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

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Nanolithography with self-assembled block copolymers (BCPs) is an emerging competitive alternative to conventional lithography, which is currently reaching its limits with regard to resolution and economic feasibility. For high-resolution lithography, both the abruptness of BCP internal interfaces between self-assembled polymer nanodomains and the processing steps used to selectively remove one of the polymers are crucial. This paper presents a detailed investigation of the chemistry, the mask wall morphology, and the line edge roughness (LER) of self-assembled nanomasks from polystyrene-\textit{b}-polymethylmethacrylate (PS-\textit{b}-PMMA) before and after selective removal of the PMMA nanodomaains. For the latter, either wet or plasma etching are employed and their impact on both the morphology and chemistry of resulting nanomasks is analysed using analytical (scanning) transmission electron microscopy (STEM), X-ray photoelectron spectroscopy and polarization-modulated infrared reflection-absorption spectroscopy. Dedicated image analysis tools are developed to determine for the first time the LER of cylindrical openings in PS masks from STEM dark-field images at sub-nanometer resolution. Applying these tools prior to and after PMMA removal from the BCP films, the statistics of feature sizes, LERs, and interfacial widths are determined. In addition, the impact of wet and dry etching processes on PS-\textit{co}-PMMA random copolymer brushes required for substrate functionalization is evaluated.

1. Introduction

Block copolymer (BCP) self-assembly (SA) is a promising approach for next-generation nanolithography.\cite{1–3} While top-down optical lithography methods are reaching their minimum feature size and economic viability limits and electron beam, ion beam, and scanning probe lithography techniques suffer from their inherent small patterning throughput,\cite{4,5} bottom-up BCP lithography today allows for a highly parallel, economic large-area patterning down to the sub-ten nanometer scale.

In BCP thin films, the self-organized microphase separation of polymer chains consisting of two immiscible polymer species into polymer nanodomains allows to create versatile periodic patterns on different solid surfaces with nanometric precision. Depending on the characteristics of the particular block copolymer, i.e., polymer species, molecular weight, and block length ratio, nanodomains can exhibit diverse geometries such as cylinders, spheres, or lamellae arranged in periodical designs.

By using chemical or topographical prepatterning of the substrate surface the local arrangement, order, and orientation of such polymer nanodomains can be controlled, which is often called directed self-assembly (DSA). DSA exploits a minimization of interfacial and strain energies to tailor complex nanometric and/or hierarchic architectures.\cite{6–12}

In BCP lithography, polymer thin films of well-defined thickness are deposited from a solution onto a solid substrate.
The nanophase separation is induced by thermal or solvent annealing, which increases the polymer chain mobility and allows the polymer to rearrange into specific nanodomains to form the desired motives. For further utilization in subsequent lithography processes, one polymer type can be selectively removed to use the remaining nanostructure as a shadow mask for, e.g., lift-off or etching processes.[13–19] To enhance the hardness of thin nanomasks in these etching processes, one polymer species can be selectively infiltrated with organometallic precursors prior to etching.[20]

PS-b-PMMA is the most commonly used polymer in BCP lithography, where the chemically less stable PMMA domains are usually selectively removed to create a PS shadow mask. In order to enable this, the PS and PMMA nanodomains need to be aligned vertically on the substrate. For SiO₂-covered silicon surfaces, this alignment is usually achieved using an interfacial layer consisting of a random copolymer (RCP) of the same monomers,[6,7,12] neutralizing the interfacial energies for the two BCP constituents. The subsequent selective PMMA removal is achieved either by (A) the degradation of PMMA by UV exposure and followed by wet chemical etching in acetic acid or by (B) preferential dry etching of PMMA in a reactive plasma. Both approaches have shown promising results and are compatible with industrial semiconductor processing standards.[10,15] However, even though various efforts have been done to minimize interface widths,[21–24] details of these PMMA removal techniques are not yet clear and their impact on the precision of resulting PS nanomasks is not yet sufficiently investigated.

In particular, it needs to be analyzed a) if the two approaches lead to a complete removal of PMMA at PS-PMMA nanodomain boundaries, b) if the MMA sections in the RCP brush between the BCP film and the SiO₂ substrate are removed as well and c) how the PMMA removal technique employed influences the line edge roughness (LER) of resulting PS nanomasks. The LER is the standard deviation of the positional difference between an actual interface and the interface of an ideal domain boundary and thus is the measure for the sharpness of an interface.[25] Since the LER should be significantly smaller than the minimum feature size of the nanomask and since the two polymers involved are chemically similar, the LER of PS-b-PMMA is hard to determine accurately. Commonly scanning electron microscopy (SEM) and grazing-incidence small-angle scattering (GISAXS) are used to characterize and quantify characteristic BCP mask parameters like feature size, feature distance, correlation length, and LER.[6] In addition, XPS was successfully applied to determine the overall surface chemistry.[26–28] To receive detailed morphological and chemical information of the nanostructure only a few newly developed techniques are available such as photoinduced force microscopy and peak force IR microscopy,[29,30] providing <10 nm spatial resolution. Unfortunately, this resolution is not yet sufficient to answer the above questions. Thus, here we exploit recent developments and improvements in the low-keV performance of state-of-the-art high-resolution spherical aberration (Cs) corrected (scanning) transmission electron microscopy ((S)TEM).

It was recently demonstrated that low-energy Cs-corrected STEM allows to observe the interfaces in microphase separated PS-b-PMMA thin films at unprecedented resolution.[31] These investigations clearly show that the PS-PMMA interfaces are not perfectly sharp but exhibit a spatially inhomogeneous and gradual change in PS-PMMA concentration. In addition, nanoscopic pockets of the minority polymer are likely to be present on either side of the microdomain boundary prior the PMMA removal. The question then of course is, how completely the PMMA can be removed by either of the two approaches (A) and (B) mentioned above and how the LER of the PS-PMMA interface is transferred into a LER of the final nanomask.

Therefore, in the present article Cs-corrected low-energy STEM is combined with X-ray photoelectron spectroscopy (XPS), polarization-modulated infrared reflection-absorption spectroscopy (PM-IRRAS), ellipsometry, and contact angle measurements to answer the above questions. The focus is placed on cylindrical masks resulting from microphase-separated PS-b-PMMA BCP after PMMA removal by either the UV/acetic acid or the reactive ion etching (RIE) approach. For the first time, the LER of cylindrical nanomask openings is determined by dedicated imaging and image analysis techniques.

2. Selective Removal of PMMA from Microphase Separated PS-b-PMMA Thin Films

The two different approaches for removing PMMA from microphase separated PS-b-PMMA (A) and (B) will be considered more closely in the following. To this end, the chemical structure of both, PS and PMMA molecules, is shown in Figure 1a, along with a numbering of bonds that can be identified by XPS and which allow for a distinction between the two polymers further below.

