Nanometer accurate fabrication of topographical guiding patterns via EUV-IL helps to improve existing energy modelling of confined block copolymers.

39x20mm (300 x 300 DPI)

Nano-confinement of block copolymers in high accuracy topographical guiding patterns: Modelling the emergence of defectivity due to incommensurability

Steven Gottlieb¹, Dimitrios Kazazis², Iacopo Mochi², Laura Evangelio¹, Marta Fernández-Regúlez¹, Yasin Ekinici², Francesc Perez-Murano¹

1: Instituto de Microelectrónica de Barcelona IMB-CNM, CSIC, 08193 Bellaterra, Barcelona, Spain

2: Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, CH-5232 Villigen-PSI, Switzerland

Abstract

We study the nanoconfinement of block copolymers in topographical guiding patterns and extend current free energy models by estimating the free energy of a defect-loaded state. The defect-loaded state appears as a consequence of the mismatch between the guiding pattern separation and the block copolymer natural pitch. We determine the relation between trench width and the emergence of defects with nanometer precision. This allows us to predict the process window for guiding pattern fabrication to achieve a low level of defects. Extreme ultraviolet interference lithography (EUV-IL) is used to manufacture topographical guiding patterns that direct the self-assembly of an 11 nm half-pitch *PS-*b*-PMMA* block copolymer. High-accuracy silicon oxide-like patterns with trench widths ranging from 68 nm to 117 nm are fabricated by exposing a *hydrogen silsesquioxane (HSQ)* resist layer with EUV light at multiple exposure doses. The excellent line width roughness of the fabricated guiding patterns enables us to minimize the influence of defect formation in the self-assembly due to guiding pattern inaccuracies and to model the emergence of the formation of defects due to guiding pattern incommensurability.

Introduction

The continuous advance of computing power would not have taken place without the progress in semiconductor manufacturing methods, whose basis is lithography. Downscaling the device dimensions all the way to the nanoscale has so far enabled semiconductor industry to fabricate ever more powerful integrated circuits. To maintain the impressive pace at which the number of transistors in integrated circuits has increased in the last decades¹, new patterning processes must be developed, so that the requirements of future semiconductor fabrication nodes in terms of resolution can be met. The high-volume manufacturing of transistors with sub-10 nm fins is planned around the year 2020. The currently-used DUV-immersion lithography² based on 193 nm wavelength light requires complicated and increasingly expensive³ multiple patterning steps to provide the resolution required for today's integrated circuit fabrication.⁴ For this reason, a number of novel patterning techniques are currently under development.

The directed self-assembly of block copolymers is one of the promising next-generation lithography techniques, as, for example, considered by the International Technology Roadmap for Semiconductors ITRS.⁵ Block copolymers consist of two chemically different polymer chains that are covalently bonded together.⁶ The materials have a complex phase behavior.^{7–9} Depending on the polymerization, the ratio of the length of the two chains and the Flory-Huggins interaction parameter of the two materials, the block copolymer self-assembles in regular structures with periodicities between 5 nm and 50 nm.^{10–13} The main application of block copolymer is the patterning of surfaces.^{14–17} To make use of the periodic structures for lithography applications, the short-range order spontaneously introduced during microphase separation is not sufficient. Chemical and/or topographical guiding patterns introduce long-range order and direct the self-assembly of the materials into lithographically relevant structures.^{18–20} The advantages of the employing the directed self-assembly DSA in semiconductor manufacturing process are the resolution and the low cost of ownership.^{5,21}

Recent developments in the field of high-volume manufacturing forecast that extreme ultraviolet (EUV) lithography will play a significant role in semiconductor manufacturing because of its capacity to fabricate features with high throughput and high resolution.²² EUV interference lithography (EUV-IL) has emerged as a promising nanolithography technique for research, which is inherently capable of producing single digit (sub-10 nm) periodic and quasiperiodic dense nanostructures (lines/spaces, dots, holes etc.), with record resolutions down to 6 nm.²³ Transmission diffraction gratings on thin Si_3N_4 membranes are used to create interference of mutually coherent beams, which, in turn, results in the desired interference patterns recorded in a

photosensitive material, as shown schematically in *figure 1) a)*. Depending on the number and configuration of the transmission gratings, several periodic structures can be produced, such as lines and spaces, square and hexagonal arrays of dots and holes, Kagome lattices etc..²⁴ *Figure 1) a)* shows a two-grating configuration, such as the one used in this work that is used to create lines and spaces. The incident beam gets diffracted by each one of the two gratings and the angles of diffraction are given by:

$$\sin\theta_m = \frac{m\lambda}{P_g}$$

where m is the order of diffraction, λ is the wavelength of the light, and P_g is the grating periodicity (pitch). When the illumination of the two gratings is identical, the resulting interference pattern has a periodicity given by:

$$P = \frac{\lambda}{2 \sin \frac{\theta}{2}}$$

where $\theta=2\theta_m$ is the angle between the two diffracted beams in the case of the two-grating mask. Combining the two equations and taking $m=1$ for first-order diffraction one finally obtains:

$$P = \frac{P_g}{2}$$

In this case, the pitch on the resist is half of the pitch of the transmission gratings, enabling frequency multiplication by a factor of 2. The EUV-IL setup used throughout our experiments is located at the XIL-II beamline of the Swiss light source (SLS) synchrotron of the Paul Scherrer Institut in Switzerland. The EUV radiation comes from an undulator (insertion device) tuned at a wavelength of 13.5 nm, which is the wavelength for next-generation EUV lithography.

One important bottleneck for the implementation of EUV lithography in high-volume manufacturing is the still large line edge roughness (LER) and line width roughness (LWR) of the features at high resolution, which improves when the technique is combined with DSA.²⁵ Moreover, achieving sub-10 nm half-pitches with EUV lithography will be challenging. On the other hand, the weak point of DSA is the still too large defect density, which is potentially attributed to an insufficient guiding pattern quality.²⁶ The fabrication of guiding patterns for the directed self-assembly of block copolymers far below 10 nm full-pitch will, therefore, require techniques with high resolution, high precision and at low LER/LWR²⁶ for DSA to meet the defect density required of semiconductor manufacturing requirements. Here, we investigate the use of

topographical guiding patterns fabricated by EUV-IL to guide the self-assembly of block copolymers and the potential to obtain DSA patterns with a low density of defects.

EUV-IL has been used before for the fabrication of chemical guiding patterns to direct the self-assembly of block copolymers^{27,28}, but to our best knowledge there are no works combining graphoepitaxy and EUV-IL. Other authors have presented graphoepitaxial guiding patterns defined by an EUV micro-exposure tool²⁹ using a positive tone resist to analyze the behavior of *PS-b-PLA* under confinement³⁰, however with relatively low guiding pattern accuracy and a significant guiding pattern LWR. DSA has moreover been used to shrink holes defined by EUV.^{31,32} A very good candidate for the fabrication of smooth guiding patterns is *hydrogen silsesquioxane (HSQ)*³³, that has recently been used to direct the self-assembly of block copolymers in combination with e-beam lithography.^{34,35} *HSQ* is particularly interesting, because the cross-linking of *HSQ* induced by EUV-IL has been demonstrated to provide high resolution patterns with excellent LWR.³⁶ The LWR of the guiding pattern features represents an important parameter in the generation of defects in the directed self-assembly of block copolymers. This has been shown both in theoretical³⁷ and in experimental^{18,26} works. In order to analyze the behavior of block copolymers in topographical guiding patterns with highest-possible accuracy and free of effects due to guiding pattern roughness, we chose EUV-IL as a fabrication technique.

We present a complete study of the directed self-assembly of an 11 nm half-pitch *PS-b-PMMA* block copolymer in trenches fabricated by the selective exposure of *HSQ* with EUV-IL. Extensive optimization of the process is carried out to achieve that block copolymers self-assemble in structures relevant for the fabrication of finFETs.^{38,39} We conducted an in-depth study of the effect of the trench width on the emergence of defects and tested different approaches of neutral brush layer deposition. The accurate control of the space between two guiding pattern ridges allows us to analyze the behavior of the block copolymer chains under confinement with nanometer precision. We have developed a model that successfully describes, how to design topographical guiding patterns to direct the self-assembly of block copolymers to obtain patterns with low defect levels. The model describes the free energy of a system with a non-zero density of defects on a semi-empirical basis.

Experimental Section

The work-flow for the fabrication of aligned block copolymer template in topographical guiding patterns fabricated by EUV-IL is depicted in *figure 1 b*).

