Modification of block copolymer lithography masks by O₂/Ar plasma treatment: insights from lift-off experiments, nanopore etching and free membranes

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Abstract
Block copolymer lithography allows for the large-area patterning of surfaces with self-assembled nanoscale features. The created nanostructured polymer films can be applied as masks in common lithography processing steps, such as lift-off and etching for pattern replication and transfer. In this work, we discuss an approach to improve the pattern replication efficiency by modification of the polymer mask prior to lithographical use by means of an O₂/Ar plasma treatment. We present a much better quality of pattern replication without loss of features, along with a precise tunability of feature sizes, that can be achieved by short mask treatment. We point out a correlation between nanopore position within the ordered arrays, expressed by its coordination number, the nanopore shape and the replication efficiency. Our experimental strategy to explain these correlations combines the indirect investigation of patterns replicated from the modified polymer masks and direct investigation of the mask top and bottom. Pattern replication is performed either in the form of gold nanodot arrays created via lift-off or nanopores transferred into a SiO₂ substrate by reactive ion etching. The direct analysis of free polymer membranes released from the substrate reveals the nanopore shape at the mask top and bottom surfaces.

Supplementary material for this article is available online

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(Some figures may appear in colour only in the online journal)

1. Introduction

Block copolymer (BCP) lithography is an emerging method for the creation of ordered nanoscale features on large surface areas [1, 2]. It is based on the microphase separation of two immiscible polymer species, which are covalently bonded to each other in a BCP chain. Their phase separation results in self-assembled nanopatterns with a variety of motives: depending on the block length ratio of the two polymer species forming the chain, cylinders, spheres, lamellae or more complex gyroidal nanopatterns can be created [3]. Recent work by Majewski et al [4, 5] demonstrates impressively how the combination of layers of different BCPs
allows for the creation of a huge variety of complex nanopatterns.

The self-assembled polymer features can be used as lithography masks in common technological processing known from semiconductor fabrication [1, 6, 7]. For instance, if one polymer species is selectively removed from the microphase separated polymer film, the remaining nano-patterned polymer layer can be used as a shadow mask in material deposition processes. Such lift-off processes can be applied for the creation of nanoparticle arrays or nanowires, when using BCPs, which microphase separate into cylindrical or lamellar structures, respectively [8]. Used as an etching mask in wet chemical or reactive ion etching processes the polymer masks are suitable templates e.g. for the creation of nanopores or nanopillars on semiconductor surfaces [6, 9–11].

For the integration of BCP lithography patterned polymer masks into high quality device production, the created patterns must meet highest requirements regarding pattern homogeneity, defect densities, pattern control, performance as resist, and so on. Especially for applications in semiconductor technology, such as for the development of fin-FET transistors [12, 13] or the improvement of storage media [14, 15] precise positional control, size tuning, shape perfection and resist edge sharpness are essential. As the nanofeatures are a direct replica of their lithography mask, the improvement of the mask is essential for the improvement of the resulting pattern homogeneity and shape. To this end, however, the understanding and control of the nanopattern self-arrangement is crucial.

So far, much work has been done to investigate the BCP pattern formation process and to compare the range of possible patterns as well as nanofeature pitch and size [16]. Fundamental research has focussed on the investigation of the interactions between the BCP and a substrate surface. These interactions determine the pattern orientation of phase separated domains on the substrate [17–20].

This understanding then allowed for the control of the self-assembly process. Directed self-assembly (DSA) was introduced as an approach to guide the nanopattern formation [17, 21–24]. Chemical and topographical surface pre-patterns allow for the control of the self-assembly process [7, 25–29] guiding the nanopatterns into long-range order [30, 31] and enable pattern density multiplication [32, 33]. DSA is also shown to be suitable for the controlled site-selective nanopattern formation, which allows for hierarchical surface pattern architectures [17, 34].