Approach (A): Exposure to UV light results in PMMA degradation, i.e., unzipping or chain scission of the MMA bonds, while the PS is ‘hardening’ due to cross-linking, resulting in a decreased solubility in organic solvents.[32–35] After UV exposure, the MMA fragments can be removed by dissolution, e.g., in acetic acid. Extensive literature can be found dealing with this PMMA removal strategy, where the UV dose and wavelength are optimized.[32,33,36] The major advantage of this wet etching approach is a seemingly 100% selectivity between PS and PMMA and the fact that such a comparably mild treatment does not affect most substrate materials. Some studies suggest that this removal approach can lead to a complete PMMA removal.[37] It is likely that the presence of PMMA residues critically depends on the duration and intensity of UV irradiation applied to damage the PMMA prior to dissolution in acetic acid. From lift-off experiments, it has been concluded that some polymer material can remain on the substrate,[34] and recent high-resolution studies[31] make it unlikely that pockets of the minority polymer can be completely removed wet chemically. Therefore, Figure 1b exhibits a more complex hypothetical model of a cylindrical mask opening, as it might emerge from a microphase separated PS-b-PMMA BCP thin film on a PS-co-PMMA RCP-neutralized SiO₂ surface after PMMA removal by approach (A). While the PMMA is completely cleared away at the center of a former vertical PMMA cylinder, some PMMA is assumed to remain at the vertical sidewalls bond to and partially embedded into the PS matrix. The result is a rough vertical side wall of this pore. It is further assumed that parts
of the RCP brush at the pore bottom have been removed. This should be mostly the MMA fraction if it was accessible to the acetic acid. Thus, a very thin polymer film, significantly thinner than the original 6.5 nm RCP brush layer and mostly consisting of PS is assumed to remain. It is obvious that such a pore morphology is less than optimal for a subsequent application for lithography purposes.

Approach (B): Dry etching using RIE processes is a suitable alternative to procedure (A) for removing PMMA. In this approach, different etching rates of PS and PMMA allow for selective PMMA removal with the major part of the PS domains remaining intact. Different plasma compositions were investigated in literature to optimize the etch selectivity between PS and PMMA, e.g., O₂/Ar,[39,40] CH₄/N₂,[41] CF₄/O₂,[39] CO/H₂,[42] CHF₃/O₂,[39] and Ar/CO.[40] All recipes rely on both physical sputtering effects and chemical etching for polymer removal. The most frequently used plasma is based on O₂ and Ar gas.[39,40] The major advantages of O₂/Ar plasmas are a good final surface roughness of the PS masks and a good etch selectivity to most substrates.[38,39] The major disadvantage of dry etching techniques, however, is the limited etch selectivity to most substrates.[38,39,42] This not only leads to a reduction of the thickness of the remaining PS mask due to a vertical etching rate, but due to isotropic character also lateral etching takes places, which enlarges the resulting features in size and changes the features in shape.[38]

Both approaches (A) and (B) have been applied in our experiments as detailed in the experimental section of this article.

3. Results and Discussion

3.1. Morphology of PMMA Cylinders and Pores

Nanophase separation of BCP films led to regular arrays of hexagonally arranged PMMA cylinders in the PS matrix as expected (see Figure S1 of the Supporting Information). For the STEM and TEM analyses, BCP films were fabricated on Si substrates covered with a sacrificial SiO₂ film and processed as detailed in the experimental section. Free-standing BCP membranes ready for TEM were released from the substrates by wet chemical etching of the sacrificial layer, followed by skimming off of the etchant using a TEM grid. The top and bottom row of Figure 2 show STEM annular dark-field (ADF) and TEM bright-field (BF) images, respectively, of individual cylinders in different processing states: the BCP thin film after nanophase separation still containing both polymer species, i.e., a PMMA cylinder in the PS matrix (Figure 2a,d), the PS membrane after PMMA removal by procedure (A), i.e., UV exposure and acetic acid etching (Figure 2b,e), and the PS membrane after PMMA removal by procedure (B), i.e., dry etching in an O₂/Ar plasma for 70 seconds (Figure 2c,f). In all cases, the SiO₂/Si substrate was removed during TEM specimen preparation.

Imaging of the intact membrane without selective staining of one polymer species for contrast improvement is demanding. The PMMA cylinder within the PS matrix is barely visible in TEM (Figure 2d), however, STEM-ADF imaging (Figure 2a) clearly reveals the PMMA domains which show a darker contrast compared to the surrounding PS. It becomes apparent that the PMMA cylinder exhibits a blurred, broad interface with PS. This interface prior to PMMA removal was investigated in detail in our previous work[31] and serves here only as a reference.

The STEM-ADF image of the membrane after PMMA removal using the UV light and acetic acid treatment (Figure 2b) shows some residual contrasts within the “hole” and reveals that the former PMMA cylinder was not perfectly perpendicularly oriented within the film, but slightly tilted or otherwise distorted along the film height. This becomes apparent from the contrast gradient at the right edge of the cylindric “hole” in Figure 2b. Contrasts in STEM-ADF imaging, so called Z-contrast imaging, are due to local differences of the projected atomic number of the sample material obtained by integration along the electron beam direction. Thus, for these samples, STEM-ADF images show contrasts resulting from a superposition of changes in material density and thickness. From Figure 2b it becomes clear at a glance that the polymer is not completely removed, and the “hole” does not penetrate the entire polymer film because the image intensity within the “hole” does not drop to zero. In addition, the contrast gradient at the domain interface indicates a certain slope of the hole wall. The TEM BF image of this membrane (Figure 2c)
confirms that the polymer is not completely removed as a material contrast typical for amorphous films remains visible within the region of the hole in the PS membrane. The thickness of the remaining film in such “blind holes” will be discussed below in more detail.

In contrast, dry etching of the polymer film using an O₂/Ar plasma results in a complete removal of the PMMA cylinder throughout the entire film. The zero-counts STEM-ADF signal (Figure 2c) and the absence of any contrast within the hole in the TEM BF image (Figure 2f) indicate that no material is left inside the hole. Compared to the intact BCP film and the wet etched film, the hole walls appear with a sharp contrast to the PS film, i.e., they seem to be well defined exhibiting a steep slope.

In order to obtain statistically relevant data on the feature morphology, we developed a MATLAB program for an automated image analysis which allows to determine the radii, nanodomain wall roughnesses and line edge roughnesses of the nanoholes as well as the hole eccentricity among other characteristics. This software, along with a detailed description on its functions and output, is made freely available by contacting the authors of this work. Briefly, to detect the hole center positions, the program first blurs the image by using a Wiener filter and strong Gaussian blurring and subsequently determines the hole center positions by detecting the local intensity minimum within each hole (Figure 3a). In this way, challenges arising from low contrast between the two phases within the usually used thresholding procedures to detect hole center positions are overcome. Radial intensity profiles starting from each hole center are then collected in different directions (in azimuthal angle steps of 5° along the hole circumference) and fitted with an error function as shown in Figure 3b,c. We define the nanostructure characteristics, which can be determined by analyzing these intensity profiles, as follows for a quantitative comparison:

- The positions of the PMMA cylinder interface (in case of the nanophase separated BCP membrane without any further PMMA removal treatment) or the hole wall (in case of PMMA removed membranes) are assumed to be at the position of 50% intensity of the error function. The local radii of cylinders/holes are thus the distance between this 50% intensity position to the cylinder/hole center for each angular position (Figure 3b). The mean hole radius is the mean value of these distances around the hole/cylinder circumference (Figure 3c).
- The interfacial width of the PS-PMMA interface and its resulting wall roughness after PMMA removal is represented by the distance between the 25%-intensity and 75%-intensity positions of the error function (Figure 3b) at each radial position around the cylinder/hole. For the intact BCP membrane, this region corresponds to the projected intermixing volume of the polymer species forming a broad interface between the PS and PMMA polymer domains. For hole-patterned membranes after PMMA removal, this area is the projected local roughness of the hole wall perpendicular to polymer film, i.e., in z-direction through the membrane.
- The line edge roughness LER of the nanoholes is defined as the difference between the local wall position at 50%-intensity determined for each azimuthal angular interval and its mean position, i.e., the local deviations of the hole wall position from a perfect circle in the x-y film plane (x- and y-directions are displayed in Figure 3a) with a radius corresponding to the mean radius of the hole.

