ADVANCED MATERIALS INTERFACES

Supporting Information

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High-Resolution Study of Changes in Morphology and Chemistry of Cylindrical PS-*b*-PMMA Block Copolymer Nanomasks during Mask Development

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1. SEM Images of all BCPs prior to removal + after UV light/acetic acid and plasma respectively.

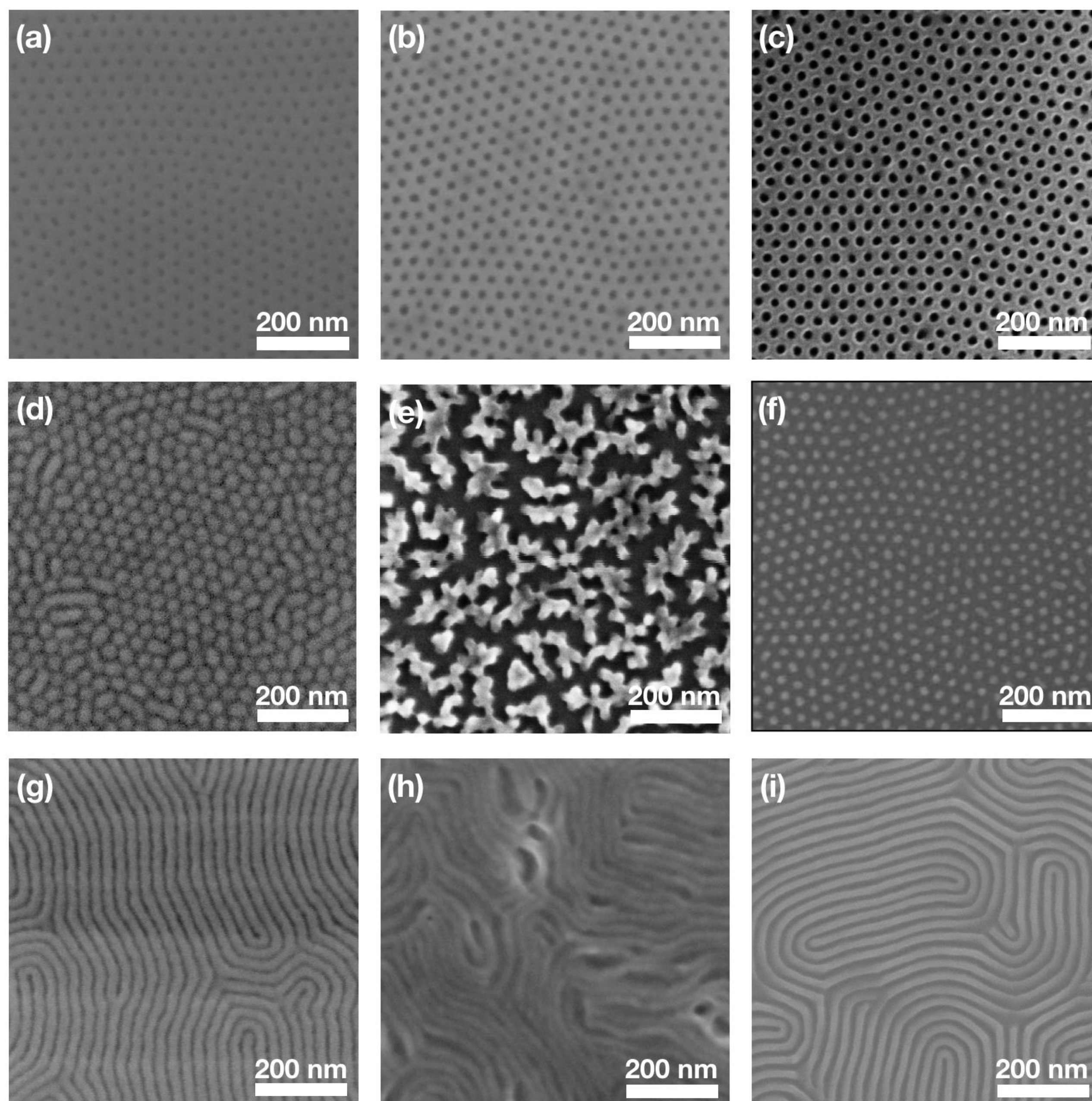

Figure S1: SEM images of PS-*b*-PMMA BCPs with block length ratios of (a-c) PS:PMMA 70:30, (d-f) PS:PMMA 30:70 and (g-i) PS:PMMA 50:50. The respective polymers are shown (a, d, g) after microphase separation with both species present, (b, e, h) after UV exposure and PMMA removal in acetic acid and (c, f, i) after PMMA removal by exposure to an O_2/Ar plasma for 40 s. The 30 and 50 % PS volume fraction BCPs exhibit a collapse of structures after the wet chemical approach, while after the RIE approach, patterns stay intact.