HSQ deposition, exposure, and development

We used flowable oxide *FOX 16* by Dow Corning Corporation diluted 1:6 in *methyl isobutyl ketone* (MIBK). Spin coating this solution at 2000 rpm for 1 min on $2 \times 2 \text{ cm}^2$ Si chips yield a film thickness of 70 nm. After spin coating, the chips are transferred in the EUV-IL exposure chamber and pumped down to a pressure of 10^{-7} mbar. Upon exposure to EUV radiation, a cross-linking process^{33,40} is initiated and the exposed areas are converted into a SiO_2 -like material. The non-cross-linked, unexposed *HSQ* is consequently developed away in an alkaline developer (Microposit 351 developer diluted 1:3 in water) for 30 s and then rinsed in deionized water, yielding the required line/space guiding patterns. The guiding patterns are fabricated by EUV-IL using transmission gratings of 300 nm pitch to create a fixed 150 nm pitch interference pattern on the chips. The transmission mask is optimized to produce 50 % duty cycle (75 nm half pitch) line/space patterns. By varying the exposure dose below and above the nominal dose, one can reduce or increase the duty cycle of the line/space patterns with great accuracy. This nanometer precision over the width of the guiding pattern is essential in helping us better understand the mechanism of directed self-assembly of block copolymers in our system. In this study, the exposure dose (i.e. dose on the mask) has been varied from 350 mJ/cm^2 to 1050 mJ/cm^2 in a step and repeat manner. The achieved duty cycles are between 23 % - 67 % which correspond to trench widths of 115 and 35 nm respectively.

Deposition of Neutral Brush Layer

In order to deposit a brush layer that grafts both to the guiding pattern walls and to the guiding pattern bottom, a solution of 1.5 % neutral brush layer in *PGMEA* is spin-coated for 30 s at 4000 rpm. For the deposition of a thin brush layer grafting only to the bottom of the trench, a 0.25 % solution in *PGMEA* is also spin-coated at 4000 rpm for 30 s. Due to the strongly diluted solution, the deposited film is thin enough to be deposited exclusively on the bottom of the trench.⁴¹ In both cases, the sample undergoes a 5 min annealing step at 230 °C. This step is required to initiate the brush layer grafting to the underlying surface. The residual, non-grafted material is removed by a rinsing step in *PGMEA*. The neutral brush layer is a *PS-r-PMMA* random copolymer containing 58 wt% *PS* and 42 wt% *PMMA* at a molecular mass $M_{\text{brush}} = 7.9 \text{ kg/mol}$ and a polydispersity index $PDI_{\text{brush}} = 1.85$.

Deposition and Self-Assembly of Block Copolymer

We work with a *PS-b-PMMA* block copolymer (BCP) with a molecular mass $M_{\text{BCP}} = 42.3 \text{ kg/mol}$. It consists of 43 wt% *PS* and 57 wt% *PMMA* with a polydispersity index $PDI_{\text{BCP}} = 1.1$. When deposited on a neutral brush layer, it self-assembles in a lamellar structure with a natural pitch of

23.4 nm. The spin coating of a 1.5 % solution in *PGMEA* at 2000 rpm for 30 s yields a 28-nm-thick film in free surface. To initiate the microphase separation process, the material is annealed in a nitrogen environment for 10 min at 230 °C.

Selective PMMA Removal

In order to fabricate technologically useful etching masks, one of the block copolymer domains has to be removed selectively. In this work, we design a selective reactive ion etching (RIE) step in an Oxford 80Plus RIE applying a gas mixture of 5 sccm O_2 and 40 sccm CHF_3 at 50 mTorr pressure. At a power of 40 W, this process etches *PMMA* at 46 nm/min and *PS* at 18 nm/min. This means that the selectivity between the two materials is 2.5.

Figure 1: Work-flow and guiding pattern fabrication. a) A schematic showing the principle of EUV-IL, where the diffracted beams create an interference pattern that is recorded on a photoresist-covered substrate, b) work-flow that has been used to fabricate the guiding patterns and to direct the self-assembly of block copolymers in EUV-IL fabricated patterns consists of the exposure and development of HSQ, the deposition and self-assembly of block copolymers and the subsequent removal of PMMA, c) guiding patterns exposed at different exposure doses yield different guiding pattern widths, d) The amount of cross-linked HSQ can be increased by raising the exposure dose. For this reason, we are capable of tailoring the trench width with nanometer precision with slight variations of the exposure maintaining the pitch of the features constant at 150 nm.

Results

Guiding Pattern Fabrication

Examples of guiding patterns resulting from three different exposure doses are depicted in *figure 1 c*). *Figure 1 d*) shows a plot of the variation of the trench width as a function of the exposure dose. The curve that relates the exposure dose with the trench width has a negative slope, since the trench width corresponds to the non-cross-linked area. The trench width is the key parameter in this work, because it defines the lateral confinement of the block copolymer lamellae.

As we have mentioned before, defects in DSA usually originate from rough or incommensurate guiding patterns. *Table 1* depicts the results of an LRW/LER analysis of four representative guiding patterns from this study confirming their extraordinarily low roughness. Image pre-processing included the bi-cubic interpolation, rotation of the image and Gaussian filtering. The threshold for the edge detection was set to 0.5 of the maximum signal of the image. The numbers displayed in *table 1* represent the 3σ -values of the analyzed image. We observe better results for LWR and LER as the exposure dose is increased, finally yielding sub-nm line edge roughness for duty cycles larger than 50 %.

<i>Exposure dose</i> <i>[mJ/cm²]</i>	<i>Trench width</i> <i>[nm]</i>	<i>LWR</i> <i>[nm]</i>	<i>std. error</i> <i>(LWR) [nm]</i>	<i>LER</i> <i>[nm]</i>	<i>std. error</i> <i>(LER) [nm]</i>
950	58.5	1.2046	0.069	0.8774	0.787
680	70.2	1.9048	0.0562	1.8376	0.2681
430	93.6	2.2618	0.1278	2.2423	0.2956
350	105.3	3.0029	0.0367	2.1555	0.6258

Table 1: Overview of analysis of four representative guiding patterns depicting the respective 3σ -LWR/LER values and their standard error.

Control over interface energy by surface neutralization

The deposition of an intermediate neutral brush layer allows to control the interaction between the block copolymer and the substrate. We considered the deposition of the neutral brush layer only after the EUV-IL step, because EUV radiation interacts strongly with *styrene* and *methyl-methacrylate*.^{42,43} The chemical integrity of the neutral brush is absolutely required⁴⁴ to study the effect of different ways to deposit the neutral brush layer.

Figure 2: Self-assembly modes and example of successful DSA in commensurate guiding pattern a)-c) Three different block copolymer assembly modes in graphoepitaxy as a function of neutral brush layer deposition conditions: thick, e.g. overing top and side walls of guiding pattern features, thin, e.g. covering only the space between the guiding pattern features and none, d) large-area defect-free self-assembly of block copolymers in topographical guiding pattern fabricated by EUV-IL. The trench width is 109 nm and reduced the block copolymer pitch about 7 % with respect to an assembly in free surface.

Through the deposition of the 1.5 wt% *PS-r-PMMA* solution not only the bottom of the trench acts as neutral layer, but also the walls, so that both *PS* and *PMMA* wet walls *and* bottom. The block

copolymer self-assembles consequently in short aligned lamellae perpendicular to the guiding pattern, as depicted in *figure 2 a*). In the present study, this behavior is not desired and for this reason we discard this result for further analysis.

The deposition of the 0.25 wt% brush layer solution yields a 3-nm-thick film on a non-patterned surface both before and after the rinsing step. After depositing and annealing the block copolymer, we observe self-assembly in lamellae parallel to the guiding pattern walls (see *figure 2 b*). This orientation can be explained by the absence of *PS-r-PMMA* macromolecules grafted to the guiding pattern walls. For this reason, the block copolymer interacts directly with the *PMMA*-attractive *SiO₂* walls and self-assembles in lamellae parallel to the guiding pattern walls. A top view of the three different block copolymer assembly configurations corresponding to the self-assembly without neutral brush, after 0.25 wt% brush layer, and after 1.5 wt% neutral brush layer deposition, is depicted in the scanning electron micrographs of *figure 2 a*), *b*) and *2 c*), respectively.

In the complete absence of a neutral brush layer (see *figure 2 c*) the block copolymer self-assembles as depicted in the sketches on the top of the structure.⁴⁵ Similar to the guiding pattern walls, the silicon substrate is preferentially wetted by the *PMMA* domain. For this reason, we expect a wetting layer on the bottom of the trench interrupting the morphological integrity of the 3-D structure and making a pattern transfer more difficult. A more detailed comparison between the two aforementioned morphologies is provided later.

Comparing the deposition modes with respect to their capability to direct the self-assembly of block copolymers into lithographically relevant structures (e.g. ordered and in ideal shape for pattern transfer), we conclude that the 0.25 wt% brush solution yields the best results.

We have achieved a defect-free directed self-assembly over several tens of micrometers after depositing and annealing of the block copolymer in a commensurate guiding pattern. *Figure 2 d*) shows an SEM image of the directed self-assembly of block copolymers in guiding pattern trenches of 109 nm. To increase contrast and facilitate the acquisition of SEM images, the *PMMA* domains have been removed before the analysis. Throughout this paper the number of *PS* domains per trench is used as reference to categorize the guiding patterns. In total we count five *PS* domains in the configuration depicted in *figure 2 d*). Two of these domains remain almost unseen in the SEM images because of the large signal originating from the edges of the guiding pattern features. To transfer three fins into the substrate, we hence need trenches to be wide enough for the self-assembly of five *PS* domains, because experiments have shown that the two outermost *PMMA*

domains do not take part in the pattern transfer process since they are not removed in the selective dry etching step.^{35,38}

Discussion

In the following, we experimentally assess the effect of the brush layer deposition mode and describe its influence on the morphology of the self-assembly below the surface. Information about the three dimensional structure was obtained by a controlled selective dry etching step as introduced in the experimental section. Due to the etching selectivity of the *PS* domain with respect to the *PMMA* domain, SEM imaging of the structures after the etching step provides useful information about the morphology of the respective structure below the surface.