These immense efforts led to a good understanding of the nanopattern formation and control in sense of overall characteristics of the nanopattern array, i.e. order, periodicity, hierarchy, which are a prerequisite for lithography purposes. On an even finer scale, the improvement and detailed control of the pattern quality of single mask features is of importance. To this end, for instance, the line edge roughness of the self-assembled nanopatterns is investigated [35] as the accuracy of features determines the efficiency in semiconductor device applications. It was investigated how the nanofeature size in the polymer mask affects the resulting feature size when the pattern is transferred into a substrate by etching [36]. It was, however, shown that the performance of polymer films as etching mask is limited regarding the maximum pattern aspect ratio, if a suitable pattern quality is required [37]. In order to overcome these aspect ratio limitations the improvement of the polymer mask resistance by different plasma treatments was investigated [38].

In this work, we investigate an approach to improve the pattern replication efficiency in lithography processes. To this end, BCP-lithographically nanopatterned polymer masks are modified with an O2/Ar plasma prior to their actual use as lithography masks. We show that a short plasma treatment allows for much better quality of pattern transfer without loosing features. We discuss the reason for this improvement in detail and demonstrate that a loss of features during lithographical replication is correlated with their local number of nearest neighbours, i.e. their coordination number, in the BCP mask prior to replication. We show that the loss of 6-fold coordinated nanofeatures, i.e. hexagonally arranged nanopores within one crystal orientation domain, can be largely avoided by plasma modification of the polymer mask. In contrast to this, nanofeatures with a non-6-fold coordination as they are typically present at pore domain boundaries, are more likely to be subjected to nanopattern loss during pattern replication. This can be explained assuming that the nanopores in the polymer mask have a conical instead of a perfect cylindrical shape. We discuss, how the plasma treatment changes the nanopore shape and thus allows for a more efficient pattern replication.

Our argumentation is based on a comparison of results gained by different experimental strategies: we use nanopatterned polymer masks, which were exposed to an O2/Ar plasma for different exposure times. For the evaluation of the efficiency of the nanofeature replication we use these masks in typical lithographical processes: we perform lift-off experiments to create Au nanodot arrays and we use the polymer masks for the creation of nanopores by reactive ion etching. In order to directly investigate the morphology of the nanofeatures in the lithography mask, we release the nanostructured and plasma modified polymer masks from the substrate surface and prepare free membranes. This allows us to compare the morphology of the nanopatterns at both mask interfaces, i.e. with air at the top and with the substrate at the bottom.

2. Experimental details

2.1. Materials

A Polystyrene-b-Polymethylmethacrylate (PS-b-PMMA) block copolymer (Polymery Source) with a molecular mass of $M_n = (46.1\, \text{b-21.0})$ kg mol$^{-1}$ was used for the PS mask preparation. The used random copolymer for surface neutralization is an α-hydroxy-ω-TEMPO-terminated Polystyrene-co-Polymethylmethacrylate (PS-co-PMMA) (Polymer Source) with a total molar mass of $M_n = 8.5$ kg mol$^{-1}$ and 66 mol% PS fraction. The polymer solutions were prepared with analytical
etching mask for pattern transfer into SiO2 by RIE exposure times.

Microphase separation of the BCP thickness was set to 35 nm and polymers were deposited onto the RCP layer by spin coating block copolymer lithography. The PS-b-PMMA block copolymer (by thermal annealing at 180°C) on SiO2 surfaces were modified in an O2 plasma using 2 sccm CHF3 and 20 sccm Ar was performed at 30 mTorr and 25 W RF power for 4 min in a ‘Oxford Instruments Plasma Lab 100’. The film thickness was monitored using a calibrated Quartz microbalance. No adhesion layer was deposited prior to Au evaporation. The PS mask was removed afterwards by ultrasonication in toluene at 40°C for 12 h.