All threshold percentages are chosen freely. Thus, for a given set of threshold values, the absolute values of average hole radius and LER are subject to a systematic error due to predetermination. Nevertheless, a direct comparison between patterns evaluated with the same set of thresholds is reliable.
Figure 3. Numerical and statistical analysis of nanofeatures observed by STEM-ADF imaging in cylinder forming PS-b-PMMA BCP membranes at different stages of membrane post-processing. a) Single pore with the pore center identified (red dot). b) Single radial intensity profile (blue) and fitted error function (purple) together with the definition of the local pore radius and interface width. c) Superposition of radial intensity profiles and their fitted error functions for different angular positions around the center in steps of 5°. d,g) STEM-ADF images of the untreated BCP membrane with PS and PMMA, e,h) the membrane after wet etching, and f,i) the membrane after dry etching. The 50%-intensity cylinder/hole contours (red lines) and interface/wall roughnesses (yellow areas) are marked in each image. j–l) 2D intensity plots of the angularly resolved radial intensity profiles of cylinder/pores in (g,h,i), respectively, with the vertical axes giving the azimuthal angle. The 50%-hole contours are similarly marked by a red line, the blue lines indicate the mean radius. m–o) Histograms of the frequency distribution of m) the mean PMMA cylinder/hole radius of individual cylinders/holes, n) the LER of all three samples, and o) the interfacial width/wall roughnesses. Statistics in (m–o) was performed over 50 cylinders/mask openings for each sample.
Figure 3d–o shows the summarized results of this analysis for the intact block copolymer membrane with PS and PMMA being present (d,g,j) and the PS membrane after PMMA removal using UV light/acetic acid (e,h,k) or plasma (f,i,l), respectively. STEM-ADF images at different magnifications are presented with the identified hole contour at 50% intensity as a red line and the interface width/wall roughness marking the area between 25% and 75% intensities as yellow areas in Figure 3d–i. Figure 3j–l depicts 2D intensity maps of the three respective samples. These maps show the angularly resolved intensity profiles for each radial position around the cylinder/hole of the high-magnification STEM-ADF images in Figure 3g–i as a function of their distance to the hole center. The red line again shows the local wall positions at 50% intensity. The blue line is the mean value of all red marked positions, i.e., the mean hole radius. Analyses of the PMMA cylinder or hole morphology for the differently treated samples were performed for 50 pores each according to these definitions. The frequency distributions of radii, interface widths/wall roughnesses, and LERs are depicted in the histograms in Figure 3m–o, respectively.

The diameter of the PMMA domains in the BCP film prior to PMMA removal measurements (11.8 ± 3.1) nm (Figure 3m), matching the previously reported values. The broad variation of the determined PMMA domain diameters is largely due to the fact that the interface between PMMA and PS domains is smeared. It is less affected by the fact that smeared interfaces are difficult to localize, since, e.g., image noise statistics are leveled out by fitting the local error functions. Each nanophase domain itself exhibits internal contrast changes (Figure 3g), which add up to the difficulties of exactly localizing the interface positions. As a result, the detected interface positions, which are marked in red in Figure 3d–g, largely deviate from those of perfect cylinders. To describe this fuzziness, the interface width within which the composition of PS and PMMA gradually changes, is introduced. It is marked by the yellow area and amounts to (5.2 ± 1.3) nm (Figure 3o). Accordingly, the line edge roughness given as the standard deviation of the 50% intensity position of the fitted error function from a position on a circle with the mean pore radius is (3.2 ± 1.5) nm (Figure 3n) for the undeveloped PS-b-PMMA film.

After PMMA removal using UV exposure and wet etching (approach A) the mean pore diameter is (19.1 ± 1.4) nm, i.e., significantly larger than the formerly identified PMMA cylinders. The shape of the formed holes is much more defined, exhibiting a much narrower size distribution of the pore radii compared to the undeveloped cylinder radii (Figure 3m). This indicates that during UV exposure and wet etching, PMMA chains within a region of comparably high PMMA concentration in the former interfacial region are removed. The wall roughness is significantly smaller than the interface width between the former polymer domains and amounts to (2.8 ± 0.7) nm (Figure 3o), which can be explained by a surface minimization of protruding polymer chains: dangling polymer strands revealed during the acetic etch are minimizing their energetic state by forming a smoother surface. The broad distribution of wall roughnesses with an average value of 0.7 nm (Figure 3n, blue histogram bars) results from the tilt of the former PMMA cylinders through the membrane which was already observed in Figure 2b. It should be emphasized that this tilt is not an imaging artifact. This can be verified as it is not unidirectional for all pores as visible in images with lower magnification (Figure 3e), allowing for a visual impression of the distribution across the sample. In addition, the implemented software (see Supporting Information section) allows to determine the eccentricity of the hole. This analysis does not show any correlation between the hole tilt and its position on the sample excluding misinterpretations due to measurement artifacts.

The 2D intensity map of the UV light/acetic acid treated sample (Figure 3k) reveals that the wall position follows a fluctuation of low frequency along the hole circumference, i.e., deviations from a perfect circle with a mean radius of $r = 9.5$ nm appear in form of undulations with an amplitude of 1 nm. These undulations are not due to statistics, as their size is large compared to the lateral distance between two profiles in Figure 3k, which is $r \cdot \tan 5^\circ = 0.83$ nm at the wall position. It was observed previously (Figure 2 and ref. [31]) that the PS and PMMA domains in undeveloped films exhibit small grains of opposite contrast within the broad interface. These grains are expected to contain entrapped coils of the opposite polymer species. As these grains are of the same size as the undulations in the hole wall, it is likely that “opposite” polymer grains are removed during UV light/acetic acid treatment. Minimization of interfacial energies then leads to a smoothing of the hole walls, resulting in this shape with an average LER of roughly (0.8 ± 0.6) nm (Figure 3p).