Scanning electron microscopy (SEM) was conducted with a Zeiss Ultra plus at 2 kV acceleration voltage using an in-lens detector. Samples were imaged as prepared, i.e. not covered with conductive metal films.

2. Full survey XPS spectra

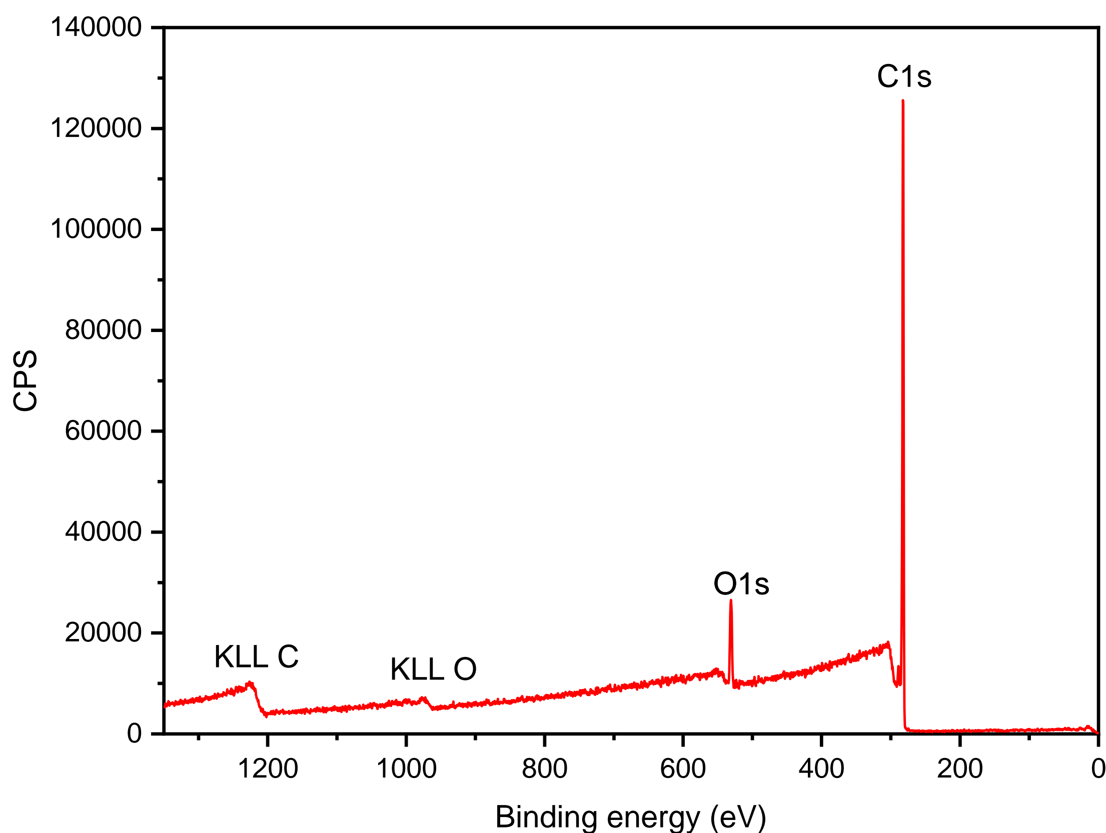

Figure S2.1: XPS survey spectrum of microphase separated PMMA-cylinder forming PS-*b*-PMMA block copolymer. C1s and O1s are core level emissions from carbon and oxygen whereas KLL C and KLL O are Auger emissions from carbon and oxygen, respectively.