Figure 3 *Comparison of different self-assembly modes assessed by reactive ion etching.* a) SEM top-view image and single line intensity profile of DSA for onion-shape morphology before RIE, b) SEM top-view image and single line intensity profile of DSA for vertical lamella morphology before RIE, c) SEM top-view image and single line intensity profile of DSA for onion-shape morphology after RIE, d) SEM top-view image and single line intensity profile of DSA for vertical lamella morphology after RIE

Figure 3 a) and figure 3 b) depict the directed self-assembly in a guiding pattern before the RIE process without and with a neutral brush layer. Figure 3 c) and figure 3 d) show a top view SEM image of the same structures after the RIE process. The morphology in cross-section is sketched in the respective in-sets.

For samples with a thin underlying brush layer, we observe that the number of *PS* domains on the surface and below the surface is the same. We deduce that the block copolymer in direction normal

to the substrate self-assembles in continuous vertical lamellae. In absence of the brush layer the number of *PS* domains decreases after the dry etching. This indicates that the domains are not continuous vertical lamella and the block copolymer is arranged in a U-shape caused by the *PMMA* wetting both the guiding pattern walls and the bottom of the trench. These results are consistent with previous studies.^{41,46}

Now, we analyze the defect density as a function of the guiding pattern width w . A short video showing the evolution of the self-assembly morphology as a function of the trench width is included in the supplemental information part. We show representative SEM images in *figure 4 a)* demonstrating the evolution of the block copolymer morphology for increasing trench width. All the images have been taken from a sample with thin brush layer and after the removal of *PMMA*. In the top part of *figure 4 a)*, we denoted the trench width at which the respective image has been taken (see white bullet points), where this trench width is located with respect to n times (blue bullet points) and $(n+0.5)$ times (orange bullet points) the natural pitch L_0 of the block copolymer. We observe that the block copolymer self-assembles in straight lamellae in the close vicinity of trench widths with dimensions of integer multiples of the natural pitch of the block copolymer. Close to $(n+0.5)$ multiples of the natural pitch the block copolymer self-assembles with a large defect density (light-orange background in *figure 4 a)*). We identify two different types of defects, which we will in the following refer to as “wiggling” and “point defects”. The wiggling morphology is referred to as a state in which the material shows a significant undulation in the block copolymer features, which is characterized by an abrupt increase in the (measured) LWR (for detailed analysis concerning the LWR measurements, refer to supplemental information, part *SI*). This state is observed at large guiding pattern incommensurability for stretched chains. We refer to chain stretching, when the trench width of the pattern is larger than the number of the self-assembled domains multiplied with the natural pitch of the block copolymer. Wiggling is the result of the reduction of chain stretching at the expense of the formation of a larger *PS/PMMA* interface area. Point defects are formed when the incommensurability of the pattern is too large for the stretching to be released by wiggling. In patterns where the block copolymer forms point defects, we simultaneously observe areas with n domains and $n+1$ domains (refer, for example, to the 106 nm pattern in *figure 4 a)*). The system creates point defects in order to change the self-assembly morphology from n to $n+1$ domains.

Figure 4 b), provides an exact overview about which trench width range yields defect-free self-assembly (blue shaded area), and which yields the defective state (light-orange shaded area). Here, we do not distinguish between the kind of defect, such as wiggling and point defects, but rather

apply a binary approach distinguishing only between defect and no-defect. The expected number of *PS* domains (*y*-axis) as a function of trench width is indicated by the grey dashed line and confirms that our measuring points follow the expected curve. When counting the *PS* domains in the trenches we have to bear in mind that the outermost *PS* domains are permanently connected to the guiding pattern features, as depicted in the in-set of *figure 4 b*). The blue vertical lines refer to measurement points taken before the *PMMA* removal and the red vertical lines refer to measurement points taken after the removal of *PMMA*. The fact that both measurements yield the same results confirms our observation of *figure 3*, that a thin brush layer yield up-right standing lamellae, for the entire covered range of trench widths. The crossover points between the defective and the non-defective state (and vice versa) are marked by the dark vertical lines. For more information about the determination of the crossover points, refer to supplemental information, part S2.

For the sake of simplicity, let us group together those trench width ranges, in which the block copolymer shows the same behavior and name them 1-5 as denoted in *figure 4 b*). The number of *PS/PMMA* interfaces equals the number lamellae across the trench, so that that there are eight lamellae assembled in group 3. Based on the location of the crossover points, the maximum compression per chain before the systems starts to form defects is 0.78 nm and the maximum stretching per chain is 0.9 nm. The same calculus for group 5 yields an average compression per chain of 1 nm and 0.94 nm respectively. The average stretching per chain for group 1 is estimated to be 1 nm. These values correspond to the capability of the chains to compress on average 8.1 % and to stretch 7.6 % with respect to their expansion at natural pitch.

Figure 4: Groups of self-assembly and 3-D morphology of the domains. a) Overview of the evolution of the self-assembly morphology as a function of the trench width, b) Graphics showing the number of PS domains n_{PS} deposited as a function of the guiding pattern trench width comparing the deposition in trenches with a thin neutral brush layer as shown in the inset. The colored areas refer to experimentally accessible trench widths, where the blue shaded areas represent those trench widths with defect-free self-assembly and the yellow areas refer to areas with a high defect-density, c) free energy per block copolymer chain in units of the free energy in unconfined state as a function of the trench width as predicted by Turner⁴⁷ (red curve, based on grey curves) and according to the calculation presented in this paper (blue curve), d) curve showing the energy difference between the two models presented in panel (c), e) graphics showing the number of PS domains deposited as a function of the guiding pattern trench when no neutral brush layer is deposited, as shown in the inset.

It should be noted that the natural pitch L_0 of the block copolymer is the result of an energy minimization process. If the block copolymer chains are stretched so that the pitch is increased, the number of IMDS (intermaterial dividing surface) per unit length along the trench width is reduced. This is one way to reduce the enthalpy of the system. Stretching the polymer chains leads on the other hand to a reduction of the entropy of the system⁴⁹. In *figure 4 c)* we present the results of the energy analysis of the system according to the model developed by Turner⁴⁷ which has afterwards been successfully employed by different authors^{30,34,50}. The underlying principle is the energy balance between formation of interfaces between *PS* and *PMMA*, and the stretching of the chains taking into account the interaction of the guiding pattern walls and the preferentially wetting polymer domain. The black parabolas in *figure 4 c)* represent the normalized free energy per chain $\frac{e_{Turner}}{e_0}$ for the self-assembly of $n = \{1;6\}$ domains in trenches of width w , given by the following equation:

$$\frac{e_{Turner}}{e_0} = \frac{1}{3} \left(\left(\frac{w}{n * L_0} \right)^2 + \frac{2 * n * L_0}{w} + \frac{2 * \Gamma * L_0}{w} \right)$$

where Γ is a measure for the energy penalty induced through the polymer-wall interaction (for calculation see supplemental information, parts *S3.1* and *S3.2*). The incommensurability of the trench is $w/n * L_0$. The surface tensions required to estimate Γ have been extracted from works of different authors.^{51–53} The free energy e_{Turner} is normalized to the bulk free energy per chain e_0 . The red curve in *figure 4 c)* represents the minimum of these parabolas and thus predicts a determined number n of domains for each trench width based on which configuration has the least free energy.

Interestingly, we always observe the creation of a high defect density in the close vicinity of trench widths with large guiding pattern incommensurability, where Turner's model predicts a crossover from n to $n+1$ domains (compare location of light-orange boxes and crossover points of red curve). The formation of a large number of defects close to crossover points is not explained by the Turner model and thus requires an extension of the model, which is provided in the following.

The blue curve in *figure 4 c)* represents a semi-empirical function to describe the free energy of the defect-loaded state. To find this curve, we have assumed that the formation of defects leads to the relaxation of the chains to their bulk energy level, and in return contributes an unknown, but constant energy penalty per chain $\frac{e_p}{e_0}$. The relaxation of the chains to bulk energy level can be implemented in Turner's formula assuming that the trenches are perfectly commensurable, e.g.

incommensurability is 1. After adding the constant energy penalty term, the modified formula to describe the free energy of the observed morphology, called $\frac{e}{e_0}$, is of the form:

$$\frac{e}{e_0} = 1 + \frac{2 * \Gamma * L_0}{3 * w} + \frac{e_p}{e_0}$$

The derivation of this formula can be found in section S3.3 in the supplemental information. We can now estimate $\frac{e_p}{e_0}$ by fitting the curve to the position of crossover points between the defect-free and the defect-loaded state. The fitting yields $\frac{e_p}{e_0} = 0.00704$ with a coefficient of correlation $R^2 = 0.9989$. Assuming that the system always self-assembles in the morphology which is characterized by the minimum free energy, we may simply calculate $\frac{\Delta e}{e_0} = \frac{e_{\text{Turner}}}{e_0} - \frac{e}{e_0}$ to predict the self-assembly morphology of the system. The curve for $\frac{\Delta e}{e_0}$ is plotted in *figure 4 d*). The defect-loaded state is energetically favorable for values $\frac{\Delta e}{e_0}(w) > 0$, while the defect-free state according to Turner is energetically beneficial for $\frac{\Delta e}{e_0}(w) < 0$. Based on this calculation, we conclude that the observed defect-loaded state is energetically unstable for trench widths larger than 130 nm.