Dry etching of the PMMA (approach B) leads to an enlargement of the hole diameter from the initial (11.8 ± 3.1) nm diameter of the untreated PMMA cylinders to (24.7 ± 1.6) nm (Figure 3m) for the plasma etching time used. As stated above, the reactive ion etching with argon and oxygen removes the PMMA but also affects the PS. Oxidation of hole walls along with desorption of volatile species and pure physical sputtering result in an increased hole diameter. This increase of feature sizes after plasma treatment was also reported in literature.[43]

Wall roughness as well as LER of the plasma treated samples are significantly smaller and exhibit a smaller fluctuation compared to the UV light/acetic acid treated sample. The wall roughness, determined in a similar way to the interfacing width in non-PMMA-removed samples, amounts to (1.6 ± 0.2) nm (Figure 3o) indicating a steep slope of the hole walls. It was argued in literature[42] that such a small wall roughness might either result from the redeposition of sputtered entities into sharp bumps created during ion bombardment or might stem from a local heating above the glass transition temperature due to energy transfer during ion bombardment and, thus, material reflow and smoothing. The average line edge roughness of the plasma etched holes is (0.5 ± 0.2) nm. Thus, it is comparable to that of the UV light/acetic acid treated sample of (0.8 ± 0.2) nm, however fluctuating much less. The wall position fluctuations, i.e., the difference between the red and blue lines in the intensity map in Figure 3i, are varying for the plasma treated samples at a higher spatial frequency than in case of the wet etched samples (Figure 3k). While low-frequency deviations after wet etching most likely result from smoothing and minimizing interfacial energies by residual PMMA chains, higher frequency deviations after plasma treatment occur most likely due to sputtering of PS from the hole walls during ion bombardment. Overall, the amplitudes of local maximum deviations from an ideally circular hole seem smaller in case of
plasma etched samples compared to wet etched samples, even though the mean values of the LER are similar (Figure 3n). It has to be emphasized that the plasma removal of the PMMA reduces the nanohole LER significantly compared to what is expected from the interfacial width between the PS and PMMA domains: while this interface width measures 4–6 nm, the actual roughness of the resulting mask opening is below 2 nm.

### 3.2. Changes in Composition and Bonding State

Energy-filtered TEM analysis was performed to further compare PS membranes from which PMMA was removed by either UV light/acetic acid or plasma etching. EFTEM thickness maps and corresponding line profiles of a UV light/acetic acid treated sample (Figure 4a,b) and of a plasma-treated sample (Figure 4e,f) were acquired. Carbon and oxygen elemental maps are shown in Figure 4c,d for the UV light/acetic acid sample and in Figure 4g,h for the plasma treated one, respectively.

Thickness mapping of the UV light/acetic acid treated samples (Figure 4a,b) reveals residual material with a thickness of 9 nm at the positions of the former PMMA cylinders and expected holes, i.e., slightly more than the 6.5 nm thick PS-co-PMMA random copolymer brush layer. Oxygen elemental mapping reveals higher O concentrations inside the “blind holes” (Figure 4d) compared to the surrounding PS membrane, indicating that PMMA and additional oxygen are still present. The height difference between the “blind hole” and membrane surface is equal to 23 nm, while the total film thickness is 30–35 nm, the latter roughly matching the sum of the initially deposited BCP thickness of 30 nm and the RCP brush layer with an initial thickness of 6.5 nm. This indicates that the RCP...
film is mostly intact but in the “blind holes” residual PMMA has remained. The sidewall slope is approximately $(63 \pm 3)^\circ$.

Plasma treatment allows to remove the PMMA cylinders completely leaving holes in the PS film. This was qualitatively observed in the STEM-ADF image in Figure 2 and is confirmed here by EFTEM thickness mapping. Inside the holes of plasma-treated masks, only signal noise can be detected (Figure 4e,f). Similarly, neither oxygen nor carbon residuals can be detected within the holes as revealed by the elemental maps (Figure 4g,h). However, it becomes apparent that the etching selectivity of the O$_2$/Ar plasma is limited and PS is partially etched—the residual membrane thickness is only 16 nm, compared to the initial BCP film thickness of 30 nm. The slope of the hole sidewall amounts to approximately $(63 \pm 4)^\circ$ in the plasma-treated film, thus identical to the UV light/acidic acid treated BCP film.

EFTEM spectroscopic imaging (EFTEM-SI) in the low-loss region was used to further increase material contrasts, exploiting plasmon excitations of individual polymer species. Figure 4i,j shows EFTEM-SI images at energy losses between 5 and 30 eV with filter widths of 5 eV. The indicated energies present mean values of the window position, i.e., an energy loss of 5 eV corresponds to an energy loss interval of 2.5–7.5 eV. It was shown before that EFTEM-SI of undeveloped BCP films exhibits a brighter PS material contrast compared to PMMA, which is due to the different plasmonic responses of PMMA and PS at an energy loss of approximately 20 eV. [34] This contrast is not observed here, which can be partially explained by the missing of PMMA domains. Instead, in case of the UV light/acidic acid treated membrane in Figure 4i, bright rings become visible at the hole circumference at energy losses from 5 to 15 eV. This area close to the side walls shows no extra EFTEM-SI contrast in case of the plasma-treated membrane (Figure 4j). It is stated in the literature that cross-linking can occur among PS and PMMA under long UV irradiation, [37] which could lead to a carbon material with a new plasmonic resonance. The emergence of ring-shaped EFTEM-SI contrasts at the circumferences of pores solely in UV/acidic acid treated films is a clear indication that the electronic structure of material present here is different from the material in the vicinity and/or material around the pores of plasma treated films. Thus, further investigations are needed to unequivocally assign these contrasts to a specific material.

XPS investigations were performed to determine the atomic composition and carbon bonding state of the polymer membranes after the different treatments (A and B) applied for PMMA removal (Figure 5). A low electron take-off angle was used to restrict the XPS information depth to the uppermost atomic layers of samples. For the XPS studies, BCP films formed on native oxide layers on silicon instead of thick sacrificial layers were used to avoid charging effects. All other processing parameters were kept the same as above. In order to analyze the acquired XPS spectra, the following assumptions are made: The BCP consists of 68.7% PS and 31.3% PMMA, i.e., the signals of the two polymer species are measured simultaneously and the spectra present a superposition of both. However, as PS contains 50 at% of C and 50 at% of H while PMMA consists of 33.3 at% C, 53.3 at% H and 13.3 at% O, the absence of oxygen in PS allows to differentiate between the two polymer species. Individual XPS investigations of neat PS and PMMA films, respectively, can be found in ref. [41].

XPS survey spectra (Figure S2.1, Supporting Information) of the polymer thin films show an elemental composition of only carbon (285 eV) and oxygen (532 eV). CIs and OIs core level spectra were acquired for further analysis and are presented in Figure 5a,c, respectively, for an untreated polymer membrane containing PMMA cylinders in the PS matrix. The CIs spectrum for a 30 s plasma treated membrane is shown in Figure 5b. The features of CIs and OIs spectra are correlated to the functional groups of PS and PMMA according to ref. [44] (see Figure 1a and Table 1 for bond assignment).

For PS, C−H, C−C, C=C as well as a π→π* signal of the phenyl ring (2), and C−H, C−H$_2$ and C−C of the polymer backbone (1) are observed. In PMMA, the methyl ester CH$_3$ and CH$_2$ (3) and C−C of carboxylic C with the polymer backbone (4) are detected. [44] The oxygen components of PMMA are C=O (5) and C−O (6) of the carboxy group and render the PMMA distinguishable from the PS. [44] The different components of the CIs and the OIs-core levels were fitted using a product of Gaussian and Lorentzian line shapes with a 30% Lorentzian fraction. It is to note that the contributions of all C−C, C=O, and C−H bonds are represented by one component as their binding energies lie within 1 eV and are not distinguishable at the given resolution. The fits of the CIs peak are further used for a semi-quantification to determine the contributions of individual bonds as shown in Figure 5d. All individual contributions are compiled in Table S1 of the Supporting Information. Along with the survey spectrum (Figure S2.1, Supporting Information), the atomic compositions of the samples are determined by using the CIs, OIs, and Si2p core level spectra (Figure 5e). For the untreated PS-b-PMMA film, the deconvoluted spectra confirm the presence of PS with a large C−C, C=C, C−H content and in particular a contribution of the π→π* transition. The PMMA is showing C−C, C=C, C−H, and in addition C=O and C=O contributions. The atomic composition resembles the expected elemental distribution with C and O.

