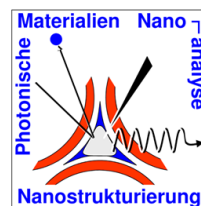




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Formation and Control of Nanostructures in High- χ PS-*b*-PDMS Block Copolymers for Next Generation Lithography

Dissertation

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Abstract

Block copolymer (BCP) self-assembly by microphase separation is an emerging technique that enables the creation of sub-10 nm periodical patterns on large surfaces at low cost. It is thus a complementary approach to EUV lithography for extending resolution beyond the current limits of optical lithography. The aim of this thesis is to analyse and control the formation of nanostructures in cylinder-forming high- χ PS-*b*-PDMS block copolymers (16 and 21 kg/mol) using solvent vapor annealing (SVA). Key processing parameters governing the ordering and orientation of the nanostructures are studied systematically. PS-*b*-PDMS is shown to self-assemble on different metallic substrates and on monolayer graphene, for which a transfer protocol from copper foils is established. Directed self-assembly in lithographically defined trenches is also explored. Morphological and chemical characterization of the nanostructures is performed using AFM, SEM, TEM, DRIFT and Raman spectroscopy. Cross-sectional TEM reveals half-cylindrical features, and DRIFT spectroscopy confirms the conversion of PDMS to SiO_x with residual carbon after plasma processing. Reducing the film thickness below the natural domain spacing enables hexagonally ordered perpendicular cylinders. Selective swelling of the PDMS block during dynamic SVA produces antidot morphologies from a cylinder-forming polymer. Building on these results, a memristor device architecture exploiting the antidot structures is proposed as a direction for future work.

Kurzzusammenfassung

Die Selbstorganisation von Blockcopolymeren (BCP) durch Mikrophasentrennung ist eine aufstrebende Technik, die die kostengünstige, großflächige Erzeugung periodischer Strukturen mit einer Breite unter 10 nm ermöglicht. Sie ergänzt die EUV-Lithografie, um die Auflösung über die Grenzen der optischen Lithografie hinaus zu steigern. Ziel dieser Arbeit ist es, die Bildung von Nanostrukturen in zylinderbildenden PS-*b*-PDMS-Blockcopolymeren (16 und 21 kg/mol) mit hohem χ mittels Ausheilung im Lösungsmitteldampf zu analysieren und zu steuern. Dabei werden die wichtigsten Prozessparameter für Anordnung und Ausrichtung der Strukturen systematisch untersucht. Es wird gezeigt, dass sich PS-*b*-PDMS auf verschiedenen metallischen Substraten, auf Graphen und lithographisch vorstrukturierten Substraten gerichtet selbstorganisiert. Die morphologische und chemische Charakterisierung der Nanostrukturen erfolgt mittels AFM, SEM, TEM, DRIFT- und Raman-Spektroskopie. Die TEM-Untersuchung zeigt halbzyklindrische Strukturen, und die DRIFT-Analyse bestätigt die Umwandlung von PDMS in SiO_x mit Kohlenstoffrückständen nach der Plasmabehandlung. Durch die Reduzierung der Schichtdicke unter den natürlichen Domänenabstand konnten hexagonal angeordnete, senkrecht stehende Zylinder erzeugt werden. Das selektive Aufquellen des PDMS-Blocks führt zu Antidot-Morphologien aus einem zylinderbildenden Polymer. Darauf aufbauend wird für zukünftige Arbeiten eine Memristor-Architektur mittels Antidot-Strukturen vorgeschlagen.

Declaration of Authorship

I hereby certify that I have written this thesis independently and without the use of any aids or sources other than those indicated. All sources are properly cited wherever the work of others has been used. This work has not been submitted, in whole or in part, to any other examining body for the purpose of obtaining a degree or similar qualification. Furthermore, I have not published any part of this work, and only non-confidential aspects are presented due to the confidentiality agreement associated with the project. Generative AI tools have been used solely for grammar checking and linguistic revision. The scientific content, analysis, and conclusions presented in this thesis are entirely my own.

Signature

Place, Date

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List of Abbreviations

AFM Atomic force microscopy.

BCP Block copolymer.

BE Bottom electrode.

BF-TEM Bright-field transmission electron microscopy.

DI Deionized.

DRIFTS Diffuse reflectance infrared Fourier-transform spectroscopy.

DSA Directed self-assembly.

EBL Electron beam lithography.

ECM Electrochemical metallization.

FWHM Full width at half maximum.

GNR Graphene nanoribbon.

HSP Hansen solubility parameter.

ICP Inductively coupled plasma.

LER Line edge roughness.

MFC Mass flow controller.

MIM Metal–insulator–metal.

OWRK Owens–Wendt–Rabel–Kaelble method.

PC Plasma cleaning.

PDI Polydispersity index.

PDMS Polydimethylsiloxane.

PECVD Plasma-enhanced chemical vapor deposition.

PMMA Poly(methyl methacrylate).

PS Polystyrene.

PS-*b*-PDMS Polystyrene-block-polydimethylsiloxane.

PVA Poly(vinyl alcohol).

RCP Random copolymer.

RED Relative energy difference.

RIE Reactive ion etching.

RMS Root mean square.

rpm Revolutions per minute.

RRAM Resistive random-access memory.

sccm Standard cubic centimeters per minute.

SEM Scanning electron microscopy.

SiO₂ Silicon dioxide.

SVA Solvent vapor annealing.

TE Top electrode.

TEM Transmission electron microscopy.

VCM Valence change memory.

List of Symbols

- D Cylinder diameter.
- L_0 Natural domain spacing.
- N Degree of polymerization.
- R End-to-end distance of a polymer chain.
- R_0 Hansen interaction radius.
- T Temperature.
- V_{reset} Reset voltage.
- V_{set} Set voltage.
- W trench width.
- ΔG_{mix} Gibbs free energy of mixing.
- ΔH_{mix} Enthalpy of mixing.
- ΔS_{mix} Entropy of mixing.
- χ Flory–Huggins interaction parameter.
- δ_d Dispersive Hansen solubility parameter.
- δ_h Hydrogen-bonding Hansen solubility parameter.
- δ_p Polar Hansen solubility parameter.
- λ Wavelength.
- f Volume fraction.
- h Film thickness.

p Pressure.

t_a Annealing time.