The key result of this analysis is that a morphology change from the defect-free to the defect-loaded state occurs as soon as the energy penalty induced through the deformation of the chains due to guiding pattern incommensurability exceeds 0.7 % of the bulk free energy level. The reason why this state for increasing trench width successively disappears is that incommensurability is compensated by a steadily increasing number of chains, such that an absolute difference between the ideal guiding pattern width and the actual guiding pattern width can be compensated by more and more molecules.

We may not forget at this point that this estimation is only true as long as the trench width is smaller or close to the correlation length of the block copolymer, which represents the limit of the directed self-assembly of block copolymers by topographical guiding patterns. For very large multiplication factors the formation of defects similar to self-assembly in free surface will play a successively larger role. Despite of the observation of two different defect formation mechanisms (e.g. domain wiggling and point defects), we find that the free energy of the defect-loaded state can be described with one single function. The energy reduction in the wiggling morphology can be qualitatively explained by a partial release of the energy stored in chain stretching through the introduction of additional *PS/PMMA* interfaces. A proposal to determine the density of point defects can be found in the supplemental information, part S3.5.

Figure 4 e) depicts the results of the analysis of the number of *PS* domains n_{PS} as a function of the trench width w on the surface and below the surface for the directed self-assembly in trenches without depositing any neutral brush layer. We observe that the number of *PS* domains after etching is lower than before the etching step for all investigated trench widths. This observation confirms the results presented in *figure 3* for the entire trench width range. This indicates that there is no trench width which enables the directed self-assembly of block copolymers in perfectly vertical lamellae unless a neutral brush layer is deposited. We do not observe the self-assembly in a morphology that displays a massive formation of defects as observed in case of the neutral brush layer deposition. A plausible explanation for this observation is that the onion-like organization of the block copolymer in the trench (e.g. the combination of vertical and horizontal lamellae) facilitates the relaxation of the chains and reduces the stretching of the domains as a result of incommensurability.

Conclusions

We have shown that EUV-IL brings the possibility of manufacturing highly accurate topographical guiding patterns for the directed self-assembly of block copolymers. EUV-IL combines high resolution, low line edge roughness and high throughput, which makes it an advantageous method compared to other lithography approaches. We have demonstrated the alignment of patterns of PS-*b*-PMMA of 11 nm pitch in perfectly vertical lamellae when a neutral brush layer is grafted to the bottom of the trenches.

We have taken advantage of the accurate control of the dimensions of the guiding patterns that EUV-IL can achieve to investigate the creation of defects as a function of the trench width while minimizing the influence of defects due to guiding pattern imperfections. We conclude that the maximum stretch/compression that the block copolymer chain can sustain is 8 % of the of the chain length in free surface. We extend the commonly used free energy models by adding the description of free energy of the self-assembly morphology that includes defects. The model successfully predicts the window of the pattern process observed experimentally.

To conclude, the experimental proof of the advantage of using EUV-IL for creation of guiding patterns in directed self-assembly of block copolymers, together with the methodology to predict the process window that provides aligned patterns without defects, will help to design process conditions for DSA using new materials, and in particular high- χ materials, to reliably obtain sub-10 nm resolution patterns.

Conflict of interest

There are no conflicts of interest to declare.

Acknowledgements

This project is partially funded by the EU project NFFA (Nanoscience Foundries and Fine Analysis) (grant agreement no. 654360) and MINECO through Nanointegra project (TEC2015-69864-R). We would like to acknowledge Christophe Navarro and Celia Nicolet from Arkema for supplying some of the polymers used in this work.

References

- 1 M. M. Waldrop, *Nature*, 2016, **530**, 144–147.
- 2 D. P. Sanders, *Chem. Rev.*, 2010, **110**, 321–360.
- 3 Y. Chen, Q. Cheng and W. Kang, *Proc. SPIE*, 2012, **8326**, 1–14.
- 4 Y. Chen, P. Xu, L. Miao, Y. Chen, X. Xu, Y. Chen, P. Xu, L. Miao, Y. Chen, X. Xu, D. Mao, P. Blanco, C. Bencher, R. Hung and C. S. Ngai, *Proc. SPIE*, 2017, **7973**, 1–8.
- 5 M. Neisser and S. Wurm, *Adv. Opt. Technol.*, 2015, **4**, 235–240.
- 6 F. S. Bates and G. H. Fredrickson, *Phys. Today*, 1999, **52**, 32–38.
- 7 M. P. Stoykovich, E. W. Edwards, H. H. Solak and P. F. Nealey, *Phys. Rev. Lett.*, 2006, **97**, 4–7.
- 8 A. Knoll, A. Horvat, K. S. Lyakhova, G. Krausch, G. J. A. Sevink, A. V. Zvelindovsky and R. Magerle, *Phys. Rev. Lett.*, 2002, **89**, 1–4.
- 9 L. Leibler, *Macromolecules*, 1980, **13**, 1602–1617.
- 10 L. Wan, R. Ruiz, H. Gao, K. C. Patel and T. R. Albrecht, *ACS Nano*, 2015, **9**, 7506–7514.
- 11 H. S. Suh, D. H. Kim, P. Moni, S. Xiong, L. E. Ocola, N. J. Zaluzec, K. K. Gleason and P. F. Nealey, *Nat. Nanotechnol.*, 2017, **12**, 575–581.
- 12 S. Park, O. Park, J. Y. Cheng, C. T. Rettner and H. Kim, *Nanotechnology*, 2008, **19**, 455304–1–6.
- 13 D. Borah, C. Cummins, S. Rasappa, R. Sentharamaikkannan, M. Salaun, M. Zelsmann, G. Lontos, K. Ntetsikas, A. Avgeropoulos and M. A. Morris, *Nanomaterials*, 2018, **8**, 1–11.
- 14 R. A. Farrell, N. Petkov, M. T. Shaw, V. Djara, J. D. Holmes and M. A. Morris, *Macromolecules*, 2010, **43**, 8651–8655.
- 15 R. A. Farrell, N. T. Kinahan, S. Hansel, K. O. Stuen, N. Petkov, M. T. Shaw, L. E. West, V. Djara, R. J. Dunne, O. G. Varona, P. G. Gleeson, S. J. Jung, H. Y. Kim, M. M. Kolesnik, T. Lutz, C. P. Murray, J. D. Holmes, P. F. Nealey, G. S. Duesberg, V. Krstić and M. A. Morris, *Nanoscale*, 2012, **4**, 3228–3236.