Si cannot be detected (Figure S2.2, Supporting Information) as it is covered with the 30 nm thick BCP film and the 6.5 nm thick RCP brush, the total thickness of which exceeds the information depth of XPS measurements.

UV exposure of the polymer membrane followed by rinsing with concentrated acetic acid (approach A) should lead to a removal of PMMA, while the energy of UV photons used in our experiments is not expected to alter the PS drastically. XPS analysis, however, reveals an increased number of O-containing bonds and a decrease of detected π→π* peak intensity after the UV/acidic acid treatment (Figure 5d,e). The presence of this latter π→π* peak suggests that some of the phenyl rings of PS are still intact. The presence of large amounts of oxygen in the UV/acidic acid treated sample film (Figure 5e) is in agreement with the EFTEM observation of oxygen, which was observed mostly at the bottom of the “blind holes,” but also on the PS matrix (Figure 4d). The increase in oxygen contribution in the PS matrix can be due to the oxidation of PS after UV exposure as reported by Zhang et al. [43] A slight increase in C=O and C−O concentration was also found in accompanying PM-IRRAS measurements (Figure 5f and Figures S4.1 and S4.2, Supporting Information). It should be emphasized that these
measurements were performed with BCP films deposited directly on Au surfaces without the RCP neutralizing layer because a mirror-like substrate is needed in PM-IRRAS. From this, it is clear that the small increase of the oxygen PM-IRRAS signal observed in the wet etched sample results from oxygen bonds on the porous PS films. It is to note that increasing $\text{C} = \text{O} / \text{C} = \text{O}$ signals due to a contamination because of PMMA fragment dissolution with acetic acid are not to be expected. Several experiments (not shown here) with different sample immersion times in water for surface cleaning were performed and did not lead to changes in the $\text{C} = \text{O} / \text{C} = \text{O}$ signal intensity.

The strong increase in the XPS measured oxygen content observed in Figure 5d,e for wet etched BCP films compared to untreated films is therefore due to oxide formation at the bottom of blind holes, in agreement to the EFTEM analysis in Figure 4d showing the largest oxygen concentrations in the residues of the etched PMMA/RCP film at the blind hole bottoms.

After PMMA removal by reactive ion etching in an O$_2$/Ar plasma (approach B), the atomic composition changes significantly with respect to the undeveloped state. The C1s semiquantification reveals strong compositional changes within the first 30 s of plasma treatment. The contribution of $\text{C} = \text{O}$ and $\text{C} = \text{O}$ bonds decreases, while the contribution of the $\pi \rightarrow \pi^*$ bonds increases. This can be explained by partial degradation of the polymer backbones and oxidation reactions at the new surface, leading to the homogenous oxygen distribution on the porous PS film detected also by EFTEM in Figure 4d. With longer plasma exposure times, the overall composition stays approximately constant, which is compatible to the idea that this oxygen is mainly located at the PS surface. The contribution of $\text{C} = \text{C}$ and $\text{C} = \text{C}$ bonds decreases, while the contribution of the $\text{C} = \text{O}$ bonds increases. This was also reported in a comparable investigation[46] of O-containing plasma treatments of neat PMMA films. Surprisingly, the $\pi \rightarrow \pi^*$ signal intensity of the PS decreases

Table 1. Binding energy contributions of PS and PMMA to C1s and O1s core level spectra. Numbers in parentheses refer to Figure 1a.

| Polymer | Core level spectra | Contribution | Binding energy [eV] |
|---------|-------------------|--------------|--------------------|
| PS      | C1s               | (1): $\text{C} = \text{H}$ | 285.0 |
|         |                   | (1): $\text{C} = \text{C}$ | 285.7 |
|         |                   | (2): Phenyll ring | 284.7 |
|         |                   | (2): $\pi \rightarrow \pi^*$ | 291.5 |
| PMMA    | C1s               | (3): $\text{C} = \text{H}$ | 285.0 |
|         |                   | (4): $\text{C} = \text{C}$ | 285.7 |
|         |                   | (5): $\text{C} = \text{O}$ | 287.8 |
|         | O1s               | (5): $\text{O} = \text{C}$ | 532.1 |
|         |                   | (6): $\text{O} = \text{C}$ | 533.6 |

The strong increase in the XPS measured oxygen content observed in Figure 5d,e for wet etched BCP films compared to untreated films is therefore due to oxide formation at the bottom of blind holes, in agreement to the EFTEM analysis in Figure 4d showing the largest oxygen concentrations in the residues of the etched PMMA/RCP film at the blind hole bottoms.

After PMMA removal by reactive ion etching in an O$_2$/Ar plasma (approach B), the atomic composition changes significantly with respect to the undeveloped state. The C1s semiquantification reveals strong compositional changes within the first 30 s of plasma treatment. The contribution of $\text{C} = \text{C}$ and $\text{C} = \text{C}$ bonds decreases, while the contribution of the $\text{C} = \text{O}$ bonds increases. This can be explained by partial degradation of the polymer backbones and oxidation reactions at the new surface, leading to the homogenous oxygen distribution on the porous PS film detected also by EFTEM in Figure 4d. With longer plasma exposure times, the overall composition stays approximately constant, which is compatible to the idea that this oxygen is mainly located at the PS surface. The contribution of $\text{C} = \text{C}$ and $\text{C} = \text{C}$ bonds decreases, while the contribution of the $\text{C} = \text{O}$ bonds increases. This was also reported in a comparable investigation[46] of O-containing plasma treatments of neat PMMA films. Surprisingly, the $\pi \rightarrow \pi^*$ signal intensity of the PS decreases

Figure 5. a–e) XPS and f) PM-IRRAS analysis of PS-b-PMMA block copolymer thin films. a) C1s core level spectra of the PS-b-PMMA film before PMMA removal. b) C1s core level spectra after 30 s O$_2$/Ar plasma treatment. c) O1s core level spectra of the untreated BCP film. d) Carbon bonding changes after UV light/acetic acid treatment and O$_2$/Ar plasma treatment for different exposure times according to C1s spectrum semi-quantification, with the colors representing the following transitions: dark blue: $\text{C} = \text{C}$, $\text{C} = \text{C}$, $\text{C} = \text{H}$; yellow: $\pi \rightarrow \pi^*$; light blue: $\text{C} = \text{O}$; green: $\text{C} = \text{O}$; e) Atomic composition histograms, with the following color assignment: dark blue: C; red: Si; light blue: O, respectively; f) PM-IRRAS spectrum of an untreated and an UV light/acetic acid treated polymer film.
after short plasma treatment—possibly due to crosslinking by UV light in the plasma—but does not vanish even after longer plasma exposure. Thus, part of the PS film stays intact despite its partial etching. Such initial surface chemistry modification of the PS followed by a constant slow-paced plasma etching of polymer thin films was also observed and discussed by Rastogi et al.[42] for PS as well as by the group of von Keudell[47,48] for other polymers. Possible explanations for this behavior include UV radiation-induced breaking of C–C and C–H bonds, crosslinking, and surface graphitization, which result in the formation of a passivation layer which then retards the etching of PS.