1 Introduction

The advancement of nanotechnology and the downscaling of semiconductor device dimensions have created an increased demand for reliable techniques in the production of nanostructures. Block copolymer (BCP) lithography is one such emerging technique for producing nanostructures in the single-digit nanometer regime [1, 2]. Unlike conventional lithography techniques, BCP lithography is cost-efficient and can be implemented over large surface areas within a shorter timescale. A diblock copolymer consisting of immiscible polymers A and B undergoes phase separation upon reaching thermodynamic equilibrium. By altering their block length ratio and combined Flory-Huggins parameter (χN), polymers A and B can form periodic nanostructures like cylinders, lamellae, spheres, and gyroids [3, 4].

The distinctive self-assembly capability of block copolymers enables the fabrication of nanostructures in the sub-10 nm regime that are simple and cost-effective. This is particularly relevant due to the feature size limitation with the conventional photolithographic methods, e.g., a 22 nm limit for immersion photolithography according to the international technology roadmap for semiconductors (ITRS 2011) [5, 6]. Similarly, BCP in combination with extreme UV-light (EUV) lithography has gained interest due to the resist pattern rectification in terms of improved local critical dimension uniformity and reduced pattern placement error [7, 8]. This motivated the implementation of block copolymer lithography in wide-ranging applications such as the fabrication of nanowires [9], fin-field effect transistors [10], magnetic storage devices [11], memristors [12–16], quantum dots [17], nanoporous membranes [18] and many more.

In BCP lithography, one of the polymer blocks is selectively removed after phase separation for the creation of nanopatterned masks. This mask can subsequently be used for pattern transfer, lift-off, or etching processes to obtain the desired nanopatterns on the substrate surface [19–21]. Achieving high-quality lithographic masks with low defect density, reduced line edge roughness, and uniform feature sizes strongly depends on the type of annealing process and subsequent patterning steps.

Among the various block copolymer species, polystyrene-block-polydimethylsiloxane (PS-*b*-PDMS) block copolymers have attracted significant attention due to their high Flory-Huggins parameter ($\chi \approx 0.26$ at room temperature), enabling the formation of sub-10 nm structures

[22]. Additionally, the high etch selectivity between PS and PDMS allows the facile selective removal of PS while PDMS is converted into silicon oxide during plasma treatment, making it an excellent hard mask material for pattern transfer. However, large differences in the surface energies between PS (40.7 mN m^{-1}) and PDMS (20.4 mN m^{-1}) [23] lead to the preferential formation of a PDMS layer at the air interface, a so-called PDMS wetting layer. This often results in the parallel orientation of all other polymer domains. While both perpendicular and parallel cylinder orderings are desirable for different applications, achieving perpendicular cylinders is challenging due to the formation of wetting layers [24].

In this work, two different high- χ PS-*b*-PDMS block copolymers with molecular weights of 16 kg/mol and 21 kg/mol are investigated for the fabrication of nanoscale structures. Solvent vapor annealing (SVA) is employed to induce phase separation by enhancing polymer chain mobility through solvent absorption. Several strategies have been proposed to achieve perpendicular cylinder orientation, including the use of electric fields [17, 25], random copolymer or brush layers [3, 26–28], and top/bottom coat [29, 30] to balance the surface interactions. However, the influence of parameters such as film thickness, SVA conditions, and substrate surface energy on the specific polymer systems has not been systematically studied and thus will be investigated in this work. Additionally, the lack of a standardized setup for a SVA system makes it challenging to reproduce results from other research.

Furthermore, the compatibility of BCP self-assembly with different substrates is investigated, including metallic surfaces and two-dimensional materials such as graphene. Graphene, an allotrope of carbon with a two-dimensional honeycomb lattice, exhibits distinctive material properties such as mechanical strength, thermal conductivity, high electron mobility, optical transmittance, biocompatibility, and so on [31–33]. BCP lithography on graphene has been successfully demonstrated for applications such as graphene nanoribbon fabrication [34] and pattern transfer to arbitrary substrates [35]. Therefore, the behavior of high- χ PS-*b*-PDMS block copolymer on monolayer graphene is also explored in this work.

Directed self-assembly (DSA) of block copolymers has demonstrated a significant role in nanolithographic applications by enabling control over domain orientation and ordering through prepatterned substrates [36, 37]. In this work, the directed self-assembly behavior of high- χ PS-*b*-PDMS system on a topographically prepatterned substrate is investigated.

The cylindrical nanostructures obtained from BCP self-assembly can be further transformed into an antidot structure, expanding their application potential. One such application is in memristive electronic devices, where the electrical resistance depends on the history of applied voltage or current, enabling non-volatile information storage. Memristors have gained significant attention due to their low power consumption, endurance, high-speed switching, ease of fabrication, and potential for memory and neuromorphic computing applications [38].

Based on the above considerations, the primary aim of this work is to achieve controlled

self-assembly of high- χ PS-*b*-PDMS block copolymers to produce well-ordered nanostructures. Systematic studies are conducted to understand the influence of key parameters, such as film thickness, SVA parameters, and surface interactions, on the resulting morphology and domain orientation. A central challenge addressed in this study is the control over domain orientation in the PS-*b*-PDMS system. Strategies such as top/bottom coatings, solvent selectivity, and substrate modification are systematically investigated to manipulate and optimize the resulting nanostructures. Furthermore, directed self-assembly is implemented to investigate the ordering of the polymer domains. In addition, morphological and chemical investigations are performed, along with pattern inversion strategies, to expand the applicability of these nanostructures, including their potential use in memristive devices. In short, this thesis aims to contribute to the development of reliable and scalable nanofabrication techniques based on block copolymer lithography for next-generation electronic devices.

The content of this thesis is divided into six chapters. Following the introduction, Chapter 2 presents the theoretical background of block copolymer lithography, including thin film physics of block copolymers and solvent vapor annealing. Chapter 3 describes the experimental methods, including BCP lithography, directed self-assembly, graphene transfer, and vibropolishing. Chapter 4 investigates the self-assembly behavior of cylinder-forming high- χ PS-*b*-PDMS, focusing on the influence of SVA parameters and substrate effects. Chapter 5 explores a higher molecular weight PS-*b*-PDMS BCP for achieving perpendicular cylinder orientation, along with pattern inversion strategies and potential device applications. Finally, conclusions and outlook are presented in Chapter 6.