- 16 R. A. Segalman, *Mater. Sci. Eng. R Reports*, 2005, **48**, 191–226.
- 17 M. Müller, W. Li, J. C. O. Rey and U. Welling, *J. Phys. Conf. Ser.*, 2015, **640**, 12010-1-12010-12.
- 18 B. S. Park, M. P. Stoykovich, R. Ruiz, Y. Zhang, C. T. Black and P. F. Nealey, *Adv. Mater.*, 2007, **19**, 607–611.
- 19 S. B. Darling, *Prog. Polym. Sci.*, 2007, **32**, 1152–1204.
- 20 D. J. C. Herr, *J Mater. Res.*, 2011, **26**, 122–139.
- 21 Y. Kasahara, Y. Seino, H. Sato, H. Kanai, K. Kobayashi, H. Kubota, K. Miyagi, S. Minegishi, K. Kodaera, N. Kihara, S. Nomura, T. Tobana, M. Shiraishi, Y. Kawamonzen and T. Azuma, *Microelectron. Eng.*, 2016, **159**, 21–26.
- 22 B. Päiväranta, A. Langner, E. Kirk, C. David and Y. Ekinici, *Nanotechnology*, 2011, **22**, 375302-1-375302-7.
- 23 D. Fan, *J. Micro/Nanolith. MEMS MOEMS.*, 2016, **15**, 33505-1-33505-7.
- 24 N. Mojarad, J. Gobrecht and Y. Ekinici, *Sci. Rep.*, 2015, **143**, 55–63.
- 25 H. Cheng, I. Keen, A. Yu and I. Blakey, *Proc. SPIE*, 2012, **8323**, 10-1–10-11.
- 26 K. Nickmans, J. N. Murphy, B. De Waal, P. Leclère, J. Doise, R. Gronheid, D. J. Broer and A. P. H. J. Schenning, *Adv. Mater.*, 2016, **28**, 10068–10072.
- 27 B. E. W. Edwards, M. F. Montague, H. H. Solak, C. J. Hawker and P. F. Nealey, *Adv. Mater.*, 2004, **16**, 1315–1319.
- 28 S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. De Pablo and P. F. Nealey, *Nature*, 2003, **424**, 411–414.
- 29 J. M. Roberts, T. Bacuita, R. L. Bristol, H. B. Cao, M. Chandhok, H. Lee, E. M. Panning, M. Shell, G. Zhang and B. J. Rice, *Proc. SPIE*, 2005, **5751**, 64–77.
- 30 I. Keen, H. Cheng, A. Yu, K. S. Jack, T. R. Younkin, M. J. Leeson, A. K. Whittaker and I. Blakey, *Macromolecules*, 2014, **47**, 276–283.
- 31 R. Gronheid, C. Boeckx, J. Doise, I. Karageorgos, J. Ryckaert, B. T. Chan, C. Lin and Y. Zou, *Proc. SPIE*, 2017, **9776**, 1W-1–1W-9.
- 32 C. Chi, C. Liu, L. Meli, J. Guo, D. Parnell, Y. Mignot, K. Schmidt, M. Sanchez, R. Farrell, L. Singh, T. Furukawa, K. Lai, Y. Xu, D. Sanders, D. Hetzer, A. Metz, S. Burns, F. Nelson, J. Arnold and D. Corliss, *Proc. SPIE*, 2017, **10146**, Q1–Q8.
- 33 I. Junarsa, M. P. Stoykovich, P. F. Nealey, M. Yyuansheng and H. H. Solak, *J. Vac. Sci. Technol. B*, 2005, **23**, 138–143.
- 34 W. Chen, J. Luo, P. Shi, C. Li, X. He, P. Hong, J. Li and C. Zhao, *RSC Adv.*, 2014, **4**, 50393–50400.

- 35 D. Borah, S. Rassapa, M. T. Shaw, R. G. Hobbs, N. Petkov, M. Schmidt, J. D. Holmes and M. Morris, *J. Mater. Chem. C*, 2013, **1**, 1192–1196.
- 36 N. Mojarad, J. Gobrecht and Y. Ekinici, *Sci. Rep.*, 2015, **5**, 1–7.
- 37 B. Kim, N. Laachi, K. T. Delaney and G. H. Fredrickson, *Proc. SPIE*, 2014, **9049**, 90491D–1–90491D–9.
- 38 H. Tsai, J. W. Pitera, H. Miyazoe, S. Bangsaruntip, S. U. Engelmann, C. C. Liu, J. Y. Cheng, J. J. Bucchignano, D. P. Klaus, E. A. Joseph, D. P. Sanders, M. E. Colburn and M. A. Guillorn, *ACS Nano*, 2014, **8**, 5227–5232.
- 39 C. Cummins, A. Bell and M. Morris, *Nanomaterials*, 2017, **7**, 304.
- 40 A. G. Caster, S. Kowarik, A. M. Schwartzberg, O. Nicolet, S. Lim and S. R. Leone, *J. Raman Spectrosc.*, 2009, **40**, 770–774.
- 41 G. Claveau, J. Hazart, N. Posseme, X. Chevalier, G. Claveau, P. Quemere, M. Argoud, J. Hazart, P. P. Barros, A. Sarrazin, N. Posseme, R. Tiron, X. Chevalier, C. Nicolet and C. Navarro, *J. Micro/Nanolithography, MEMS, MOEMS*, 2016, **15**, 31604-1-31604–11.
- 42 Y. Sun, C. Wang and J. Liou, *Soft Matter*, 2016, **12**, 2923–2931.
- 43 H. Bartnik, A. Fiedorowicz, R. Jarocki, R. J. Kostecki and M. Szczurek, *Appl. Phys. A*, 2010, **98**, 61–65.
- 44 P. Mansky, Y. Liu, E. Huang, T. P. Russell and C. Hawker, *Science*, 1997, **275**, 1458–1460.
- 45 A. Erdmann, P. Michalak, M. Ismail, T. Fühner, M. Argoud, G. Claveau, R. Tiron, M. Müller and C. Cayrefourcq, *Talk 2nd DSA Symp. Grenoble*.
- 46 B. E. Han, H. Kang, C. Liu, P. F. Nealey and P. Gopalan, *Adv. Mater.*, 2010, **22**, 4325–4329.
- 47 M. S. Turner, *Phys. Rev. Lett.*, 1992, **69**, 1788–1791.
- 48 R. Ruiz, N. Ruiz, Y. Zhang, R. L. Sandstrom and C. T. Black, *Adv. Mater.*, 2007, **19**, 2157–2162.
- 49 D. Walton, G. J. Kellogg, A. Mayes, P. Lambooy and T. P. Russell, *Macromolecules*, 1994, **27**, 6225–6228.
- 50 J. O. Y. Y. Cheng, A. M. Mayes and C. A. Ross, *Nat. Mater.*, 2004, **3**, 823–828.
- 51 D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, 1969, **13**, 1741–1747.
- 52 C. J. Carriere and R. L. Sammler, *Rheol. Acta*, 2000, **39**, 476–482.
- 53 T. Suzuki and Y. Yamada, *J. Cryst. Process Technol.*, 2015, **5**, 43–47.

Supplemental information

Nano-confinement of block copolymers in high accuracy
topographical guiding patterns: Modelling the emergence of
defectivity due to incommensurability

Steven Gottlieb¹, Dimitrios Kazazis², Iacopo Mochi², Laura Evangelio¹, Marta Fernández-Regúlez¹,
Yasin Ekinici², Francesc Perez-Murano¹

1: Instituto de Microelectrónica de Barcelona IMB-CNM, CSIC, 08193 Bellaterra, Barcelona, Spain
2: Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, CH-5232 Villigen-PSI, Switzerland

S1: Line width roughness (LWR) analysis as a function of the trench width 2

S2: Determining the crossover points from defect-free to defect-loaded state 3

S3: Determining the free energy for the defect-free and the defect loaded state 5

S3.1: Adapting the free energy model for block copolymers confined between two plates according to Turner to our system5

S3.2: Understanding the influence of Γ on the determination of characteristic points in the Turner model6

S3.3: Derivation of a model to predict the self-assembly mode as a function of the trench width7

S3.4: Contributions to the free energy in block copolymers under nanoconfinement10

S3.5: Implementing a mixed state of stretched chains and point defects13

S4: References Supplemental Information..... 18

S1: Line width roughness (LWR) analysis as a function of the trench width

The line width roughness of a line is defined as the standard deviation of the width of a line, which is defined by the distance between a right and a left border. Due to the undulations of the block copolymer domain in the defective state – as in group 2 and 4 – it is only natural that the result of the LWR measurement increases significantly, when the direction of the . Representative LWR measurements for each of the groups are depicted in *figure S 1 a*). We observe that the LWR increases for high-defect-density block copolymer patterns. This is not the case because the LWR of the block copolymer actually increases by such a large factor, but because the measurement direction is defined in one determined direction x indicated by the black arrow in *figure S 1 a*) and a deviation from this direction is expressed by a larger measured line width at this position.

Figure S 1: *LWR as a function of the trench width. a) Representative results of LWR analysis for the groups 1-5, b) LWR as a function of the trench width w yields significantly higher values for trench widths far away from the commensurate guiding patterns.*

S2: Determining the crossover points from defect-free to defect-loaded state

One challenging part of this work was the accurate determination of the trench width, at which the block copolymer system changes from the defective morphology to the defect-free morphology and vice versa. Fortunately, the length of the mask transmission gratings and therefore of the interference pattern is finite and the guiding pattern feature width becomes successively smaller towards the border of the pattern. In these last micrometres towards the border of the guiding pattern width decreases at a rate of roughly 1 nm per 100 nm. This position is ideal to determine the specific trench widths, at which the self-assembly mode changes from one morphology to the other. Examples of this part of the guiding pattern is depicted in *figure S 2 a)-c)*.

To minimize measurement uncertainties, we extracted the trench widths from 49 morphology changes.

The results of this analysis can be found in the table below.

Group x → Group y	Mean [nm]	e/e ₀ [-]	Std Dev [nm]	Nat pitch [nm]	# Chain [-]	Chain Length [nm]	Delta Chain Length [nm]	Delta Chain Length [%]
1→2	76.25	1.413	1.75	70.2	6	12.7	1.00	8.6
2→3	87.3	1.369	2.49	93.6	8	10.9	0.78	6.7
3→4	100.8	1.316	1.74	93.6	8	12.6	0.90	7.7
4→5	107	1.299	1.80	117	10	10.7	1.00	8.5
5→6	126.4	1.253	0.89	117	10	12.6	0.94	8.0

Table S 1: Determination of the crossover points between defective and non-defective state in block copolymer self-assembly.