The atomic composition analysis of the samples reveals that a major amount of the PMMA cylinders must be already removed after 30 s plasma treatment, as signal intensities from the Si substrate become detectable (Figure S2, Supporting Information). The inelastic mean free path (IMFP) of electrons calculated using the IMFP module of the software QUASES[49] for electrons from the C1s level in polymers amounts to approximately 4 nm. The upper limit of the information depth for XPS measurements is commonly estimated to be three times the IMFP, i.e., up to 12 nm. With an initial polymer film thickness of 37 nm (BCP+RCP brush), this means that PMMA must be largely removed, leaving holes in the PS membrane. The Si contribution to the surface composition increases further with increasing plasma exposure time indicating the ongoing PMMA removal.

3.3. Removal of PMMA from PS-co-PMMA Brush Layers

As outlined above, to align the orientation of nanodomains perpendicular to the substrate surface during the microphase separation, polymer brushes are frequently used to functionalize the substrate surface and also have been used in this work. In the present case of cylinder-forming PS-b-PMMA BCPs, PS-co-PMMA random copolymer brushes are grafted to SiO2 surface to create surface energies and polarities which are comparable for PS/substrate and PMMA/substrate interfaces.[11,50] As we have seen above, these RCP brushes may remain on the substrate surface during further BCP lithography processing, depending on the development process used. Therefore, in the following, we have studied the effect of the two PMMA removal processes (A) and (B) on this polymer brush using samples solely consisting of a brush layer formed on the native SiO2/Si surface, without additional BCP film on top. Figure 6 gives an overview of the surface characteristics and properties of the random copolymer brush in its initial state and after either UV light/acetate acid (approach A) or O2/Ar plasma treatment (approach B, for different treatment durations), as determined by ellipsometry for the layer thickness (Figure 6a), water contact angle (CA) measurements (Figure 6a) and XPS analysis (Figure 6c–f).

The untreated intact RCP brush layer has a thickness of 6.5 nm directly after grafting, and its contact angle with water measures 90.5° (Figure 6a). This neither particularly hydrophobic nor hydrophilic nature is to be expected as the surface termination randomly comprises PS and PMMA with a slight excess of PS (66 mol%). XPS investigations allow to determine the atomic composition of the RCP brush (Figure 6c) as well as the bond compositions (Figure 6b) of the Cs and Os core level spectra (Figure 6d,f). Spectra are analyzed as explained above for the BCP samples. All individual contributions are compiled in Table S2 of the Supporting Information. Estimating that the brush layer contains 34% of PMMA, which has an oxygen content of 13.3 at% one would expect 4.5% of C–O and C=O bonds. Analysis of the atomic composition results in a fraction of 10.0% O in the untreated RCP brush (Figure 6c), which is the sum of oxygen atoms contained in PMMA and bonded to the SiO2/Si surface.

UV exposure of the PS-co-PMMA brush followed by rinsing with concentrated acetic acid is expected to lead to a destruction of PMMA bonds at all bond positions randomly distributed along the brush chains. In fact, ellipsometry shows that this treatment leads to a reduction of the brush thickness from 6.5 to 4.4 nm (Figure 6a), i.e., no complete removal, in agreement with above results. The surface is still covered with a partially cut brush and still exhibits a contact angle of 77°, which is large compared to a bare SiO2 surface (typical water contact angle 35°). Also, XPS analysis does not reveal drastic compositional changes of the remaining brush, indicating that together with destroyed PMMA fragments attached polystyrene fragments are removed as well, at a rate given by the PS:PMMA volume fractions. As expected, the PS is not largely affected by the UV light/acetate acid treatment and the spectrum still shows the π→π* peak suggesting intact phenyl rings (Figure 6b). A small increase of the contribution of C–O and C=O bonds can be observed (Figure 6c) after PMMA removal using route (A). This increase may result from a slight oxidation of the PS.[51,52] All in all, these studies after applying procedure (A) suggest that the PMMA is not fully removed but only the most surface-near area of the brush layer is affected by the UV light/acetate acid treatment and partially removed.

The plasma treatment (procedure B) of the RCP brush shows a clear trend with increasing plasma treatment time (Figure 6a–c). Please note that the longest treatment time (30 s) considered here corresponds to the shortest plasma treatment time used to develop the much thicker BCP films in the previous sections of this paper. With increasing plasma exposure time, the brush is more and more destroyed up to the complete removal after 25 s. AFM investigations (not shown here) confirmed a homogeneous removal as no surface roughness (root mean square roughness rms < 1 nm) is detectable. The CA decreases with increasing plasma exposure time from 90° to 24.5° after 25 s, which is most likely due to the partial oxidation of the polymer in the O2 containing plasma and the revealing of an oxidized substrate surface. Thus, the contact angle finally increases to the typical equilibrium water contact angle of bare SiO2 of approximately 35° which is reached after 30 s at a nominal brush thickness of 0 nm.

XPS data suggest that the sample surface composition is strongly affected by the O2/Ar plasma already after a short plasma treatment of 10 s (Figure 6b,c). In particular, the fraction of oxygen containing components drastically increases while the fraction of aliphatic species decreases. This also explains the decreasing water contact angle. With further increasing plasma exposure time, the C=O contribution strongly decreases while the C–O contribution increases, most likely due to deterioration of the carboxy group in PMMA and...
C=O substitution by C−O and C−C bonds, as observed above in PS-b-PMMA BCP films. Removal of the brush is also indicated by the vanishing of the π→π* signal of phenyl rings in PS already after 10 s (Figure 6b). Analysis of the atomic composition shows that after a plasma treatment for 20 s the Si from the underlying substrate, which was so far covered by the brush layer, becomes more detectable. This again indicates that the RCP brush is nearly completely removed as was also concluded from ellipsometry. After 25–30 s plasma exposure, surface characteristics are similar to those of the bare SiO2 reference sample, as also observed by CA measurements. Remaining signals from aliphatic and C−O bonds after 30 s are most likely due to adsorbents from ambient atmosphere at which the samples were stored.

4. Conclusions

The morphological and chemical state of nanophase separated, cylinder forming block copolymer (BCP) thin films of both, PS-b-PMMA (suitable as for applications in nanolithography masks) and PS-co-PMMA (needed to control the orientation of BCP nanodomains on SiO2/Si surfaces) are analyzed for the first time at sub-nanometer lateral resolution prior to and after PMMA removal. For the PMMA removal, the two most commonly used removal techniques are applied, namely UV light exposure followed by acetic acid etching and treatment in an O2/Ar plasma. Both techniques are compared for their selectivity for PMMA and the morphology of resulting nanopores.

In order to gain a molecular-level understanding of polymer alterations in these frequently used BCP and RCP films, we exploit state-of-the-art Cz-corrected analytical low-keV STEM, TEM and EFTEM with dedicated image analysis software and combine this with XPS, PM-IRRAS, contact angle, and ellipsometry measurements. Using newly developed image analysis routines for ADF-STEM images, the interfacial width of nanophase separated PMMA cylinders in a PS matrix prior to PMMA removal and the line edge roughness (LER) of cylindrical nanomask openings resulting after PMMA removal from the PS masks are directly measured for the first time and analyzed statistically. It should be emphasized that this analysis is done without any staining of the polymers, thus giving reliable results at the molecular level.