2 Theoretical Background

2.1 Fundamentals of block copolymers

Polymers are macromolecules composed of repeating structural units, the monomers [39]. The number of monomer species, arrangement, and number of monomeric units represent specific polymers, and the properties of a polymer are tailored by these factors. The degree of polymerization N describes the total number of monomers in a polymer chain. The entire polymer sample consists of individual molecules with a distribution of the degree of polymerization, determined by the method of synthesis [40]. A polymer can be classified as a homopolymer or a copolymer based on its composition. Polymers composed of only one type of monomer are called homopolymers, whereas polymers made of two or more different monomer species are referred to as copolymers.

The size of a polymer is characterized by its molecular weight, and the distribution of molecular weights within a polymer sample is described by the polydispersity index (PDI), defined as the ratio of the weight-average molecular weight to the number-average molecular weight. A PDI value of 1 corresponds to a monodisperse system in which all polymer chains have equal length. In practice, a narrow molecular weight distribution ($\text{PDI} \approx 1$) is desirable for achieving uniform and well-ordered nanostructures in block copolymer self-assembly [41].

The investigation of copolymers was initiated back in the 1930s after synthetic rubber was developed [42]. Copolymers are typically categorized based on the arrangement of the different monomers. The unique feature of block copolymers is that the monomeric species are present as discrete blocks that are bonded covalently [43]. The advancement in polymer synthesis, e.g., controlled radical polymerization (CRP) or living anionic polymerization (LAP) techniques, has made it possible to produce BCPs with controlled and well-defined block length and block length ratios [44].

A diblock copolymer is the simplest form of a block copolymer with a combination of two distinct homopolymers as blocks (e.g., A-*b*-B) as depicted in Figure 2.1. A certain degree of incompatibility can exist in a mixture of chemically distinct components [43]. Thus, the coexistence of two different polymer blocks within a block copolymer results in complex phase

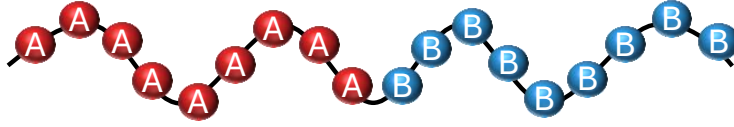


Figure 2.1. Schematic representation of a diblock copolymer with polymer A (red) and B (blue) as different monomer types.

behavior, and the polymer blocks will attract or repel each other. A phase separation will happen when the distinct homopolymers of a diblock polymer are immiscible, thus reducing the free energy. Since the blocks are covalently bonded, the phase separation is restricted to the nanoscale. As a result, the system's equilibrium state is governed by the balance of enthalpic and entropic contributions to the total free energy [45]. The free energy of mixing ΔG_{mix} for a BCP system can be expressed as:

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}, \quad (2.1)$$

where ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing. The driving force of this phase separation can be quantified using the Flory-Huggins interaction parameter χ and the overall degree of polymerization N . The Flory-Huggins interaction parameter χ describes how unfavorable it is for two chemically distinct polymers to mix. A larger value of χ indicates stronger repulsion between the blocks, promoting phase separation, whereas a smaller χ favors mixing [46]. The interaction parameter depends on the temperature and can be approximated as:

$$\chi = A + \frac{B}{T}, \quad (2.2)$$

where A and B are material-specific constants, and T is the absolute temperature. The degree of polymerization N describes the total number of monomeric units in a polymer chain [46, 47]. In a diblock copolymer (A-*b*-B), it corresponds to the total number of monomeric units from each polymer species and is expressed as below:

$$N_{A-b-B} = N_A + N_B. \quad (2.3)$$

The product χN is defined as the segregation strength, and if it exceeds the critical value (≈ 10.5 [48]) corresponding to the order-disorder transition, the polymer blocks self-assemble to ordered domains. The equilibrium morphology formed upon microphase separation primarily depends on the volume fraction of individual blocks and the segregation strength, as discussed in the following section.

2.1.1 Phase behavior and morphology

During the phase separation process, the block copolymers cannot phase separate macroscopically as the blocks are covalently bound together. Instead, they undergo microphase separation, forming ordered nanodomains [49]. The equilibrium morphology after phase separation in bulk systems is governed by the volume fraction f of the components and the segregation strength χN [50]. In this context, bulk refers to an unconfined system in which surface and interfacial effects are negligible. Thus, by controlling these factors, it is possible to achieve particular architectures. The volume fraction is the ratio of the volume occupied by one polymer to the total volume of all blocks. In a diblock copolymer, the volume fraction of block A can be expressed as:

$$f_A = \frac{V_A}{V_{total}} = \frac{\frac{M_A}{\rho_A}}{\frac{M_A}{\rho_A} + \frac{M_B}{\rho_B}}, \quad (2.4)$$

where V is the volume, M corresponds to the molecular mass, and ρ is the density of the respective block A or B.

Figure 2.2 illustrates the phase diagram for a diblock copolymer consisting of monomeric units A and B. The phase diagram depicts the relation between the combined Flory-Huggins parameter (χN) and the volume fraction (f) of one polymer species. The volume fraction deter-

