Mat deposition	Commercial NLD-128 = 8 nm	XPMOST 0.5 wt.% PGMEA 3000 RPM = 9 nm	XPMOST 0.5 wt.% PGMEA 600 RPM = 19 nm
Brush composition (see Table 1)	BB-71	BB-68	BB-68
BCP deposition	0.75 wt. % MIBK 1500 RPM = 33 nm	0.75 wt. % MIBK 1500 RPM = 33 nm	0.75 wt. % MIBK 1500 RPM = 33 nm
Top coat deposition	0.5 wt. % methanol 1500 RPM = 19 nm	0.5 wt. % methanol 1500 RPM = 19 nm	0.5 wt. % methanol 1500 RPM = 19 nm
Anneal	205°C 5 mins	205°C 5 mins	205°C 5 mins
CD to image for best feature formation	18 nm	18 nm	14 nm

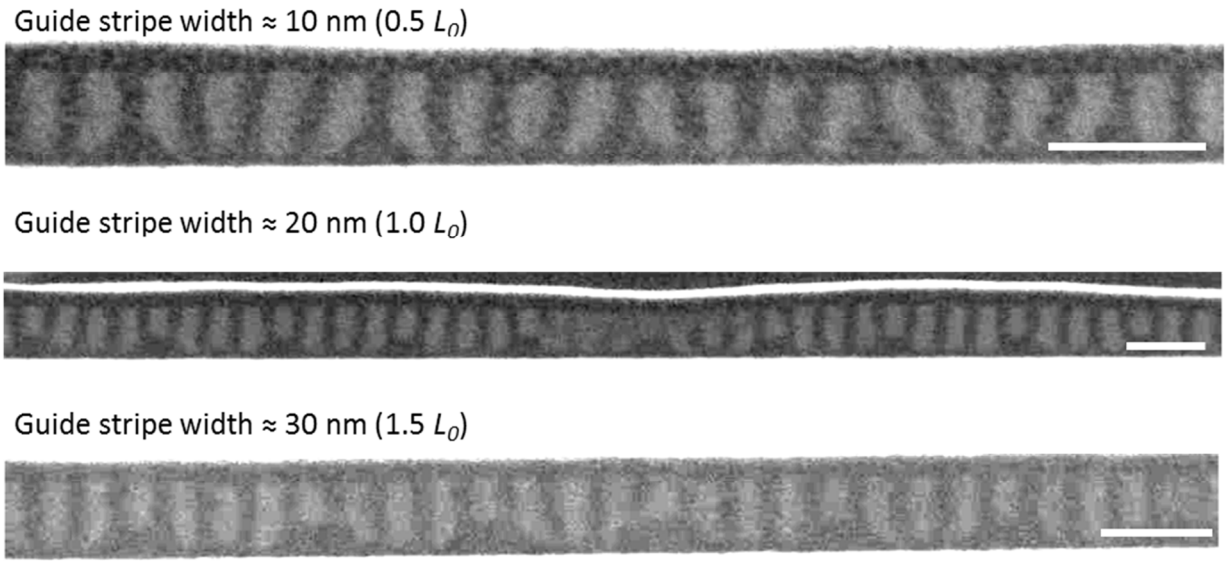


Figure S1. STEM micrographs of unetched BCP DSA cross-sections. The labels indicate the approximate guide stripe width, which changes how many components sit on top of the guide stripe. Small regions of these micrographs were used to construct the EELS images in seen in Figure 3. The pitch of the guide stripe in all cases is 79 nm. Scale bar = 50 nm. The contrast was enhanced in all three images. The domain tilting is either due to thermal drift during STEM rastering, the cross-sectioning process, or a real phenomenon that is largely fixed by the etch process (See Figure S2).