In particular, we found that in PS-b-PMMA BCP films deposited on a PS-co-PMMA neutralizing brush layer and in pure PS-co-PMMA films grafted to SiO2/Si substrates, UV exposure and subsequent acetic acid wet etching leaves PMMA residuals in the polymer film. A thin polymer film rich in oxygen was clearly seen in such wet etched films at the bottom of pores, thus forming “blind holes” instead of open cylindrical mask openings. MMA residuals also stay in the cylinder side walls of etched BCP films on brush layers. These cylinder sidewalls emerge from a 4–6 nm thick transition region between the PS host matrix and PMMA rich cylinder cores which are present in the as-nanophase separated state prior to wet etching, as shown by ADF-STEM. After the UV light/acetic acid treatment the statistical evaluation of ADF-STEM images shows that resulting pores are significantly larger than the previous...
PMMA cylinders. In addition, they have a much-decreased radius distribution, a significantly reduced LER of less than 2 nm (average <1 nm) and a strongly reduced interface width. Thus, it is obvious that wet etching sharpens the interfaces, indicating that the residual polymer chains dangling into the opened cylinders bend to create a smoothened surface. According to EFTEM thickness mapping the sidewall slope amounts to about 63° which needs to be considered if subsequent lithography processes are to be added.

If an O₂/Ar plasma dry etching is used instead of the UV/ wet chemical for PMMA removal, the brush layer is completely removed after a few seconds and again an altered surface chemistry of the remaining PS mask material with an enhanced oxygen content is observed. The thickness of the PS mask is reduced, and at sufficiently long treatment time PMMA is completely removed, i.e., the lithography mask is opened, leaving nanoholes with a very small LER below 2 nm (average < 1 nm). Here the fluctuations are even a little smaller than for wet etching, and again much smaller than the interfacial width of undeveloped PS-b-PMMA.

The detailed description compiled in this article of the morphological and chemical changes occurring in PS-b-PMMA BCP films upon processing them into nanomasks is certainly important for any subsequent lift-off and pattern transfer processes, the fabrication of vias in semiconductor circuits as well as the creation of nanopore filters. While these insights may help to understand a crucial process step in block copolymer nanolithography with PMMA-cylinder forming PS-b-PMMA, we emphasize that the presented experimental approach comprising microscopic and spectroscopic surface analysis at high spatial resolution and numerical evaluation can be applied also to other BCP species. This is exemplarily shown in the Supporting Information section of this paper for PS-b-PMMA with other block length ratios. With the advent of novel high-χ (Flory-Huggins parameter) BCPs our approach will contribute to render block copolymer nanolithography to the next state-of-the-art technique in semiconductor lithography and many other fields of nanotechnology requiring high-precision sub-10 nm features.

5. Experimental Section

**BCP Films**: For substrate functionalization, an α-hydroxy-α-TEMPO-terminated PS-co-PMMA random copolymer (RCP) brush was spin coated on Si substrates covered with a native SiO₂ film. The RCP has a molecular weight of $M_r = 8.5 \text{ kg mol}^{-1}$ with a polydispersity index (PDI) of 1.45 and contains 66 mol% PS. A polystyrene-b-polymethylmethacrylate (PS-b-PMMA) block copolymer with a molar mass of $M_n$, PS-b-PMMA = 46.1-21.0 kg mol$^{-1}$, i.e., a block length ratio of PS:PMMA = 68.7:31.3, with a PDI of 1.09 was used to create hexagonally ordered PMMA cylinders in a PS matrix. While this paper focuses on the BCP forming PMMA cylinders in a PS matrix, PS-b-PMMA with other block length ratios was also used to obtain PS cylinders in a PMMA matrix and PS/PMMA vertical lamellae. Results on these additional block copolymers are shown in the Supporting Information of this paper. All polymers were purchased from Polymer Source Inc.

**Polymer formation of PS-b-PMMA**: Nanophase separation of PS-b-PMMA was conducted as described previously.$^{[20]}$ Briefly, 30 nm thin films were spin cast from a 1.2 wt% polymer solution in toluene. The thin films were then vacuum annealed at 180 °C/10⁻⁷ mbar for 24 h. If not stated otherwise, Si (100) wafers with their native oxide layer were used as substrate and functionalized with a 6.5 nm thick PS-co-PMMA random copolymer brush. This brush was created by spin coating of a 50 nm thick RCP layer from solution in toluene onto the Si wafer. The RCP film was annealed at 180 °C/10⁻⁷ mbar for 24 h to enable grafting of the hydroxy-terminated polymer chains to the SiO₂ surface. After annealing, the residual unbound RCP was removed by rinsing in analytical toluene.

In the first strategy (A) to remove the PMMA, a combination of exposure to UV light and a subsequent wet chemical etching was applied. Samples were exposed to the UV radiation of a Hg light with a peak wavelength of 254 nm at a power of 50 mW cm⁻² for 20 min. Samples were then immersed into concentrated acetic acid (Carl Roth, analytical grade, 99.5%) at room temperature for 30 min followed by rinsing in DI water for 5 min.

In the second strategy (B), PMMA was removed by dry etching in a plasma. Samples were exposed to an O₂/Ar plasma in an Oxford Instruments reactive ion etching system Plasmalab 80plus. Samples with a size of 1.5 cm × 1.5 cm were exposed for different times (10–80 s) to a plasma of 2 sccm O₂ and 8 sccm Ar at a pressure of 75 mtorr, a RF power of 20 W at 1.1 V.

**Characterization Techniques**: Analytical (scanning) transmission electron microscopy ((S)TEM) was performed using a probe-side Cs-corrected JEOL JEM-ARM200F at 60 kV acceleration voltage equipped with an imaging energy filter Gatan GIF Quantum ER. Details of the acquisition conditions can be found in ref. [31]. TEM bright-field images (TEM BF) were collected using a 4k × 4k CMOS camera (GATAN OneView). Energy filtered TEM (EFTEM) analysis was conducted using the GIF image filter with a 2k × 2k CCD camera. Maps of the projected film thickness are calculated by applying the EFTEM log ratio technique$^{[53]}$ using energy filter slit widths of 10 eV, in combination with the model of Iakoubovskii et al.$^{[34]}$ for the estimation of electron mean free paths. A slit with a width of 10 eV is centered at the zero-loss peak for the acquisition of the elastic image. Elemental maps of carbon and oxygen are obtained using the three-window method$^{[34]}$ at the C–K and O–K edges at 284 eV (pre-edge 1: 246 eV; pre-edge 2: 268 eV; post-edge: 294 eV) and 532 eV (pre-edge 1: 484 eV; pre-edge 2: 514 eV; post-edge: 547 eV), respectively, and slit widths of 20 eV (C–K edge) and 50 eV (O–K edge). EFTEM spectroscopic imaging (EFTEM SI) series were captured by adjusting the acceleration voltage in 5 eV steps using a filter slit width of 5 eV with the full width at half maximum of the zero-loss peak being 0.7 eV. STEM images were recorded at 60 kV with a semiconvergence angle of 16.6 mrad and collected on an annular dark-field (ADF) detector with collection angles from 69 to 147 mrad.

Samples for (S)TEM analysis were prepared using an additional 700 nm thick sacrificial SiO₂ layer underneath the RCP brush layer, created by thermal oxidation of the substrate. The BCP self-assembly was otherwise performed as stated above. After nanophase separation and either UV light/acidic acid treatment or plasma treatment for 70 s, samples were dipped into 10 wt% HF$_3$ to etch the sacrificial SiO₂ layer. The released polymer membranes were then skimmed off the etchant with an Au TEM Quantifoil grid (1.2 μm holes, bought from Plano GmbH), the same procedure is used in refs. [14, 31].