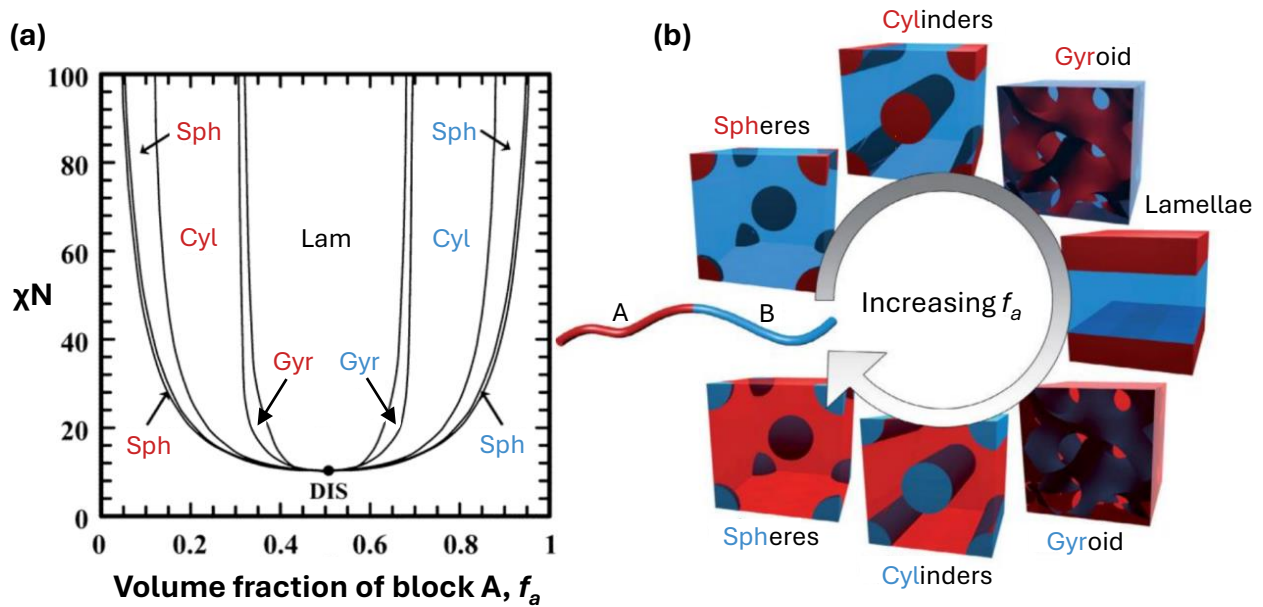


Figure 2.2. (a) Typical phase diagram of a diblock copolymer A-*b*-B. Depending on the volume fraction f , the Flory-Huggins interaction parameter χ and the degree of polymerization N , the BCP phase separation can be tailored. The shapes are Sph: body-centered spheres, Cyl: hexagonally packed cylinders, Gyr: double gyroid phase and Lam: lamellae. (b) Different BCP orientations as described in (a) with increasing volume fraction [51].

mines the resulting equilibrium morphology while the parameter χN controls the segregation strength between two blocks. By varying these parameters, i.e., by increasing the volume fraction of polymer (f_a) as seen in Figure 2.2 (b) phase-separated polymer domains of the minority species with a geometry of spheres (Sph), cylinders (Cyl), gyroid (Gyr) and lamellae (Lam) in a matrix of the majority polymer species can be achieved. These geometries can also be inverted if the concentration exceeds 50%, with the previously minority block forming the continuous matrix phase.

In Figure 2.2, "DIS" corresponds to the disordered phase. The order-to-disorder transition occurs when the temperature is high, such that the polymer chains are mobile or at a lower value of χN , resulting in a relatively small interaction between polymer blocks A and B. Under these conditions, entropic contributions dominate the free energy, favoring a disordered state in which the polymer blocks are mixed on a molecular scale [52]. Conversely, at lower temperatures or a higher χN value, the chemically distinct blocks will tend to reduce the interaction energy by separating from each other. However, because the blocks are covalently bonded, a macroscopic separation is not possible. Instead, they undergo microphase separation, resulting in the formation of ordered morphologies [52]. The characteristic length/domain spacing L_0 of this ordered structure depends on the total chain length N . As the product of χ and N must be larger than about 10.5, high- χ BCPs allow for the fabrication of periodic patterns with L_0 of a few nanometers.

2.2 Thin film block copolymer physics

While the phase behavior of block copolymers in bulk systems is well understood, their behavior when processed as thin films on a substrate deviates significantly due to confinement and interfacial effects. As a result, the film thickness and interfacial energies also affect the resulting morphology in thin BCP thin films in addition to the volume fraction and segregation strength χN [53]. Particularly low surface energies of one polymer species compared to the other can lead to the assembly of a lower energy polymer in a surface film called a preferential wetting layer. This wetting layer influences the polymer domain orientation (parallel or perpendicular to the substrate surface) in the rest of the film and the degree of lateral ordering of the nanostructures (long-range order). Consequently, the final morphology in thin films is governed by a balance between bulk thermodynamic driving forces and interfacial energy contributions. In the following subsections, the effects of BCP film thickness and the surface energies are discussed, followed by an analysis of the domain orientation in cylinder-forming block copolymers.

2.2.1 Confinement and film thickness effects

During the microphase separation, the polymer chains redistribute to minimize the total free energy of the system. At this stage, the periodic nanostructures will reach their equilibrium periodicity, defined as domain spacing L_0 . The value of L_0 primarily depends on the degree of polymerization [54, 55]. In thin film systems, the film thickness h acts as an additional geometric constraint which influences the final morphology. The influence of film thickness on the equilibrium morphology depends on interfacial boundary conditions. In systems with preferential interactions at one or both interfaces, the film thickness acts as a geometric constraint, and commensurability with the natural domain spacing determines the energetically favorable morphology. In contrast, for neutral interfaces where both blocks experience similar interfacial energies, perpendicular domain orientation is generally favoured and becomes independent of film thickness. For a lamellar-forming BCP, the final morphology of the BCP thin film is energetically favorable if the film thickness satisfies the condition:

$$h = nL_0, \quad (2.5)$$

where n is an integer number of domain layers. When these conditions are met, the polymer domains can form without any significant distortion. On the other hand, if the film has an initial thickness that deviates from the above condition, the thin film system experiences a confinement constraint that disturbs the equilibrium morphology. This results in an increase in the elastic free energy as the polymer chains undergo stretching or compression to compensate for the film thickness. As a result, the associated energetic penalty may promote defect formation, distorted domains, or a different domain orientation [55, 56]. Thus, the BCP film thickness plays a crucial role in determining the order and morphology of the nanostructures. In this work, the role of film thickness is exclusively studied for PS-*b*-PDMS BCPs, where it is shown to influence the resulting morphology (4.1.1).

2.2.2 Surface and interfacial energies

The influence of film thickness is explained in the previous section 2.2.1. In addition to thickness effects, the orientation and morphology of BCP nanostructures are strongly influenced by the interfacial interactions, as the thin film is confined between the substrate and the free interface (air interface). This is because each polymer species at the interface will interact with the substrate or air, contributing an additional interfacial energy [55]. The total free energy for a BCP thin film is the sum of different energy components and can be expressed as [57, 58]:

$$F = F_{mix} + F_{elast} + F_{interface}, \quad (2.6)$$

where F_{mix} is the free energy of mixing, F_{elast} is the elastic free energy, and $F_{interface}$ is the free energy at the interfaces. Out of these, F_{mix} arises from the thermodynamic incompatibility between chemically distinct blocks. The elastic free energy F_{elast} evolves from the deviations of the polymer chain from its undisturbed conformations, such as compression or stretching required to accommodate confinement. The equilibrium morphology and domain spacing result from a balance between the free energy of mixing and the elastic free energy [57]. The interfacial energy $F_{interface}$ accounts for the intermolecular interaction between each polymer species and the substrate or air interfaces.