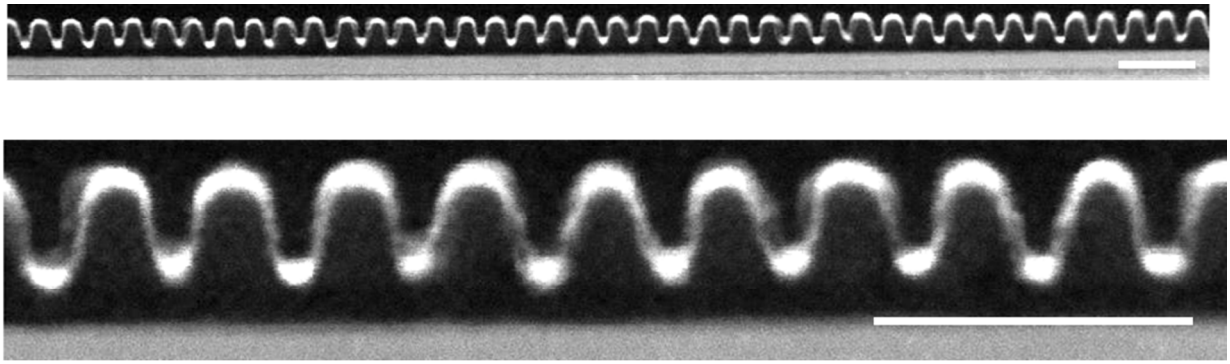


Figure S2. STEM micrographs of partially-etched BCP DSA cross-sections at two magnifications, showing the relative uniformity of the BCP features despite the domain tilting seen in the cross-sections in Figure S1. The micrograph was taken at guide stripe width ≈ 1.5 L_0, pre-pattern pitch = 79 nm. Scale bar = 50 nm. A capping layer of chromium oxide was deposited on the features before cross-sectioning.

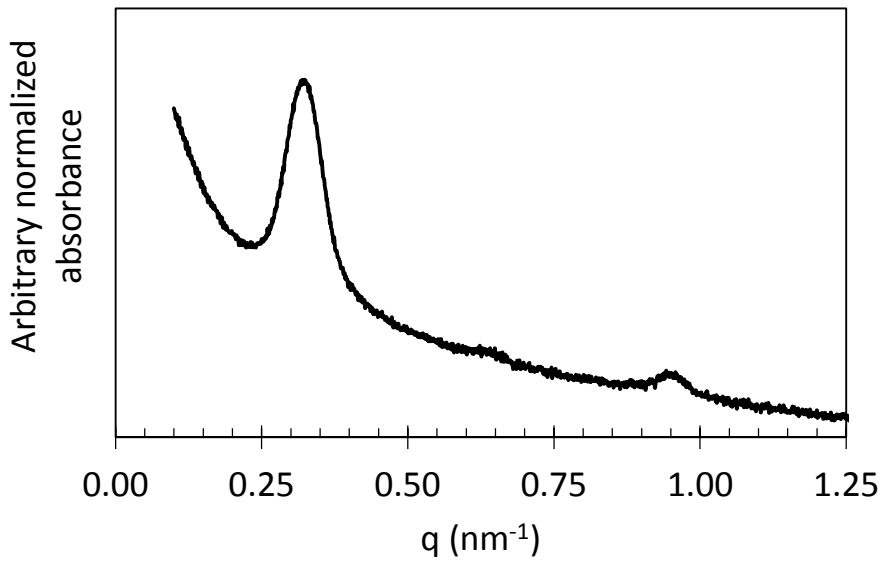


Figure S3. Small angle X-ray scattering (SAXS) data of circa 20 nm PMOST-*b*-PTMSS. q* peak at approximately 0.319 nm^{-1} indicates a 19.7 nm L_0 estimate. Data taken at room temperature of a sample annealed at approximately 200 °C then quickly quenched.