The surface composition was analyzed by means of X-ray photoelectron spectroscopy (XPS) in an ESCA+ facility (Oxford Instruments). The spectra were acquired at a base pressure of <5.0 × 10⁻¹⁰ mbar and at a take-off angle of 20° with respect to the surface such that information depth is restricted to the very near surface region of samples. Calculating the inelastic mean free path of C1s electrons in corresponding polymers by means of the QUASES-Tougaard program based on the work of Tanuma et al.$^{[59]}$ and assuming that the information depth is about 3λ, the XPS information depth can be estimated to be 3–4 nm at our experimental conditions. No charge neutralization was used. Spectra were measured using monochromatic Al Kα irradiation (1486.7 eV). The energy calibration was performed using the Cls signal at 285.0 eV of aliphatic carbon following the
convention for polymers according to Beamson and Briggs. For the investigation of the atomic composition, spectra were normalized to the peak maxima. For concentration and stoichiometry investigations a Shirley background was subtracted, and the peak areas were multiplied by the corresponding normalization factors. Spectra analyses and peak assignments were performed according to refs. [44,56].

Polarization-modulated infrared reflection-absorption spectroscopy (PM-IRRAS) was performed using a Bruker VERTEX 70 instrument with a polarization module PMA-50 as photoelastic modulator and a liquid nitrogen cooled MCT detector. All spectra were acquired with a resolution of 4 cm\(^{-1}\). The IR angle of incidence was 80°, the aperture of incident light was 2 mm. All measurements were performed at ambient atmosphere. The spectra were acquired for 512 scans between 4000 and 4000 cm\(^{-1}\). The PM-IRRAS spectra were processed, i.e., baseline corrected and cut, using the OPUS 6.5 (Bruker) software.

As PM-IRRAS measurements require a highly reflective substrate, prior to BCP deposition a 70 nm thick Au film was deposited on the Si substrates by thermal evaporation using 2 nm Ti as adhesion promoter. In this case, BCP microphase separation was performed directly on Au substrates by thermal evaporation using 2 nm Ti as adhesion promoter. A successful BCP self-assembly on bare Au surfaces was shown previously. [30] It is probably worth emphasizing that PM-IRRAS probes the whole thickness of the BCP film on the reflecting substrate, with an enhanced sensitivity next to the near-surface region. [31] unlike XPS, which is most sensitive to the near-surface region.

Sessile drop contact angle (CA) measurements were done using a Krüss drop shape analyzer DSA 25E. Water contact angles were measured using ultrapure water. Droplets with a volume of 5 µL were deposited and their contact angles were obtained by fitting a baseline to the substrate and an ellipse to the drop silhouette using the Krüss Advance software. Given contact angles are mean values of 10 CA individual fits to three different droplets, each at a different sample position.

Ellipsometry was performed using an Accurion GmbH EP3 nulling ellipsometer at an angle of incidence of 70°. The wavelength was changed between 364 and 883 nm in steps of 3 nm. Reflective indices and film thicknesses were extracted and displayed after standard ground subtraction. All other statistical data treatments are described in the main body of this article.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available in the supplementary material of this article.

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[1] C. M. Bates, F. S. Bate, Macromolecules 2017, 50, 3.
[2] M. Luo, T. H. Epps III, Macromolecules 2013, 46, 7567.
[3] S. B. Darling, Prog. Polym. Sci. 2007, 32, 1152.
[4] R. García, A. W. Knoll, E. Riedo, Nat. Nanotechnol. 2014, 9, 577.
[5] R. Menon, A. Patel, D. Gil, H. J. Smith, Mater. Today 2005, 8, 26.
[6] K. Brassin, J. K. N. Lindner, Adv. Mater. Interfaces 2020, 7, 1901656.
[7] F. Ferrarrese Lupi, T. J. Giarmannia, G. Seguinia, F. Vita, O. Francescangeli, K. Sparracci, D. Antonioli, V. Gianotti, M. Laus, ACS Appl. Mater. Interfaces 2014, 6, 7180.
[8] F. S. Bates, G. H. Fredrickson, Annu. Rev. Phys. Chem. 1990, 41, 525.
[9] L. Leibler, Macromolecules 1980, 13, 1602.
[10] H. Hu, M. Opinadhan, C. O. Osuji, Soft Matter 2014, 10, 3867.
[11] K. Brassin, D. Kool, C. G. A. Nallet, J. K. N. Lindner, Adv. Mater. Interfaces 2020, 7, 1901605.
[12] F. Ferrarrese Lupi, T. J. Giarmannia, A. Miti, G. Zuccheri, S. Carignano, K. Sparracci, G. Seguinia, N. De Leo, L. Boarino, M. Perego, M. Laus, ACS Nano 2018, 12, 7076.
[13] S. Xiao, X. Yang, E. W. Edwards, Y. H. La, P. F. Nealey, Nanotechnology 2005, 16, S324.
[14] K. Brassin, D. Kool, J. K. N. Lindner, Nanotechnology 2019, 30, 225302.
[15] C. J. Hawker, T. P. Russell, MRS Bull. 2005, 30, 952.
[16] V. Gowrishankar, N. Miller, M. D. McGeehe, M. J. Misner, D. Y. Ryu, T. P. Russell, E. Dronckenmuller, C. J. Hawker, Thin Solid Films 2006, 513, 289.
[17] J. Bang, U. Jeong, D. Y. Ryu, T. P. Russell, C. J. Hawker, Adv. Mater. 2009, 21, 4769.
[18] D. O. Shin, J. R. Jeong, T. H. Han, C. M. Koo, H. J. Park, Y. T. Lim, S. O. Kim, J. Mater. Chem. 2010, 20, 7241.
[19] A. Andreozzi, L. Lamagna, G. Seguinia, M. Fanciulli, S. Schamm-Chardon, C. Castro, M. Perego, Nanotechnology 2011, 22, 335303.
[20] A. Subramanian, G. Doerk, K. Kisslinger, H. Y. Daniel, R. B. Grubbs, C. Y. Nam, Nanoscale 2019, 11, 9533.
[21] D. F. Sunday, M. J. Maher, A. F. Hannon, C. D. Liman, S. Tein, G. Blachut, Y. Asano, C. J. Ellison, C. G. Willson, R. J. Kline, Macromolecules 2018, 51, 173.
[22] M. Longanecker, A. Modi, A. Dobrynin, S. Kim, G. Yuan, R. Jones, S. Satija, J. Bang, A. Karim, Macromolecules 2016, 49, 8563.
[23] D. F. Sunday, R. J. Kline, Macromolecules 2015, 48, 679.
[24] J. M. Kim, Y. H. Hur, J. W. Jeong, T. W. Nam, J. H. Lee, K. Jeon, Y. J. Kim, Y. S. Jung, Chem. Mater. 2016, 28, 5680.
[25] P. N. Patrone, G. M. Gallatin, Macromolecules 2012, 45, 9507.
[26] T. Xu, J. Stevens, J. A. Villa, J. T. Goldbach, K. W. Guarini, C. T. Black, C. J. Hawker, T. P. Russell, Adv. Funct. Mater. 2003, 13, 698.