Unlike in bulk systems, these interfacial energies can significantly compete with the bulk thermodynamic driving forces, resulting in the polymer species showing affinity to the substrate or air interfaces [55, 59]. When one polymer block exhibits lower interfacial energy to the substrate, it will preferentially adhere to the substrate interface; as a result, preferential wetting occurs. On the other hand, differences in the surface energy at the air interface result in the formation of a wetting layer at the air interface [60, 61].

In the case of lamellar or cylinder-forming block copolymers, domain orientation is governed by interfacial interactions between the polymer blocks and the substrate or air interfaces. When both interfaces preferentially attract the same polymer block (e.g., block A), a symmetric wetting condition is established and a parallel domain orientation is energetically preferred. In cases where only one interface is selective, either to substrate or air, an asymmetric wetting condition arises. A perpendicular orientation would require both blocks to be exposed at the selective interface, resulting in an energetically unfavorable condition for the non-preferred block. To avoid this increase in interfacial energy, the system adopts a parallel domain orientation. In contrast, when both polymer blocks experience similar interfacial energies, the substrate is considered neutral, and perpendicular orientation of cylinders or lamellar domains becomes energetically favorable [53, 62].

2.2.3 Domain orientation: parallel vs perpendicular cylinders

As discussed in section 2.2.2, interfacial interactions strongly influence the orientation of domains in thin films. In cylinder-forming block copolymers, the cylindrical domains may orient perpendicular or parallel to the substrate surface. In perpendicular orientation, the cylinders will align as hexagonally packed domains normal to the substrate surface. In contrast, in the parallel configuration, the cylinders lie parallel to the substrate, forming a fingerprint-like nanodomain when observed in top-view. The examples of parallel and perpendicular cylinder orientation to the substrate are shown in Figure 2.3. For clarity and simplicity, the cylinders in this schematic are represented as perfectly ordered and straight. However, in practice, the parallel-oriented cylinders form a fingerprint-like morphology because the cylinders have no

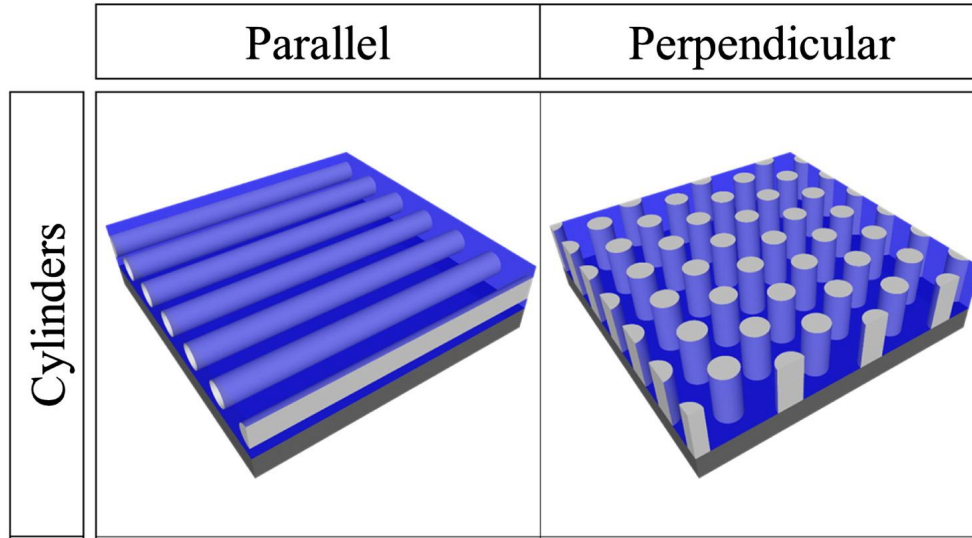


Figure 2.3. Schematic representation of parallel and perpendicular cylinder orientations in block copolymer thin film [64].

preferred in-plane direction on a flat substrate, causing nucleation of multiple grains with different local orientations and resulting in the absence of long-range order. The mismatch between grains with cylinders arranged in different directions is accommodated by grain boundaries containing topological defects such as dislocations, disclinations, and line terminations [63].

In addition to the interface energy, film thickness, and commensurability effects also affect the orientation. Thus, the system will end up in an orientation that minimizes the total free energy under the specified conditions based on the balance of the above-mentioned constraints.

Perpendicular cylinders are of utmost interest in the nano-fabrication of electronic device applications because of the ease of vertical pattern transfer to the substrate [17]. On the other hand, parallel-oriented cylinders can also be implemented for surface templating or directed self-assembly applications [2]. Thus, tuning of the thermodynamic and interfacial parameters during the processing is essential to obtain well-ordered nanostructures. A widely used method to achieve this is by solvent vapor annealing (SVA) and is discussed in the following section.

2.3 BCP phase separation by solvent vapor annealing

In block copolymer thin films, microphase separation can be induced by various techniques such as thermal annealing, rapid thermal annealing, solvent vapor annealing (SVA), laser spike annealing, and microwave annealing [65]. In this work, solvent vapor annealing is employed to induce microphase separation in PS-*b*-PDMS block copolymer thin films. It modifies the

thermodynamic state of the block copolymer thin film by introducing solvent molecules into the polymer film.

SVA enhances the polymer chain mobility through solvent uptake, which can accelerate the ordering kinetics compared to thermal annealing [64]. The introduction of solvent molecules lowers the glass transition temperature, thereby facilitating chain rearrangement toward equilibrium morphologies. In addition, SVA is usually performed at a lower temperature, where the BCP does not degrade and enables faster ordering of the polymer blocks compared to conventional thermal annealing. Depending on the solvent selectivity, temperature, and annealing time, the whole process can be performed within minutes to several hours [65]. Solvent vapor annealing provides independent control over solvent selectivity and swelling ratio, enabling precise tuning of polymer chain mobility and morphology evolution. This makes it particularly suitable for inducing microphase separation in block copolymer thin films where thermal annealing alone does not provide sufficient control over morphology. In a system incorporating a top coat (discussed in detail in Section 2.4.1), SVA performed at low temperatures can preserve the temperature-sensitive layers. PVA top coat starts degrading at temperatures above 110 °C, limiting their compatibility with thermal annealing [66].