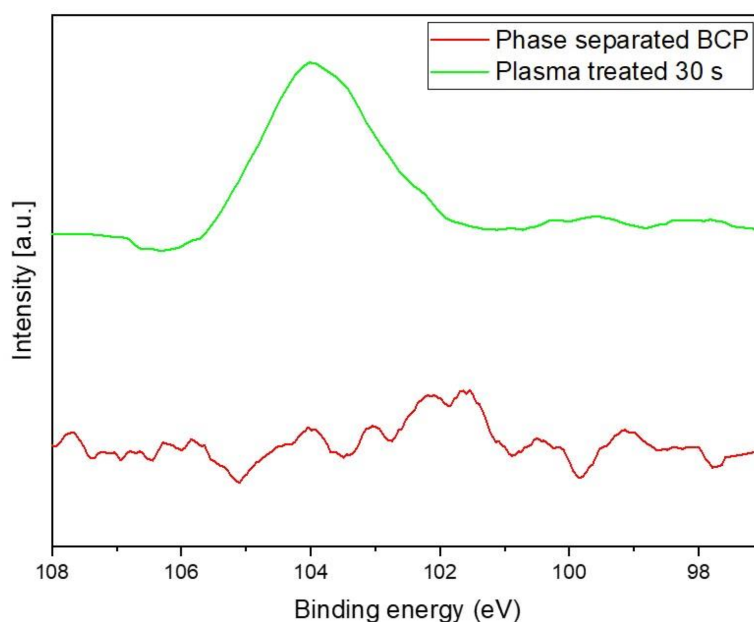

Figure S2.2: Si2p core level XPS spectra of microphase separated and plasma treated (30 s) PS-*b*-PMMA block copolymer.

3. Bond fractions in BCP

Table S1: Bond fractions in PS-b-PMMA with block length ratio (70:30 PS:PMMA) determined from fitted deconvoluted peaks in C1s core level XPS spectra for the undeveloped BCP, after UV/acetic acid treatment and after O_2/Ar plasma treatment for different durations.

Components	**und. BCP**	**UV/a**	**30 s**	**40 s**	**50 s**	**60 s**	**70 s**
C=C/C-C/C-H	90.86	74.88	72.36	78.18	79.19	82.6	84.74
C=O	2.38	12.03	6.83	6.07	5.68	5.71	4.57
C-O	2.31	12.66	19.74	14.73	14.17	10.69	9.57
π-π*	4.45	0.43	1.07	1.02	0.96	1	1.12

4. PM-IRRAS spectrum BCP

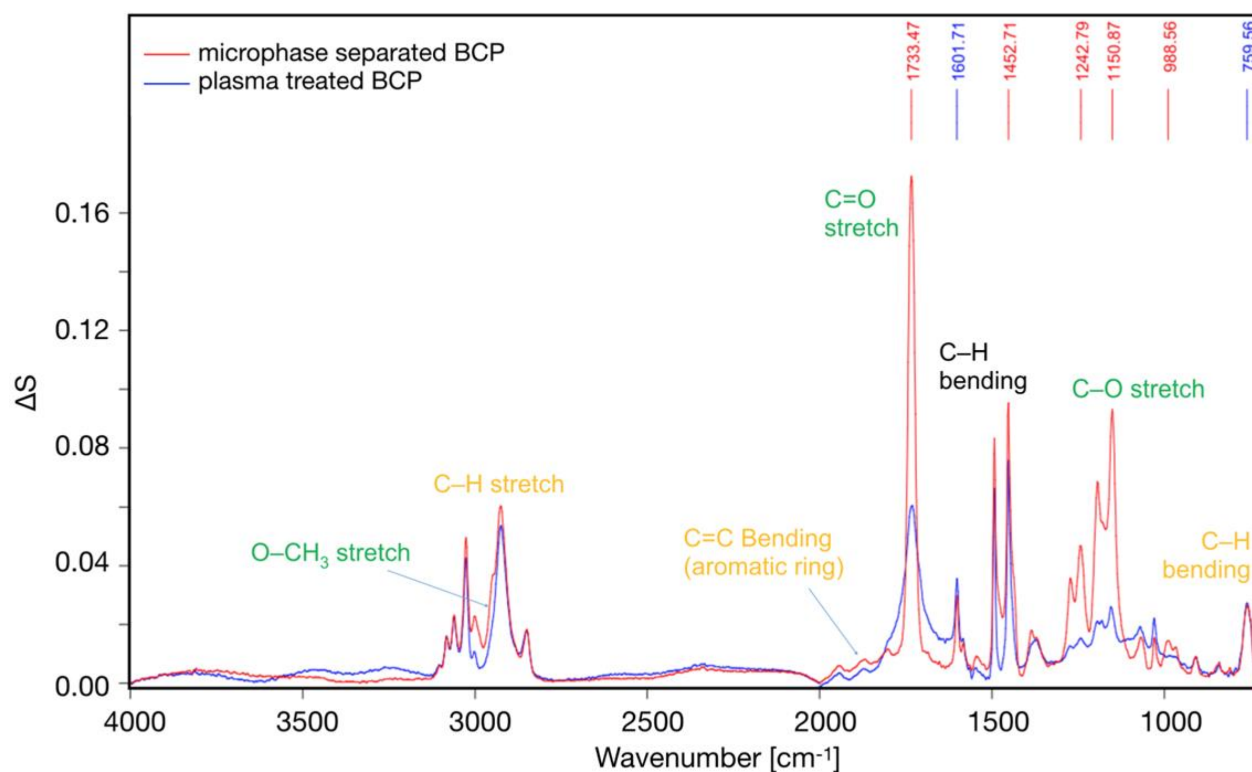

Figure S4.1: PM-IRRA spectra of microphase separated block copolymer (PS-*b*-PMMA 70:30) prior to (red) and after (blue) plasma treatment. Yellow labels are marking peaks predominantly stemming from PS and green labels from PMMA; black labelled peaks are found in both species [1,2].