Figure S 2: *Examples of how to determine the cut-off values for each group. The numbers in the images indicate, which group this part of the guiding pattern belongs to. The dashed line indicates the approximate height of the crossover point.*

S3: Determining the free energy for the defect-free and the defect loaded state

S3.1: Adapting the free energy model for block copolymers confined between two plates according to Turner to our system

According to Turner, the free energy per block copolymer chain of a system confined between two parallel plates normalized to the bulk free energy per chain e_0 can be written as ^{1,2}:

$$(S1) \quad \frac{e_{Turner}}{e_0} = \frac{1}{3} \left(\lambda^2 + \frac{2}{\lambda} + \frac{2 * \Gamma}{n * \lambda} \right)$$

The energy per chain in this system depends on the parameter λ (indicates the incommensurability of the trench with respect to an integer multiple of the natural pitch of the block copolymer; see *formula S2* and Γ (which balances the interface energy between one of the blocks and the confining wall, and the interface energy between the two blocks; see *formula S3*).

$$(S2) \quad \lambda = \frac{w}{n * L_0}$$

$$(S3) \quad \Gamma = \frac{\gamma_{SiO_2-PMMA}}{\gamma_{PS-PMMA}}$$

The interface free energy between two materials can be calculated by an extension of Young's equation, as presented by Owens and Wendt ³. The parameters required to do the calculus are the dispersive (γ_D) and polar (γ_P) contributions to the surface free energy of the respective materials.

$$(S4) \quad \gamma_{A-B} = \left(\sqrt{\gamma_{P,A}} - \sqrt{\gamma_{P,B}} \right)^2 + \left(\sqrt{\gamma_{D,A}} - \sqrt{\gamma_{D,B}} \right)^2$$

Using literature values for, this calculus yields $\Gamma = 2.1$. ⁴⁻⁶. Here, material A is PMMA and material B is SiO₂. Filling this result into *formula S1*, we can determine the curves for the free energy per chain as a function of w for $n = \{1; 2; 3; \dots\}$, where n corresponds to the number of PS-PMMA repeat units. This calculation provides us with the free energy per chain, when a number of n repeat units is confined in a trench with width w . The corresponding curves are depicted in *figure S3* in pink ($n=2$), brown ($n=3$), green ($n=4$), blue ($n=5$) and cyan ($n=6$). The preferred self-assembly mode is always the one that exhibits the minimum free energy per chain, which is symbolized by the black dashed line. The light blue shaded area in *figure S2* represents the trench widths that we have worked with in the course of our experiments and the beige boxes represent those zones, where we observe a defect-loaded state, which cannot be explained with Turner's formula.

Figure S 3: *Free energy per chain according to Turner.* Colored parabolas: free energy per chain as a function of trench width w for $n = \{2;6\}$ PS and PMMA domains. Black dashed curve: Minimum of all colored curves. Blue shaded area: Process window in this work. Light-orange-shaded areas: Defect-loaded self-assembly.

S3.2: Understanding the influence of Γ on the determination of characteristic points in the Turner model

Reliable information about the polar and the dispersive surface free energy of SiO_2 (crosslinked HSQ is chemically very similar to amorphous SiO_2) is somehow hard to find and we would like to probe the justifiable concern that some inaccuracy has been introduced to the calculation of the crossover points due to that. Filling in *formula S2* into *formula S1*, yields

$$(S5) \quad \frac{e_{vert}}{e_0} = \frac{1}{3} \left(\left(\frac{w}{n \cdot L_0} \right)^2 + \frac{2 \cdot n \cdot L_0}{w} + \frac{2 \cdot \Gamma \cdot L_0}{w} \right)$$

Furthermore,

$$(S6) \quad \frac{\partial \left(\frac{e_{vert}}{e_0} \right)}{\partial w} = 0$$

yields

$$(S7) \quad w_0 = \sqrt[3]{\frac{n+2 \cdot \Gamma}{n^2 \cdot L_0}}$$

Therefore, we can tell that the minimum free energy in a confined system is proportional to the cube root of Γ . Looking closely at *figure S 3*, we observe surprisingly that the minimum free energy curve does not necessarily pass by the minimum of the parabola. The defect-loaded morphology of the block copolymers always occurs in the vicinity of connection points between two of minimum free energy curves c_n and c_{n+1} . The crossover points have the mathematical property

$$(S8) \quad \left(\frac{e_{vert}}{e_0} \right)_n = \left(\frac{e_{vert}}{e_0} \right)_{n+1}$$

, which by using *formula S5* becomes

$$(S9) \quad \frac{1}{3} \left(\left(\frac{w}{n \cdot L_0} \right)^2 + \frac{2 \cdot n \cdot L_0}{w} + \frac{2 \cdot \Gamma \cdot L_0}{w} \right) = \frac{1}{3} \left(\left(\frac{w}{(n+1) \cdot L_0} \right)^2 + \frac{2 \cdot (n+1) \cdot L_0}{w} + \frac{2 \cdot \Gamma \cdot L_0}{w} \right).$$

Here, the term containing Γ is easily cancelled out. This means that an inaccurate estimation of the wall/polymer interaction Γ does not affect the position of the crossover points and is therefore no essential parameter for our analysis.

S3.3: Derivation of a model to predict the self-assembly mode as a function of the trench width

In this section we will explain, why block copolymers in certain trench width regimes abruptly change their morphology from stretched vertical lamellae with no or almost no defects to a state with a very high defect density (e.g. the regime where the block copolymer shows wiggling or forms point defects). To do so, we will derive a mathematical expression that allows us to describe the free energy per chain normalized to e_0 in the defect-loaded state, fit it to our experimental data and compare it to the model presented by Turner. Therefore, we assume that the block copolymer always self-assembles in the morphology with the minimum free energy.

Let us now assume that the energy of the system we investigate is the sum of four energy components E_{tot}

$$(S10) \quad E_{tot} = E_{S,L0} + E_{AB,L0} + E_{AW} + E_P$$

The components introduced above are defined as follows:

$E_{S,L0}$: Energy stored in the stretching of the chains in bulk conditions, e.g. when the block copolymer pitch equals the equilibrium pitch L_0 . Here, one single chain is stretched to the length of $L_0/2$

$E_{AB,L0}$: Energy contribution due to the interface between the blocks A and B of the block copolymer in bulk conditions

E_{AW} : Energy contribution due to the interaction between the block A and the walls (we assume that only one block, namely PMMA interacts with the wall ^{1,2})

E_P : An energy penalty that covers every possible energy component in our system that is not included in the first three terms, including mainly the formation of defects, but possibly also energetic components related to stretching and the increase of interface area. This term does

not appear in any way in the model of Turner, because he does not consider any defects in his system.

As our system consists of a total number of b chains, we state that the total free energy of the system E_{tot} equals the product of b chains and their respective free energy e , such that *formula S10* can also be written as:

$$(S11) \quad E_{tot} = b * e = b * (e_{S,L0} + e_{AB,L0} + e_{AW} + e_P)$$

From now on, minuscule letters refer to energies describing one chain, while capital letters refer to the energy of the entire system.

As Turner's model analyzes the energy per chain normalized to the bulk free energy, we will have to divide *formula S11* by the number of chains and the energy of a single block copolymer chain in bulk configuration ($b * e_0$), which yields:

$$(S12) \quad \frac{e}{e_0} = \frac{e_{S,L0} + e_{AB,L0} + e_{AW} + e_P}{e_0} = \frac{e_{S,L0} + e_{AB,L0}}{e_0} + \frac{e_{AW}}{e_0} + \frac{e_P}{e_0}$$

The sum of free energy due to chain stretching and the creation of *PS/PMMA* interfaces in bulk configuration $e_{S,L0} + e_{AB,L0}$ is precisely defined as e_0 , so that *formula S12* can be simplified to:

$$(S13) \quad \frac{e}{e_0} = 1 + \frac{e_{AW}}{e_0} + \frac{e_P}{e_0}$$

Now, let us have a closer look at the energy formula derived by Turner (*formula S14*):

$$(S14) \quad \frac{e_{Turner}}{e_0} = \frac{1}{3} * \left(\lambda^2 + \frac{2}{\lambda} + \frac{2 * \Gamma * L_0}{3 * w} \right)$$

The first summand in brackets accounts for the chain stretching, the second term accounts for the interface energy between the blocks and the third term corresponds to the energy contribution through the interaction between one of the block copolymer blocks and the wall. Assuming that $\lambda = 1$ (i.e. no incommensurability, as defined in *formula S2*, yields

$$(S15) \quad \frac{e_{Turner}}{e_0} = \frac{1}{3} + \frac{2}{3} + \frac{2 * \Gamma}{3 * n} = 1 + \frac{2 * \Gamma * L_0}{3 * w}$$

After clarifying this, we are capable of isolating the interaction term between the wall and the block copolymer, and estimate the contribution of the wall/block copolymer interaction to the free energy per chain in the system (with $\Gamma = 2.1$ and $L_0 = 23.4$):

$$(S16) \quad \frac{2 * \Gamma * L_0}{3 * w} = \frac{e_{AW}}{e_0} = \frac{32.76 \text{ nm}}{w [\text{nm}]}$$

Filling in this term into *formula S13* yields:

$$(S17) \quad \frac{e}{e_0} = 1 + \frac{32.76}{w} + \frac{e_P}{e_0}$$

Let us furthermore assume that the term $\frac{e_P}{e_0} = \text{const.} \neq f(w)$. This makes sense because we expect the major energy component of this term to originate from the energy penalty through the formation of defects or the introduction of wiggling. In principal it seems to be a reasonable assumption to claim that the number of defects increases linearly proportional with the number of chains in the system, so that the dependence with w cancels out. We assume that the formation of defects primarily leads to a relaxation of the chains into an energy state close to the one of the bulk at the expense of the creation of additional free energy. This additional free energy component originates primarily from the increase of the area of *PS/PMMA* interfaces.