The SVA method uses solvents to induce microphase separation, and it is done by exposing the BCP film to the solvents, which causes swelling of these polymers. The solvent-swollen polymer chains gain mobility, allowing them to arrange themselves towards a thermodynamically favorable configuration to such an extent that they can separate into microphases. The process of SVA can be explained with the help of a schematic as depicted in Figure 2.4.

The SVA process can be divided into 3 steps: solvent absorption, BCP-solvent concentration equilibrium and solvent desorption [64]. In the first stage, the spin-coated BCP film undergoes solvent absorption, causing the BCP film to swell. Swelling reduces the polymer chain entanglement, decreases the effective segregation strength χN , and plasticizes the polymer chain by lowering the glass transition temperature of the BCP/solvent mixture, collectively enhancing

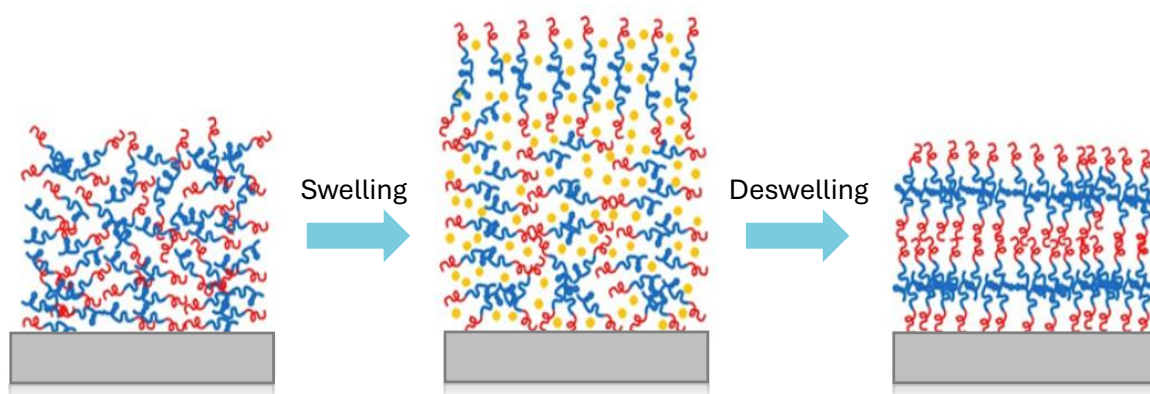


Figure 2.4. Schematic explanation of steps involved in solvent vapor annealing [64].

the polymer chain mobility [67, 68]. This creates a kinetic pathway for the solvent-swollen BCP units to arrange as they absorb more solvent. The increased chain mobility enables the polymer block to reorient to a lower energy configuration. The degree of swelling, which is quantified by the swelling ratio, defined as the ratio of swollen film thickness to the initial film thickness, influences the structure reorganization of the block copolymer [69, 70]. When the film's solvent concentration approaches equilibrium, the morphology in the swollen state is determined by the effective volume fraction of the polymer blocks, effective segregation strength χN , and the interfacial energies at the substrate and free surface. Finally, the desorption of the solvent is initiated by removing the solvent atmosphere. As the solvent leaves, the polymer film deswells, thereby increasing the entanglement of polymer chains and traversing the glass transition temperature, locking in the self-assembled structure.

The swelling and deswelling rates play a crucial role in the final structure after microphase separation. Swelling is supposed to increase the mobility of the BCP chains to such an extent that they can separate into microphases. However, it is also possible to over-swell the polymer film; for sufficiently high solvent fractions, the film may get disordered. Deswelling of the polymer film may cause reorientation or reduction in film volume, which causes deformation or collapse of the microdomains [71]. Therefore, the film thickness and swelling ratio, the interfacial energies at the substrate and free surface, solvent composition and vapor pressure, and the absorption and desorption rates all have a significant impact on the final morphology formed by SVA of a BCP film. Quantifying the impact of these variables on the self-assembly process is challenging because they are strongly interdependent; changing one parameter often affects several others at the same time.

Selection of the swelling solvent is another significant aspect in the annealing process. The solvent's selectivity toward one of the polymer blocks plays a crucial role in determining the morphology after phase separation. Solvents for BCPs can be classified into two types: selective and non-selective solvents. A selective solvent is one that preferentially interacts with one block over the other, whereas a non-selective solvent will swell both similarly. In the case of a selective solvent, preferential swelling leads to asymmetric swelling of these polymer blocks. As a result, the effective volume fraction (f_{eff}) of the block changes, and the presence of solvent modifies the effective interaction parameter (χ_{eff}). These changes shift the position of the system within the BCP phase diagram (Figure 2.2) and can induce morphological transitions. In contrast, for a non-selective solvent, the uniform swelling results in the absorption of solvent by both blocks, which reduces the effective segregation strength ($\chi_{\text{eff}}N$) without significantly changing f_{eff} . This results in increased chain mobility and promotes defect annihilation while preserving the equilibrium morphology [59, 72]. In short, solvent selectivity influences the effective block fraction in the swollen state, resulting in morphology transitions or changes in domain orientation [72].

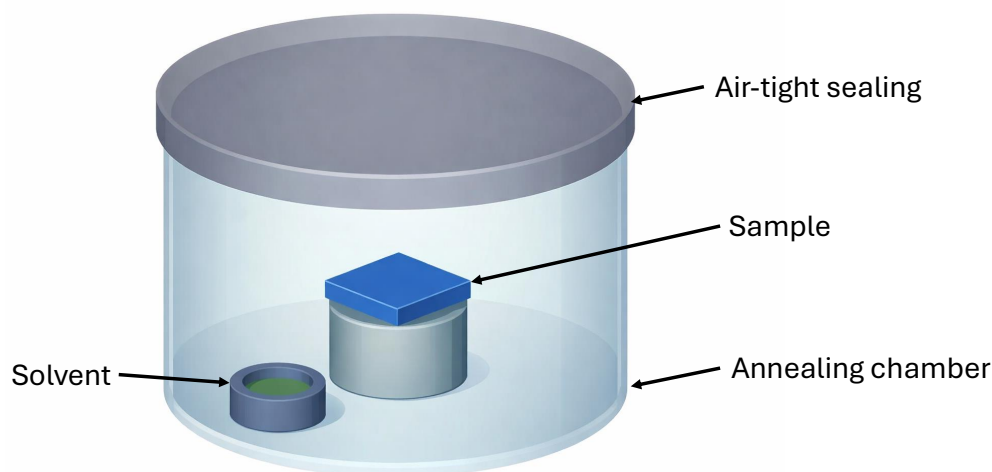


Figure 2.5. Schematic of static SVA setup [74].