2.3. Mask modification

The nanostructured PS thin films on the RCP-functionalized SiO2 surfaces were modified in an O2/Ar plasma (figure 1(b), option III) a 800 nm thick thermal SiO2 film on a Si wafer was used as a sacrificial layer in a wet chemical HF etching process. To this end, the samples were dipped into 15% HFaq for 3 s, removed from the solution for 1 min and immersed again for 3 s. This procedure results in the dissolution of the SiO2 and floating-off of the PS membrane at the solution surface. The floating membrane was then skinned off the surface with a piece of a Si wafer, which was shortly immersed into the HF solution directly prior to the membrane skimming in order to remove the native oxide.
2.7. Characterization

Samples were imaged by scanning electron microscopy (SEM) with a Zeiss Ultra Plus at an acceleration voltage of 2 kV with an in-lens detector. Images are analysed as described previously [17] with a grey scale thresholding technique for pore size distributions and a Delaunay triangulation based software for determination of pore densities and coordination numbers. For each case studied, a number of roughly 3000 nanostructures was analyzed numerically in order to obtain good statistics. High-resolution transmission electron microscopy (HR-TEM) was used to analyse the cross-sectional geometry of nanopores etched into SiO2 by RIE. Cross-sectional samples were thinned mechanically and by ion milling. TEM analysis was performed at 200 kV in bright-field mode with a JEOL ARM 200 F.

3. Results and discussion

Nanopatterned polystyrene (PS) masks created by block copolymer (BCP) lithography were modified with an O2/Ar plasma and the influence of the plasma exposure time on the mask morphology was investigated. The mask modification is evidenced by different experimental strategies: directly by mask imaging (figure 1(a) (right), figures 2(a)–(c)) and indirectly by using the PS masks in typical lithography processes, i.e. pattern replication by a lift-off process (figure 1(b) —option I, figures 2(d)–(f)) and pattern transfer into the substrate by reactive ion etching (RIE) (figure 1(b) - option II, figures 2(g)–(i)). Figure 2 compiles SEM top view images of all these nanostructures created with the untreated mask (0 s) and modified masks for 20 and 40 s plasma exposure, respectively. SEM images of masks after 10 and 30 s exposure can be found in figure SI 1 is available online at stacks.iop.org/NANO/30/225302/mmedia in the supplementary information.

The mean diameters and size distributions of the nanostructures are quantified by SEM image evaluation with a grey scale thresholding technique. The evolutions of the feature sizes with increasing mask modification time are summarized in figures 2(k)–(n). Figures 2(k)–(m) show normalized Gaussian fits of the size distributions of the nanopores in the PS mask, the Au nanodots and the SiO2-etched nanopores, respectively. A representative Gaussian fit with corresponding experimental data is shown in figure SI 2 in the supplementary information. Figure 2(n) visualizes the correlation between nanostructure sizes created using the different lithographical processes by plotting their mean diameters for different O2/Ar plasma exposure times.

Figure 2(a) shows a top view SEM image of the PS mask prior to any plasma treatment. The PS film (grey) with nanopores (black dots) is created by removal of the former PMMA cylinders, which were formed by the microphase separation of the PS-b-PMMA BCP. The nanopores have a diameter of (16.8 ± 2.2) nm and are hexagonally arranged. The order is occasionally disturbed by domain boundaries. The pore density is 9.4 × 1010 cm−2.

Exposure of such a PS film to an O2/Ar plasma (figures 2(b) and (c)) results in an increase of the nanopore diameter. This modification is expected to result from both, sputtering of the polymer by Ar+ ion bombardment and the oxygen species in the plasma causing chemical modification of the polystyrene, i.e. oxidation and introduction of carbonyl groups. This reactive ion etching process then results in a partial erosion of the PS mask. In the investigated parameter regime from 0–40 s treatment time the mean nanopore diameter increases from 16.2 to 23.1 nm, as shown in figure 2(k). The widths of the size distributions stay approximately constant. The increase of the nanopore diameter goes along with an increase of the surface coverage ratio between pore and PS matrix. While the nanopores are still well defined in shape after 20 s of plasma treatment, a 40 s treatment results in nanopores only being separated by very thin PS walls. Here, the nanopores appear more irregular in shape and, occasionally, the PS walls are removed and neighboring nanopores are merged, which broadens the size distribution. Thus, this is the maximum exposure time investigated here.