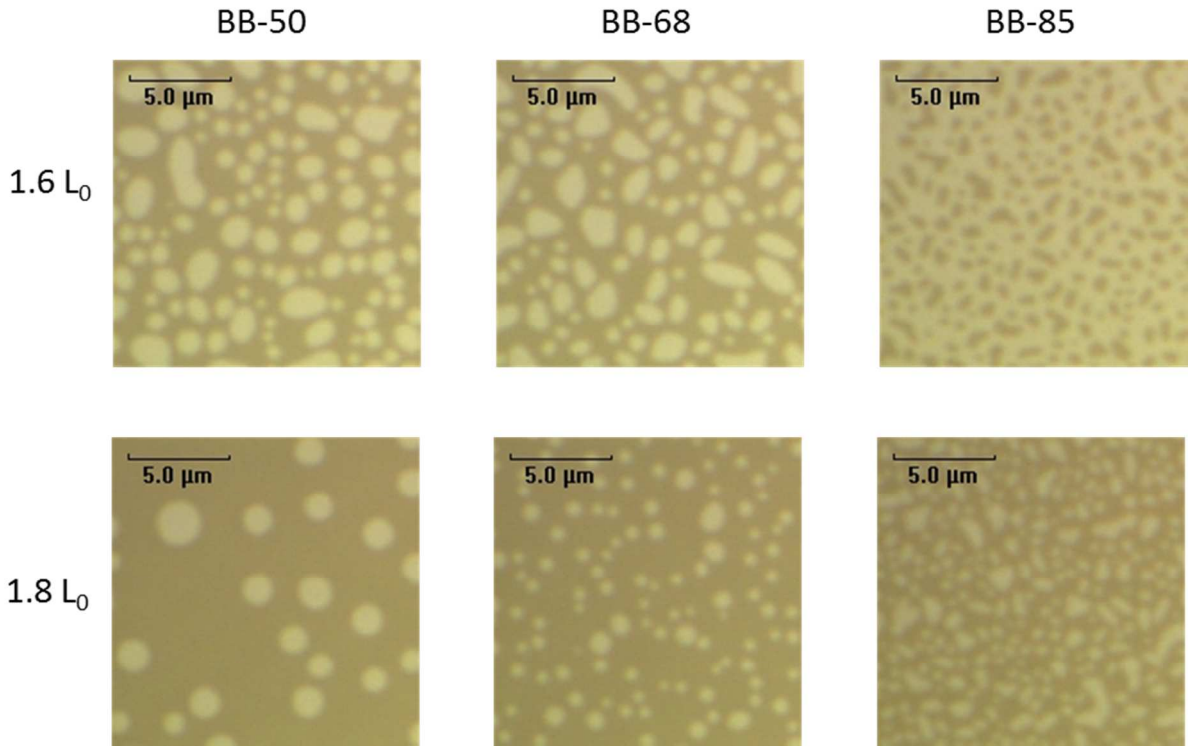


Figure S4. Optical micrographs of PMOST-*b*-PTMSS films annealed on blank substrates treated with the three brushes used for DSA. Anneals were performed at 205 °C for five minutes on hotplates open to N_2. The presence of holes at both film thicknesses for BB-50 and BB-68 implies symmetric (PTMSS) wetting substrates. BB-85 shows a feature flip (islands to holes) between the two film thicknesses, implying the existence of an incommensurability condition at 1.75 L_0, indicative of neutral wetting behavior.

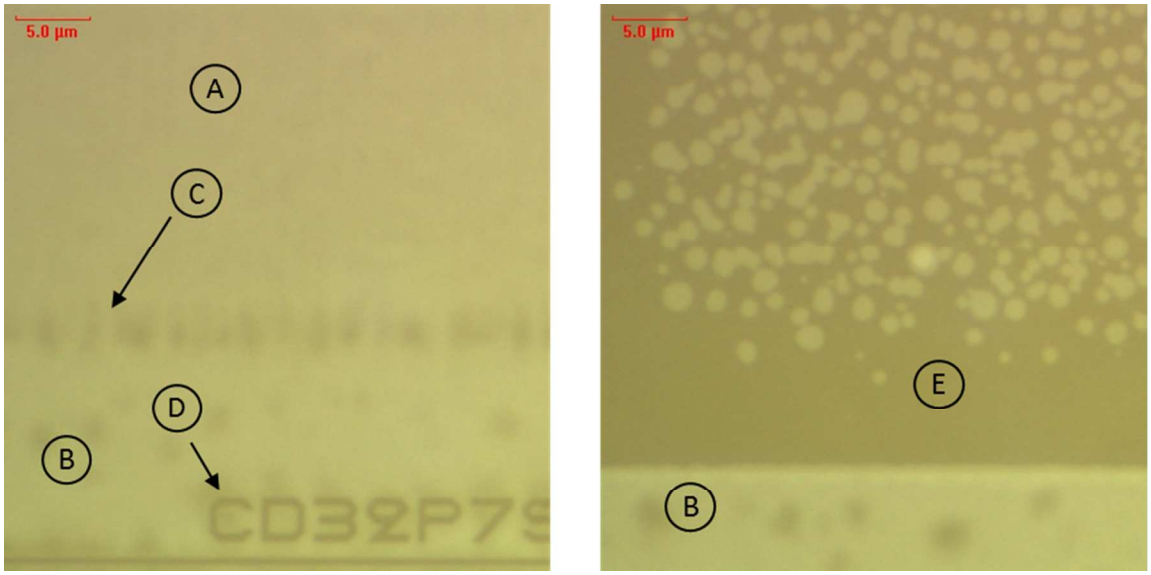


Figure S5: Optical micrographs of select regions of a fully processed XPMOST chemo-epitaxy wafer including a patterned region (left) and an unpatterned region containing XPMOST (right). The labels correspond to different regions: (A) patterned area containing DSA showing very smooth film, (B) unpatterned area (in both left and right images) backfilled with brush, (C) approximate location of boundary of regions (A) and (B) which evidently helps to nucleate features, (D) macroscopically patterned XPMOST, (E) unpatterned XPMOST, clearly showing white spots characteristic of hole BCP topography (in this case, half-holes). Region (B) also seems to produce topography, but the contrast of these features is very low and are presumably not explicitly quantified BCP features. BCP was coated at 36 nm = 1.87 L_0.