We know that the curve we search for intersects with the curve derived by Turner exactly in the crossover points.

For this reason, we fit the curve

$$(S18) \quad \frac{e}{e_0} = 1 + \frac{32.76}{w} + C$$

to the five experimentally determined points depicted in as presented in *table S 1*, 2nd and 3rd column. This analysis yields $C=0.007074$ with a coefficient of determination of $R^2=0.9989$. The curve represents the given data therefore excellently.

The curve that describes the free energy of the self-assembly of block copolymers in a state with many defects is thus:

$$(S19) \quad \frac{e}{e_0}(w) = 1 + \frac{32.76}{w} + 0.007074$$

To fulfil the objective of this work and to find an expression that helps us predict, in which morphology the block copolymer self-assembles, we will have to take a look at the energy difference between the two models $\frac{\Delta e}{e_0}$, which is defined as follows:

$$(S20) \quad \frac{\Delta e}{e_0} = \frac{e_{Turner}}{e_0} - \frac{e}{e_0} = \min \left\{ \frac{1}{3} \left(\left(\frac{w}{n_0 * L_0} \right)^2 + \frac{2 * n_0 * L_0}{w} + \frac{2 * \Gamma * L_0}{w} \right) \right\}_{n_0 \in \{1; j\}} - \left\{ 1 + \frac{32.76 \text{ nm}}{w} + 0.007074 \right\}$$

This function is plotted in *figure S 4* for the trench width $w=\{23.4 \text{ nm}; 200 \text{ nm}\}$ and $n=\{1;9\}$. Whenever the free energy of Turner's model is larger than the free energy of the model we have developed here, the curve plotted in *figure S 3* is positive, which predicts that the block copolymer self-assembles in defect-free lamellar morphology. For those trench widths where $\frac{\Delta e}{e_0}(w) > 0$, the block copolymer self-assembles with a large number of defects. The light blue box represents those trench widths that have been experimentally accessible for us. The yellow boxes indicate those trench widths, where the defect-loaded state is energetically preferable. These areas become consistently narrower and disappear for trench widths larger than 130 nm. On a molecular basis this is mainly due to the fact that upon stretching, the energy required to stretch a molecular chain increases in a quadratic manner. For this reason, in case of an incommensurable trench, the energy penalty is smaller if the system must stretch many chains a little bit, than if it has to stretch few chains a lot.

Figure S 4: Difference in free energy between Turner's model and the model derived in this document. A value $\Delta e/e_0 < 0$ indicates an energetic advantage of self-assembly in defect-free stretched lamellae, a value $\Delta e/e_0 > 0$ indicates an energetic advantage for the block copolymer to self-assemble in a defect-loaded state. The light blue box indicates the area for which we have experimental data available. The light yellow boxes indicate the area where we observe or predict the existence of the defect-loaded state.

S3.4: Contributions to the free energy in block copolymers under nanoconfinement

Let us now understand which energy contributions play a role in the two models that we work with in this document. This will also help us deepen our understanding of the parameter C , e.g. e_p/e_0 . This is a good opportunity to bear in mind, that in neither one of the models we included the interface

energy contributions between the substrate and the block copolymer, and the surface tension of the block copolymer. As the two models we investigate are a form of upright-standing lamellae (even though the one has defects, the other does not), the two contributions are considered to be the same for both models.

Figure S 5: Different energy components that contribute to the calculation of the free energy according to Turner and according to the model derived in this work.

Turner's model takes chain stretching (e_s), the inter-block interface (e_{AB}) and the block-wall interaction (e_{AW}) into account (see *formula S14*). The energy contributions of the chain stretching and inter-block interface in bulk conditions ($e_{S,L0}$; $e_{AB,L0}$) can be understood as the sum of a bulk condition contribution ($e_{S,L0} + e_{AB,L0} = e_0$). Moreover, two additional contributions account for the stretching (/compression) ($e_{S,\lambda}$) and the resulting reduction (/increase) of interfaces ($e_{AB,L0}$) due to the incommensurability λ .

$$(S21) \quad \frac{e_{Turner}}{e_0} = \frac{e_S + e_{AB} + e_{AW}}{e_0} = \frac{(e_{S,L0} + e_{S,\lambda}) + (e_{AB,L0} + e_{AB,\lambda}) + e_{AW}}{e_0} = \frac{e_0 + e_{S,\lambda} + e_{AB,\lambda} + e_{AW}}{e_0}$$

The respective energy contributions are sketched in *figure S 5*. From this plot we learn that a great proportion of the free energy of the system originates from the bulk free energy $e_{S,L0} + e_{AB,L0} = e_0$ (blue curves, where $e_{S,L0} = 1/3$ and $e_{AB,L0} = 2/3$).

Another important, but strictly monotonically declining part of the free energy comes from the interaction of the A block (e.g. *PMMA*) and the wall (green curve). We have isolated this contribution in *formula S16*. The characteristic $1/w$ -dependence of this curve can be explained by the fact that wall free energy E_{PMMA-W} , is not a function of the trench width, but rather equivalent to $2 * A * \gamma_{PMMA-W}$. In this equation, A stands for the area of the guiding pattern wall which is in contact with the *PMMA* block and γ_{PMMA-W} is the respective interface free energy (see *formula S4*). As the trench width increases, this energy contribution is to be distributed among a consistently increasing number of chains. For an infinitely wide trench, this energy would be zero.

The characteristic spikes in Turner's curve originate from additional increase in stretching and interface energy due to the incommensurability ($e_{S,\lambda} + e_{AB,\lambda}$) with the trench. It is only natural that this curve is always positive, because the bulk free energy is defined as the minimum free energy, so that any deviation from the equilibrium point at L_0 leads to an energy penalty. Here, we only plot the sum of both contributions represented through the red dashed line. The interface energy term, however, becomes negative in case of chain stretching, because the density of interface areas is reduced. In case of a chain compression, the interface energy term is positive, because the density of interfaces is reduced.

Based on this analysis, let us now do the same analysis for the model we have developed to describe the defect loaded system. Exactly like Turner's model, our system takes the bulk energy into account and analyzes the energetic deviation of the system from the bulk energy. Therefore, we include both the bulk free energy ($e_{S,L0} + e_{AB,L0} = e_0$) and the wall interaction energy e_{AW} exactly like in the previous section. In contrast to that, our approach does not take the stretching of chains and the change of interface energy due to incommensurability ($e_{S,\lambda} + e_{AB,\lambda}$) into consideration, and replaces it by a constant penalty term $\frac{e_P}{e_0}$. This term primarily accounts for the increase in free energy due to the creation of defects.

$$(S22) \quad \frac{e}{e_0} = \frac{e_{S,L0} + e_{AB,L0} + e_{AW} + e_P}{e_0} = \frac{e_0 + e_{AW} + e_P}{e_0}$$

If we now subtract *formula S22* from *formula S21*, we figure out that $\frac{\Delta e}{e_0}$ (plotted in *figure S 4*) can also be written as:

$$(S23) \quad \frac{\Delta e}{e_0} = \frac{(e_{S,\lambda} + e_{AB,\lambda}) - e_P}{e_0}$$

This confirms once again, but on a more general level, that our results are independent from the interaction energy of the block copolymer and the guiding pattern wall, and are therefore not a

function of Γ . This finding is surprising but pleasant, given the fact that one of the major sources of uncertainty of our method is the estimation of Γ .

Previously, we have found that $\frac{e_p}{e_0} = 0.00704$ which corresponds to a value of 0.704 % of e_0 .

To set this value in a relation, let us now calculate the bulk free energy per chain as proposed by Ohta and Kawasaki^{7,8} normalized to kT , which is given by:

$$(S24) \quad \frac{e_0}{kT} = \frac{3}{8} * \frac{L_0^2}{N*b^2} + \frac{2*N*b}{L_0} * \sqrt{\frac{\chi}{6}} = 2.99$$

The block copolymer periodicity $L_0=23.4 \text{ nm}$, $N=424$ and the Flory-Huggins interaction parameter $\chi=0.037$.⁹ For the determination of the average Kuhn segment length b of our block copolymer, we use $6.6 \text{ \AA}$.¹⁰

Based on this calculus we estimate that

$$(S25) \quad e_p = 0.00704 * e_0 = 0.021 \text{ kT}$$

We can thus conclude that the additional energy induced in the system compared to the bulk energy quantitatively only accounts for a relative small fraction of the total free energy of the system. We will now assume, that the energy penalty term is exclusively used to form defects and that the formation of these defects results in the relaxation of all those chains in the system that do not contribute to the formation of defects. A defect in a block copolymer like the one used in this example yields an energy penalty of $E_D=200 \text{ kT}$.¹¹ The volume of a single chain v can be estimated by

$$(S26) \quad v = \frac{M_{L22}}{(f_{PS}*\rho_{PS}+f_{PMMA}*\rho_{PS})*N_A}$$

We can now estimate that the average distance l between two defects in a 105 nm wide trench w with block copolymers of 50 nm height h is

$$(S27) \quad l = \frac{E_D*v}{e_p*h*w} = 117 \text{ nm}$$

Comparing the result derived above with the actual defect density we observe in such a trenches, we notice that the predicted defect density is larger than the one we observe in the actual structure. This may be because the stretching and the interface terms are actually non-zero.