Temperature is another critical parameter in SVA as the solvent vapor pressure depends exponentially on temperature (Clausius–Clapeyron relation) [73]. The vapor pressure determines the degree of solvent uptake and therefore the extent of swelling. A modest increase in the annealing temperature induces large changes in the swelling driving force, making the SVA process highly sensitive to thermal control.

The SVA process can be implemented in two different ways: static or dynamic SVA. Static solvent vapor annealing is the simplest way for annealing BCP thin film, where the sample is placed in a sealed beaker with the swelling solvent placed nearby. Figure 2.5 shows the schematic of a static SVA setup. In this technique, the swelling of the BCP thin film is influenced by the type and amount of solvent, vapor pressure (set by temperature), annealing time, and humidity [75]. The process can be carried out at temperatures below the glass transition temperatures of the polymer species and the boiling point of the selected solvents [72]. Here, the vapor pressure stays constant throughout the process as the temperature and volume of the annealing chamber stay the same. The solvent evaporation process is finished by taking the sample out or removing the lid, which is difficult to quantify. Additionally, it can also be done by introducing a leak to let all the solvent evaporate [76, 77].

In dynamic solvent vapor annealing, the solvent reservoir and the annealing chamber are separately placed, and a carrier gas (usually an inert gas) is used to transport the solvent vapor into the annealing chamber. Figure 2.6 shows a schematic of a dynamic SVA in which the sample is placed in an isolated annealing chamber. The SVA process begins with the generation of solvent vapor by passing the carrier gas through the solvent reservoir (bubbler), where it becomes enriched with solvent vapor. This solvent vapor is subsequently transported into the annealing chamber, enabling controlled exposure of the block copolymer film to the solvent

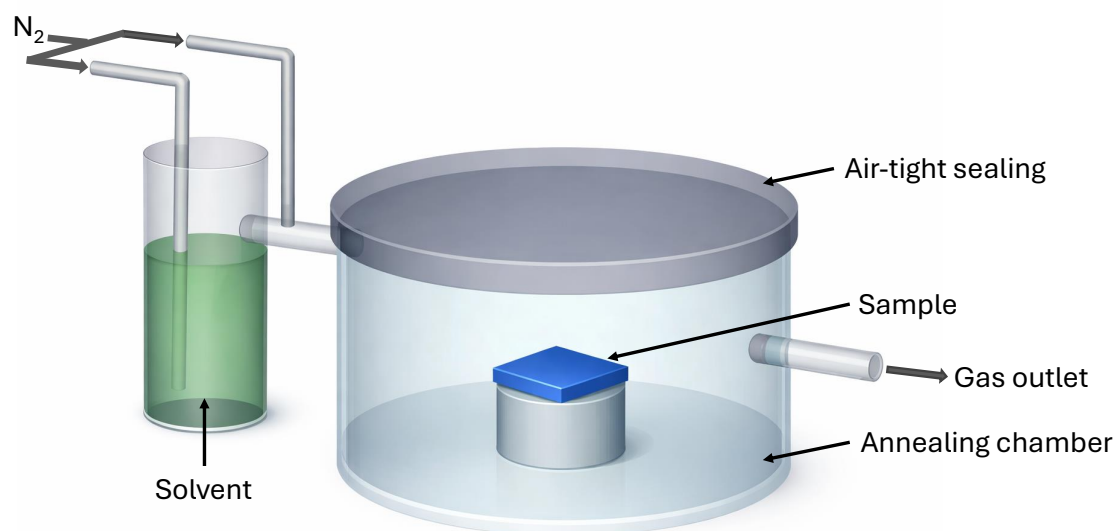


Figure 2.6. Schematic of dynamic SVA setup [74].

environment. The process is ended by purging the annealing chamber with the carrier gas.

The solvent environment inside the chamber is governed by temperature and the partial pressure of the solvent in the carrier gas stream. When a carrier gas such as nitrogen is passed through the bubbler, it becomes saturated with solvent vapor, and the resulting vapor concentration is determined by the solvent vapor pressure at a given temperature. The solvent concentration in the annealing chamber can be further tuned by adjusting the composition of the gas mixture, i.e., by mixing solvent-saturated gas with a pure carrier gas. In contrast, the total carrier gas flow rate determines the rate of solvent delivery to the film and thus influences the kinetics of swelling and deswelling. Increasing the flow rate enhances the flux of solvent molecules to the film without significantly altering the solvent concentration. This independent control of the solvent concentration and flow rate enables precise tuning of the solvent environment as well as the degree and rate of swelling of the polymer film. In dynamic SVA, the continuous flow of carrier gas prevents the establishment of thermodynamic equilibrium within the chamber, due to spatial variations in solvent concentration across the chamber and changes in solvent concentration over time at a given location. As a result, achieving fully saturated vapor conditions throughout the chamber is more challenging compared to static SVA, where equilibrium can be readily established [74]. Additionally, the deswelling process can be dynamically controlled by regulating the vapor concentration over time by adjusting the flow rate and gas composition. Furthermore, integrating these setups (static or dynamic SVA) with in-situ characterization techniques, such as reflectometry, aids in real-time monitoring of the film thickness and swelling behavior. This provides a detailed insight into the kinetics of microphase separation during the SVA process.