The differently modified PS masks were then used as shadow masks in the deposition of 10 nm Au by electron beam evaporation. The resulting Au nanodots shown in SEM images in figures 2(d)–(f) are formed by a lift-off of the PS mask by chemical dissolution. The Au nanodots replicate the nanopore patterns of the masks. Thus, the nanodot diameter increases with increasing nanopore diameter with increasing plasma exposure times, as expected. However, replication of the nanopores using the untreated PS mask gives a poor result with many missing nanostructures and a broad size distribution, as is obvious in the SEM image in figure 2(d). The poor replication efficiency becomes apparent when comparing the nanostructure densities, which decrease from 9.4 × 1010 nanopores per cm2 in the as-deposited PS mask (figures 2(a) to 9.0 × 1010 Au nanodots per cm2 (figure 2(d)). In contrast, the Au dots created by the lift-off from the 20 s plasma treated mask (figure 2(e)) appear much more homogeneous in shape, order and size, the nanodot density (9.4 × 1010 cm−2) matches the one of nanopores in the mask. Analysis of the evolution of the nanodot size distribution in figure 2(f) reveals that (i) the average Au nanodot diameter is generally 2.8 nm (no plasma treatment) to 5.4 nm (40 s plasma treatment) smaller than the measured mean pore diameter in the PS mask and (ii) that the nanodots created with shortly plasma treated masks have an even narrower size distribution than the nanopores in the PS mask. Especially for a 20 s mask treatment, the nanodots are very homogeneous with a standard deviation of only 1.1 nm at a mean diameter of 16.1 nm. The short treatment of the PS mask with an O2/Ar plasma thus allows for a complete mask replication without feature loss, while the increase of plasma exposure time can be used to tune the mean Au nanodot diameter in the range of 14.0–17.7 nm in a controlled manner. Only for long plasma exposure (40 s), the nanodot size distribution becomes broader again, as the PS mask is gradually consumed and shows more defects (thin PS wall, irregular shape, merging pores, figure 2(f)) as described above.
Figure 2. Top-view SEM images of PS masks created by BCP lithography and after subsequent O₂/Ar plasma exposure for 0–40 s (a)–(c). These PS films are used as lithography masks to form Au nanodots by a lift-off process (d)–(f). Nanopores are transferred into SiO₂ by RIE in (g)–(i). Scale bars are 200 nm. Corresponding evaluation of the size distributions of nanopores in the PS mask (k), Au nanodots (l) and nanopores etched into SiO₂ (m) after different mask plasma exposure times. (n) Comparison of mean diameters of nanopores in PS mask, Au nanodots and etched nanopores for different etching times. Error bars indicate the FWHM of Gaussian size distributions.
Similar effects of the mask plasma modification on the efficiency of the lithographical nanopore replication can be observed when using the differently modified PS masks as etching masks for pattern transfer into the SiO₂ substrate. We performed reactive ion etching experiments in a CHF₃/Ar plasma (20 sccm/20 sccm) at 25 W and 30 mTorr for 4 min and removed the PS mask afterwards by ultrasonication in toluene. Top view SEM images of the etched nanopores are shown in figures 2(g)–(i), a cross-sectional high-resolution TEM image of the etched nanopores can be found in the supplementary information figure SI 3.

Again, the pattern transfer from the untreated PS mask (figure 2(g)) shows poor pattern quality: the shape of the nanopores appears irregular and many nanopores are missing. The size distribution of these nanopores cannot be properly evaluated, as the irregular pore shape along with the poor image contrast do not allow for an image analysis with the software used otherwise. However, an O₂/Ar plasma treatment of the PS mask for 20 s results in a high-quality pattern transfer (figure 2(h)). All nanofeatures are transferred, the density of nanopores etched into the SiO₂ is with 9.3 × 10¹⁰ cm⁻² approximately the same as in the PS mask (9.4 × 10¹⁰ cm⁻²). The nanopores appear equal in shape and the size distribution (figure 2(m)) resembles that of the corresponding PS mask. Thus, the improved PS mask quality achieved by 20 s plasma modification allows for a controlled pattern transfer. The homogeneity of the mask modification is also apparent from the homogeneous etching depth visible in the cross-section HR-TEM image (figure SI 3). For longer plasma treatment however, again, the pattern transfer is poor and nanopores are barely visible in the SEM image in figure 2(i). This poor pattern replication most likely results from the fact, that the PS mask thickness is already reduced by the O₂/Ar plasma modification (see supplementary information, Table SI 1) and thus, the PS mask was consumed in the CHF₃/Ar RIE pattern transfer process resulting in a very broad nanopore size distribution.