Sample setup: 70 nm e-beam evaporated Au film with 2 nm Ti adhesion promoter; BCP directly on the Au film (as in [3]). Then UV and acetic acid treatment to remove PMMA and 20 s plasma.

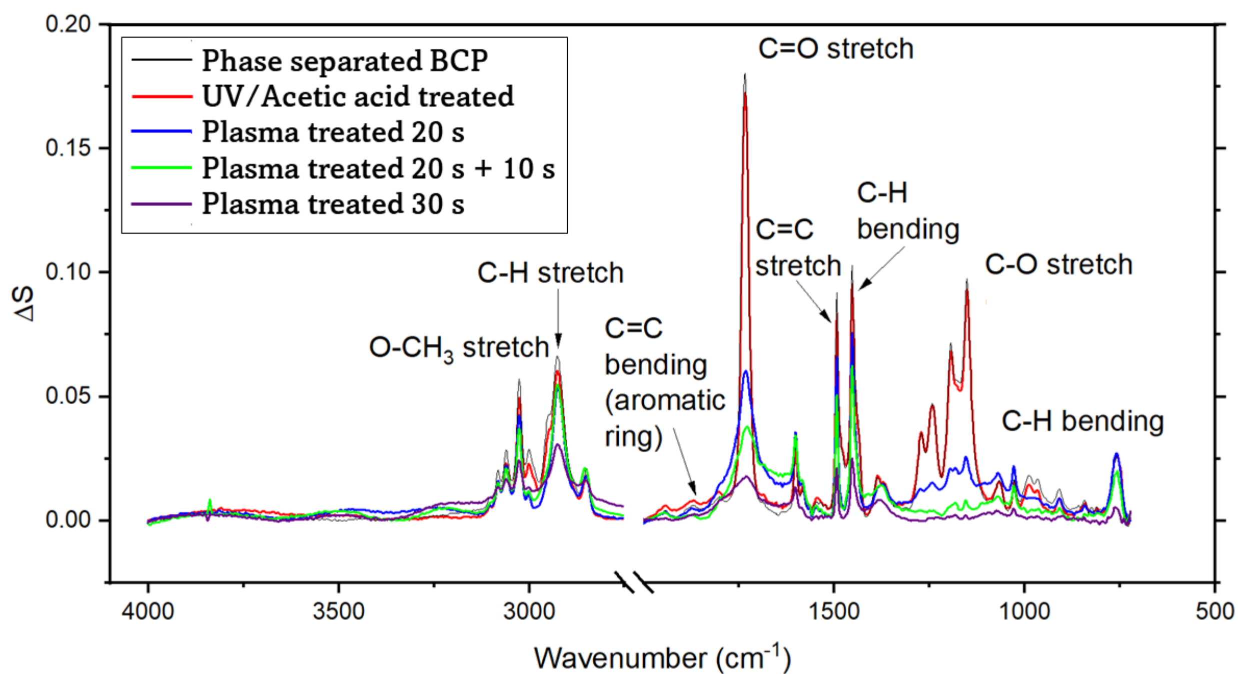

Figure S4.2: PM-IRRA spectra for samples with gold as reflective surface at different steps of BCP lithography. Black line: microphase separated but not developed BCP. Red line: PMMA removed by UV/acetic acid. Blue, green, and violet lines: plasma treated PS mask for 20 s, 20 s + 10 s separately, and 30 s, respectively. The 20 s + 10 s plasma treated sample is exposed to atmosphere after first etching, leading minor changes at the surface prior to the second plasma etching.

5. Bond fractions in RCP brush

Table S2: Bond fractions in RCP brush films determined from fitted deconvoluted peaks in C1score level XPS spectra for the undeveloped BCP, after UV/acetic acid treatment and after O_2/Ar plasma treatment for different durations.

Components	unt. RCP	UV/a	10 s	15 s	20 s	25 s	30 s
C=C/C-C/C-H	87.74	84.68	60.68	41.85	41.25	64.65	77.81
C=O	4.04	5.04	15.9	12.92	17.3	8.94	4.5
C-O	5.98	8.51	23.42	45.23	41.45	26.41	17.69
π-π*	2.24	1.77	0	0	0	0	0

References:

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[3] K. Brassat, D. Kool, J. Bürger, J. K. N. Lindner, *Nanoscale* **2018**, *10(21)*, 10005-10017.