S3.5: Implementing a mixed state of stretched chains and point defects

In the previous paragraph we have noticed that modeling the energy contribution of the defective state e_p/e_0 as a constant that does not depend on w is a simple and versatile way to predict, for which

trench widths the system cannot compensate the incommensurability of the trench with further stretching and compression of the chains, and must consequently change its self-assembly mode. We have, however, also shown that this simplified model fails to properly predict the defect density of the defective state. This is because we have not taken into account, that the formation of point only a part of the system can be relaxed by the formation of defects and the rest of it is still self-assembled in a stretched manner. This concept is clarified in *figure S 6*, where the self-assembly in trenches of two different widths are depicted.

Figure S 6: Experimental result of the deposition of a block copolymer in a 104 nm wide trench (left) and in a 106 nm wide trench (right). Scale bar is 150 nm.

We can generally say, that a determined volume fraction of the block copolymers in the system is self-assembled in the stretched/compressed mode as described by Turner, and another part contributes to the formation of defects. The volume fraction of the material self-assembled in Turner's mode is referred to as a , while we refer to as $(1-a)$ to the volume fraction the contributes to the formation of defects. Consequently, chains belonging to the latter group are characterized by the bulk free energy e_0 and the energy penalty e_p that we have calculated in the previous sections. The first group is further divided in two sub-groups, which consist of chains that have the free energy of n and those that have the free energy of $n+1$. In the example of *figure S 6* we observe a mixed state with $n=4$ (red area) and $n+1=5$ (blue area). The observation of the samples supports the thesis that areas of self-assembly with n and $n+1$ domains can be found, despite of the fact that always either n or $n+1$ domains are energetically clearly favorable. In addition to that, we observe that point defects always occur, when the system changes its morphology from n to $n+1$ domains.

We will now calculate the free energy of the defective state for the trench widths from $w_1 = 101.5 \text{ nm}$ to $w_2 = 107.5 \text{ nm}$, that we have previously referred to as group 4. For this reason, $n = 4$ and $n+1 = 5$. We subtract the wall contribution and the bulk free energy from the free energy of each chain and

only balance the contributions through stretching, interface creation and the energy penalty due to the creation of defects.

The equation to describe a for a known evolution of the proportions between block copolymers self-assembled in n domains and $n+1$ domains is given below. The said proportions are functions of the trench width and referred to as $p_{n=4}(w)$ and $p_{n=5}(w)$.

$$(S28) \quad a * \left(p_{n=4}(w) * \frac{e_{S,\lambda} + e_{AB,\lambda}}{e_0}(w)_{n=4} + p_{n=5}(w) * \frac{e_{S,\lambda} + e_{AB,\lambda}}{e_0}(w)_{n=5} \right) + (1 - a) * \frac{e_p}{e_0} \leq MIN\left(\frac{e_{S,\lambda} + e_{AB,\lambda}}{e_0}(w)_{n=4;5}\right)$$

In the following, we will model the free energy of the defect-rich regime based on two different functions describing this proportion. In *figure S 7 a)* we have plotted the two possible scenarios for the evolution of this proportion as a function of the trench width in the range where we observe the defective state; namely linearly and based on logistic growth. In both cases the proportion p_n is 1 at the first crossover point and p_n is 0 at the second crossover point. Both scenarios are symmetric to the point $(104.5/0.5)$ and obey the boundary condition of $p_n + p_{n+1} = 1$.

The energetic situation for $a=1$ is depicted in *figure S 7 b)*. There, the solid line shows the free energy as a function of the trench width for the linear evolution of $p_n(w)$, and the dashed line for the logistic growth solution. The fact that these two states predict a higher free energy for all trench widths w , justifies to set $a < 1$ to lower the free energy density of the system by the introduction of defects.

We can now solve *formula S28* for the linear and the logistic growth of the curves to find expressions for $a(w)$. This yields

$$(S29) \quad a(w) = \frac{MIN\left(\frac{e_{S,\lambda} + e_{AB,\lambda}}{e_0}(w)_{n=4;5}\right) - \frac{e_p}{e_0}}{p_{n=4}(w) * \frac{e_{S,\lambda} + e_{AB,\lambda}}{e_0}(w)_{n=4} + p_{n=5}(w) * \frac{e_{S,\lambda} + e_{AB,\lambda}}{e_0}(w)_{n=5} - \frac{e_p}{e_0}}$$

The solution of this equation for the both scenarios of $p_n(w)$ is plotted in *figure S 7 c)*. The dashed line represents the solution of $a(w)$ for the logistic growth, whereas the solid line represents the solution of the linear scenario. The values of a have to be understood as maximum values for a , so that the total free energy of the system is below the free energy of Turner's model.

Figure S 7: *Graphic solution of the extended model of free energy in the defect-loaded state.* (a) Two different scenarios on how the fractions of block copolymers self-assembled in n (and $n+1$) domains evolve as a function of w over the area where we observe the defective state. The solid line represents a linear approach and the dashed line represents a logistic approach, (b) evolution of free energy per chain normalized to the bulk free energy as a function of w for the two scenarios (linear and logistic). For both scenarios the free energy is constantly larger than the free energy proposed by Turner, (c) Minimum values for “ a ” to decrease the free energy per chain below the free energy of Turner, (d) estimation of the volume of chains that are relaxed by the creation of a defect using the example of a defect observed in a trench of 106 nm.

As we can tell from the images depicted in figure S 6, a is significantly larger than 0.5. The linear model predicts, however, a minimum value of $a \approx 0.6$ for trench widths of 106 nm, while the logistic growth model predicts a maximum of $a \approx 0.9$ (see figure S 6 c)). For this reason, we consider the logistic growth model to represent the situation more realistically than the linear model. The solution for the parameter a represents a maximum value, so that the free energy of the defect-loaded state does not to exceed the free energy of the Turner state.

In this way, it is possible to make an estimation of the minimum distance between two defects. Based on the observation of the defect depicted in figure S 7 d), we believe that it is reasonable to assume that the creation of one defect relaxes all the chains inside a volume $h * w * 2 * L_0$:

$$(S30) \quad \frac{V_{sys}}{V_{rel}} = \frac{w * h * l}{w * h * 2 * L_0} = \frac{1}{1-a}$$

Claiming that the ratio of total block copolymer volume in our system to the volume of block copolymers relaxed through the creation of defects equals $1/(1-a)$, and for $a \approx 0.85$ yields:

$$(S31) \quad l = \frac{2 * L_0}{1-a} = 312 \text{ nm}$$

This means that the length of a system with one single defect (e.g. the mean distance between two defect centers) corresponds to a maximum of 312 nm.

This estimation is significantly more realistic than the result derived in *section S3.4*.

S4: References Supplemental Information

- 1 I. Keen, H. Cheng, A. Yu, K. S. Jack, T. R. Younkin, M. J. Leeson, A. K. Whittaker and I. Blakey, *Macromolecules*, 2014, **47**, 276–283.
- 2 M. S. Turner, *Phys. Rev. Lett.*, 1992, **69**, 1788–1791.
- 3 D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.*, 1969, **13**, 1741–1747.
- 4 C. J. Carriere and R. L. Sammler, *Rheol. Acta*, 2000, **39**, 476–482.
- 5 T. Suzuki and Y. Yamada, *J. Cryst. Process Technol.*, 2015, **5**, 43–47.
- 6 <http://www.surface-tension.de/solid-surface-energy.htm>, .
- 7 T. Ohta and K. Kawasaki, *Macromolecules*, 1986, **19**, 2621–2632.
- 8 D. Walton, G. J. Kellogg, A. Mayes, P. Lambooy and T. P. Russell, *Macromolecules*, 1994, **27**, 6225–6228.
- 9 T. P. Russell, R. P. Hjelm and P. A. Seeger, *Macromolecules*, 1990, **23**, 890–893.
- 10 E. Helfand and Y. Tagami, *Polym. Lett.*, 1971, **9**, 741–746.
- 11 S.-M. Hur, V. Thapar, A. Ramírez-Hernández, G. Khaira, T. Segal-Peretz, P. A. Rincon-Delgadillo, W. Li, M. Müller, P. F. Nealey and J. J. de Pablo, *Proc. Natl. Acad. Sci.*, 2015, **112**, 14144–14149.