Figure 2(n) summarises all the above results: the mean diameters of the nanopores in the PS masks, the Au nanodots and the etched nanopores into SiO₂ are plotted as a function of the mask plasma exposure time. The standard deviations from the mean feature diameter are given by error bars. A linear increase of all nanofeature sizes with increasing plasma exposure time is found in the investigated time regime. It becomes apparent, that a direct pattern transfer is achieved by nanopore etching via RIE. The mean diameters of etched nanopores in SiO₂ exactly match those of the nanopores in the PS masks. Only the data point for 40 s mask treatment does not follow this trend. We do neglect this in the linear regression as no defined pattern transfer could be achieved here due to PS mask degradation. The diameter of Au nanodots created by the lift-off process follows a linear trend of increasing diameter with increasing mask treatment time, too. The regression has a slope comparable to that of the PS mask nanopore evolution. This allows for a prediction of the Au nanodot diameter, which is about 20% smaller than the nanopore diameter in the corresponding PS mask.

All the above results indicate a drastic difference in pattern transfer efficiency between untreated and plasma treated PS masks. In order to understand the influence of the plasma treatment on the PS mask morphology, we further investigated exactly which nanopores from the PS mask are lost during pattern transfer. To this end, we evaluated the position of the missing nanofeatures within the overall nanopore arrangement. In particular, we analyzed the local number of nearest neighbors of lost features. These coordination numbers give detailed insight into the effect of the mask modification with O₂/Ar plasma treatment on the mask morphology.

The coordination numbers were determined from SEM images of Au nanodot arrays by an algorithm, which translates the nanofeatures by grey scale thresholding and centroid identification into an array of data points. The number of neighbors within a defined radius of these data points is counted and displayed as a colour-coded map. Figures 3(a) and (b) show these coordination number maps superimposed with the original SEM images of Au nanodots (individual images can be found in figure SI 4 in the supplementary information). These Au nanodots were obtained by lift-off from an untreated PS mask in figure 3(a) and from a 20 s plasma modified PS mask in figure 3(b). In particular, we evaluate the number of 5-, 6- and 7-fold coordinated nanofeatures present in these nanodot arrays.

The most frequent deviations from the perfect 6-fold coordination of hexagonally arranged nanodots consist in rings of 5-fold coordinated dots around voids (white dashed circles in figures 3(a) and (b)), i.e. single missing nanofeatures within one domain of the crystal orientation, and alternating 5- and 7-fold coordinated dots at domain boundaries (white dashed lines in figures 3(a) and (b)). These types of defects, of cause, occur both in the PS mask formed by BCP lithography and the replicated Au nanodot arrays. However, our investigations show that the number of non-6-fold coordinated nanofeatures is affected by the pattern replication process and the modification of the PS mask.

The sketches in figure 3(c)–(f) depict how the number of the 5-, 6-, and 7-fold coordinated nanofeatures is affected by the loss of one nanofeature (grey stars) at different positions: the typical arrangement of nanopores is shown in figure 3(c) with 6-fold coordinated pores within one domain and 5- or 7-fold coordinated pores along a domain boundary. If a 6-fold nanopore inside a domain is removed from such an array, e.g. due to loss during pattern replication, six additional 5-fold coordinated nanopores are left behind, as shown in figure 3(d). If a 7-fold coordinated pore at a domain boundary is removed, five new 5-fold coordinated pores and two 4-fold coordinated pores are left behind. This is shown in figure 3(e). Loss of a 5-fold coordinated pore at the domain boundary creates three 5-fold and two 6-fold coordinated pores (figure 3(f)).

The histogram in figure 3(g) gives a comparison of the distribution of 5-, 6- and 7-fold coordinated nanofeatures in the PS mask, the replicated Au nanodots obtained by lift-off from an untreated PS mask and Au nanodots from a PS mask treated for 20 s with the O₂/Ar plasma. In addition, the
coordination numbers of nanopores visible at the membrane back side of the untreated PS mask released from the substrate are evaluated; these values will be discussed later.

The comparison of the distribution of nanofeature coordination in the PS mask (blue bars) and the direct replication by Au nanodots (figure 3(a)) without any plasma treatment (orange bars) reveals significant deviations. The perfect 6-fold coordination decreases during replication by 7%, i.e. more defects are apparent in the Au nanodot arrangement (orange bar) than in the original mask (blue bar). The total increase of defects results in a Au nanodot density of $9.0 \times 10^{10}$ cm$^{-2}$, which is clearly lower than the initial nanopore density of $9.4 \times 10^{10}$ cm$^{-2}$ in the PS mask. However, only 3.4% of Au dots are 7-fold coordinated, which is 58% less than in the untreated PS mask. Nearly 17% of all Au nanodots are 5-fold coordinated, which is twice as much as 5-fold coordinated pores in the PS mask. Such a change of coordination number distribution gives insight into the feature loss mechanism by comparison with the sketches in figures 3(c)–(f): even though feature loss at each position of the nanopore arrangement leads to an increase of the number of 5-fold coordinated features, its increase is most distinct when a formerly 6-fold

Figure 3. Evaluation of the PS nanopore replication by analysis of pattern coordination at mask defects. (a) and (b) show Au nanodots formed by lift-off from an untreated PS mask and a PS mask after 20 s plasma treatment, respectively. (a) and (b) display SEM images with an overlay of colour-coded coordination numbers. Domain boundaries (DB) are marked by white dashed lines, point defects by circles. (c)–(f) Sketches of effect of the loss (grey star) of a nanopore during pattern replication on the local coordination of neighboring pores. The grey dashed lines mark the domain boundary. The colour of dots indicates the coordination number of particles as in (a) and (b). (g) Histogram of the 5-, 6- and 7-fold coordinated nanopores in the PS mask, on the PS mask back side and the Au nanodots from (a) and (b).
coordinated feature within a domain is lost (figure 3(d)). Thus, the drastic increase of 5-fold coordinated nanodots found for the case of direct replication without any plasma treatment indicates that during pattern replication predominately formerly 6-fold coordinated nanopores, which were positioned within a domain, are lost.

The coordination number distribution of Au nanodots created from a 20 s plasma-treated PS mask, again, shows a very different behavior (red bars in figure 3(g)). The number of 6-fold coordinated nanodots is comparable to, or even a little bit higher than for the untreated PS mask and the total nanodot density measures $9.4 \times 10^{10} \text{ cm}^{-2}$. The fraction of 5-fold coordinated nanofeatures is roughly equal in the PS mask and the Au nanodot arrays. Contrary to the case without plasma treatment, a comparison with the sketches in figures 3(c)–(f) reveals that in this case only few nano-features from the interior of a domain are lost. However, the fraction of 7-fold coordinated Au nanodots is here much smaller than it was for the PS nanopores and even smaller than in case of the Au nanodots from an untreated mask. This means, that in case of the replication from a PS mask, which was modified by an O$_2$/Ar plasma for 20 s, nanofeatures are predominantly lost at domain boundaries. As visible in the sketches (e) and (f), feature loss at the domain boundary decreases the number of 7-fold coordinated features, while basically maintaining the fraction of 5- and 6-fold coordinated features. Otherwise, i.e. for feature loss within a domain, the 5-fold coordination number would have been further increased along with a decrease of 6-fold coordination.

These observations reveal that an O$_2$/Ar plasma treatment changes the PS mask in a way, that is more distinct for nanopores within a domain than for nanopores at domain boundaries. This means that feature loss within a domain can be overcome with a mask plasma treatment, while feature loss at domain boundaries still occurs. This site-selective change in feature loss during replication suggests that some nanopores do not resemble a clean mask opening, but are excluded from mask replication in lithography processes. One explanation for the poor pattern transfer with untreated PS masks could result from the underlying random copolymer brush layer which is used for SiO$_2$ surface functionalization. This polymer layer covers the whole substrate surface and also remains at the bottom of the nanopores in the PS mask after PMMA cylinder removal in the block copolymer lithography. The role of the RCP layer as inhibitor of RIE pattern transfer processes was discussed in [39], where an improvement of the pattern replication after a plasma treatment was reported as well. However, since the majority of pores gets replicated by Au nanodots even without plasma treatment, it is reasonable to assume that replication failures, especially by lift-off, are not related to the RCP neutralization layer. A more likely reason might be a deviation from a perfectly cylindrical nanopore shape, i.e. a conical geometry with decreasing nanopore diameter to the PS mask interface with the substrate. Such a non-ideal nanopore shape could lead to a removal of those Au nanodots which are trapped inside nanopores, which are not open at the bottom. An O$_2$/Ar plasma treatment could remove the extra material, leading to a more cylindrical pore shape allowing for a better pattern replication.

Our observations compiled in figure 3 also imply that non-ideal pore geometries of 6-fold coordinated pores within a domain are easily modified even during a short mask plasma treatment of 20 s while wrong-coordinated nanopores at domain boundaries are not. This can be seen as a hint that pattern replication inhibition results from a deformation of the pores which is strongest at the domain boundaries.

In order to get a more immediate picture of the nanopore morphology throughout the PS film, we released the differently modified PS masks from the substrate surface making them accessible for direct imaging. The nanopore morphology at both sides of these free PS membranes was investigated by SEM (figures 4(a)–(e)). In the following, we call the former interface between PS mask and air, which is visible in standard SEM top view images, the ‘membrane top’; the former interface between PS mask and substrate is called ‘membrane bottom’ (see inset in figure 4(f)).

The free PS membranes were obtained by removal of the 800 nm thick sacrificial thermal SiO$_2$ layer on the substrate. Figure 4(a) shows a SEM image section of an untreated PS mask released from the surface, in which the membrane folded during skimming, revealing the membrane top as well as the membrane bottom. At a glance, the two membrane surfaces show similar patterning. It is to note that nanopores (especially at domain boundaries) near the edge of the membrane are torn apart, resulting in a stretched nanopore shape with thinned PS walls. These areas are not evaluated for the further morphology investigation, but only areas are taken into account where the membrane was not obviously damaged by the preparation process.

Figure 4(f) shows the results of the evaluation of nanopore diameters at the membrane top (solid lines) and the membrane bottom (dashed lines) for PS masks which were treated with an O$_2$/Ar plasma for different times (0, 10, 20 s). For the untreated mask (black lines) the mean diameter of the nanopores at the membrane bottom is smaller than at the top and the size distribution on the bottom is much broader than at the top. This observation supports our hypothesis of a non-cylindrical nanopore shape with decreasing nanopore diameter towards the substrate interface. Furthermore, evaluation of the nanofeature density reveals, that the nanopore density decreases from $9.4 \times 10^{10} \text{ cm}^{-2}$ at the top to $8.4 \times 10^{10} \text{ cm}^{-2}$ at the bottom interface. This means, that nanopores are not only smaller at the bottom, but some are partially closed by a PS layer. This obviously explains the loss of nanofeatures in the lift-off experiments discussed above (figures 2 and 3). Comparison of the nanopore coordination numbers at the top and bottom interfaces (figure 3(g)), again, evidences an increased fraction of 5-fold coordinated nanopores by 380% and a decreased fraction of 7- and 6-fold coordinated nanopores at the membrane bottom, which explains a high feature loss within a domain. Accordingly, the fraction of 6-fold coordinated nanopores is decreased by 32%, while the fraction of 7-fold coordinated pores is decreased by 52%. Thus, few of the 7-fold coordinated pores visible at the membrane top reach the
bottom, which explains the observation of preferential nano-feature loss at the domain boundaries.

Upon plasma treatment, the discrepancy between nanopore diameter at the membrane top and the bottom decreases after 10 s and nearly vanishes after 20 s (figure 4(f)). Also the widths of the size distributions converge. Corresponding SEM images of membrane tops and bottoms of plasma-treated masks are shown in figures 4 (b)–(d). The evaluation of size distributions for 30 s plasma-treated masks are not added in figure 4(f), as the areal ratio between nanopore and PS walls is already so large that one can not clearly distinguish between folded overlapping membrane layers. Thus, in

![SEM images of membrane tops and bottoms](image-url)
figure 4(d), the edge between top and bottom surface is marked by a dashed line, as the membrane is already rigid due to the long plasma treatment and the underlying membrane surface is visible through the folded part. For PS masks which were plasma treated for 40 s, the membrane could not be released from the substrate, as the PS layer is too rigid and the membrane breaks to pieces. This could be expected due to the very thin PS walls visible in the SEM image in figure 2(c).

In order to exclude a possible coverage of the nanopore bottom with adhered RCP causing the decreased nanopore bottom diameter, we prepared a PS mask on a TiO2 surface. As reported previously [17] on TiO2 surfaces nanopores (former PMMA cylinders) can be produced perpendicularly oriented to the substrate without a surface functionalization with a RCP brush layer. Disregarding the absence of the RCP layer the BCP lithography on TiO2 was performed identically to the procedure on SiO2 surfaces, only the spin casted BCP film thickness was 45 nm on TiO2 instead of 35 nm on the SiO2/RCP surfaces. For the preparation of the TiO2 surface a sacrificial layer of 50 nm Ti was deposited by electron beam evaporation onto a Si wafer covered with the native oxide. A native TiO2 layer was formed by exposure of the film to the atmosphere. Membrane release and skimming was performed as stated above. Figure 4(e) shows top and bottom surfaces of an untreated PS mask released from a TiO2 substrate. The nanopores at the bottom interface of this membrane are completely closed, i.e. a PS wetting layer is formed on the TiO2 surface. The incommensurate wetting of the PS-b-PMMa at the interfaces, i.e. neutral wetting at the air/vacuum top interface while preferential wetting of the substrate bottom interface with PS, leads to a highly asymmetric nanopore geometry. This example presents the crucial effect of interfacial energies on the nanopore shape which can largely differ from a perfect cylinder. At the same time it demonstrates the minor role of the RCP brush on the performance of the PS mask in lithography processing.

4. Conclusions

In this paper, we investigated how polymer masks created by block copolymer lithography can be modified by an O2/Ar plasma treatment. The mask modification results in a better performance of the mask in lithographical applications in terms of pattern replication and transfer. We found that a short plasma treatment of the mask can significantly improve pattern replication efficiency, i.e. the complete replication of nanofeatures without losses. We evaluated this improvement applying standard lithography processing, i.e. lift-off and reactive ion etching. We also showed that the mask modification allows for a controlled tuning of the nanofeature size with nanometer accuracy.

From a statistical analysis of SEM images of nanopatterned surfaces we found a correlation between the coodination number of nanofeatures and their loss probability in pattern replication processes. We observed that the plasma treatment prevents the extensive loss of 6-fold coordinated nanofeatures, typically apparent within the interior of a domain of ordered nanopores, when untreated masks are used for replication. Pattern transfer from plasma modified masks, however, only reveals losses of 5- or 7-fold coordinated nanofeatures, which are usually found at domain boundaries. This result led us to the hypothesis of a non-cylindrical but conical nanopore shape, which is even more pronounced at domain boundaries, leading to poor pattern replication efficiency. We analysed how the plasma treatment improves the nanopore morphology towards a more cylindrical shape and thus leads to improved pattern replication.

To verify our hypothesis the nanopore morphology was directly imaged at the top and bottom of untreated and plasma-modified polymer membranes after releasing them from the substrate. In fact it is clearly visible that nanopores are wider at the top surface of masks than at the bottom. Upon O2/Ar plasma treatment, the pore size distributions at the top and bottom interface converge with increasing treatment duration, which corresponds to a shape modification towards more cylindrical instead of conical pores.

In total, the detailed analysis of the influence of plasma modification of polymer masks on the nanofeature distribution along with the investigation of free polymer membranes gives insight into the nanopore morphology and its change by plasma modification. Our approach improves the pattern replication efficiency by avoiding nanofeature loss.

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