2.4 PS-*b*-PDMS as a high- χ block copolymer system

Polystyrene-block-Polydimethylsiloxane (PS-*b*-PDMS) block copolymers are among the various block polymers investigated for nanoscale pattern formation due to their high segregation strength and excellent etch contrast. Figure 2.7 shows the chemical structure of PS-*b*-PDMS block copolymer and one can observe a huge chemical dissimilarity between the silicon-containing PDMS block and the hydrocarbon-based polystyrene. This results in a high Flory-Huggins interaction parameter of $\chi \approx 0.26 - 0.30$ at room temperature, enabling microphase separation even at lower molecular weights [72, 78]. The significant research on these block copolymers is due to the exceptionally high Flory-Huggins interaction parameter [2, 4]. As the Flory-Huggins interaction parameter χ governs the driving force for the microphase separation, it also influences the defect density [78], i.e., any deviation from a completely regular pattern. A high χ leads to a higher driving force, which can decrease the defect density and yield in improving the long-range ordering of the nanostructures [79]. Theoretical studies further show that with increasing χ , interfacial width decreases ($w \propto 1/\sqrt{\chi}$), resulting in sharper domain interfaces. This reduction in interfacial width suppresses interfacial fluctuations and therefore decreases the line edge roughness (LER) [80, 81]. Moreover, it has also been reported that with these high- χ polymers, nanopatterns in the single-digit nanometer regime can be created [36, 82, 83]. Overall, high- χ block copolymers facilitate the formation of well-ordered, low-defect nanopatterns with reduced line edge roughness.

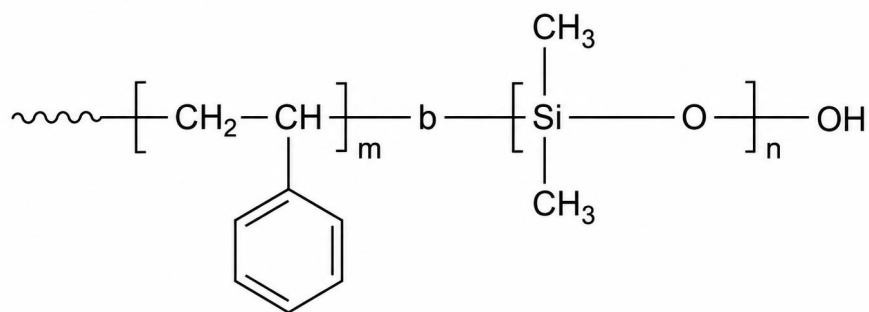


Figure 2.7. Structural formula of a PS-*b*-PDMS block copolymer with silanol termination. m and n are the degree of polymerization for PDMS and PS, respectively.

For any lithographic application, a patterned mask is required in order to transfer the required pattern into the substrate. In block copolymer lithography, one of the polymer species is selectively removed after microphase separation, resulting in the nanopatterned mask. In the case of PS-*b*-PDMS, PDMS is a highly etch-resistant block, and PS can be removed easily. When treated in an oxygen plasma, the high density of silicon in PDMS results in large etch

contrast between PS and PDMS. The PDMS blocks can be selectively oxidized to silicon oxide nanopatterns, which can be used as a hard mask for pattern transfer [17]. Thus, the high- χ and high etch selectivity of PS-*b*-PDMS block copolymers have attracted much attention in the nano-fabrication community.

2.4.1 Role of top/bottom-coat as a neutralizing layer

As discussed in Section 2.1, the morphology resulting from the microphase separation depends on various factors, among which are the surface energies at the interfaces to the ambient atmosphere and the substrate. It is therefore possible to influence the nanostructure by applying a top or bottom cover layer. A neutral layer is defined as a surface that exhibits equal interfacial energies toward both polymers, thereby eliminating preferential interactions. The use of such neutral layers as a top or bottom coating layer promotes an energetically favorable perpendicular orientation of polymer domains. In the absence of a neutralizing layer, one of the polymer blocks preferentially wets either the substrate or the air interface due to differences in interfacial energies. If the substrate is neutral with respect to the polymers, then an additional bottom neutral layer is not required. In that case, a top coat can be used to suppress preferential wetting at the free surface, thereby preventing the formation of a wetting layer by the polymer block with lower interfacial energy at the free surface.

In PS-*b*-PDMS thin films, PDMS ($\approx 20.4 \text{ mN m}^{-1}$) has a lower surface energy than PS ($\approx 40.7 \text{ mN m}^{-1}$) [23], and it tends to accumulate at the air interface [29]. This covers the underlying structure, which means that the structure after microphase separation will be covered by a PDMS wetting layer. In order to prevent the formation of a PDMS wetting layer, a top coat can be applied with a surface energy that lies between the surface energies of the polymers involved. In this work, we used polyvinyl alcohol (PVA, see Section 3.1 for more details) as a top coat. The surface energy of the PVA can be tuned by the degree of hydrolysis, which refers to the fraction of acetate groups converted into hydroxyl groups along the polymer chain. A partially hydrolyzed PVA, e.g., 40% degree of hydrolysis, exhibits intermediate surface energy and balanced interactions with both PS and PDMS, making it suitable for suppressing the preferential wetting and promoting the desired domain orientation in the thin film [29, 30].

2.4.2 Implications of solvent selectivity for PS-*b*-PDMS

During solvent vapor annealing, solvent selectivity refers to the preferential interaction of a solvent with one polymer block over the other in a block copolymer system. A selective solvent preferentially swells one block, while a non-selective solvent interacts similarly with both blocks. This selectivity plays a crucial role in determining the swelling behavior of the block

copolymer film. Solvent selectivity is determined by differences in thermodynamic interactions between the solvent and individual polymer blocks. To quantify these interactions, the solubility of the polymer in a given solvent must be considered.

A quantitative framework was established by Hansen [85] in 1967 to check the compatibility of the polymer and the solvents. The Hansen solubility parameter (HSP) theory splits the total solubility into three contributions: polar interactions δ_p , dispersion forces δ_d (van der Waals interaction), and hydrogen bonding tendency δ_h of both solvent and polymer species [85]. These three contributions define a three-dimensional space (Hansen space), in which both solvents and polymers can be represented. A polymer is described by a solubility sphere that defines the range of compatible solvents, as illustrated in Figure 2.8. In the Hansen sphere, a polymer is represented by a solubility sphere centered at its Hansen parameters (δ_d , δ_p , δ_h), which define the position of the polymer in the three-dimensional space. The radius of the sphere is R_0 , which is defined as the interaction radius and is considered the maximum distance at which a solvent is considered to be compatible with the polymer. The value of R_0 is typically determined experimentally by solubility tests. A solvent with parameters close to or within this Hansen sphere exhibits good compatibility and can effectively dissolve or swell the polymer [84]. The compatibility between a polymer p and solvent s is evaluated using the Hansen distance R_a , which is expressed as [85]:

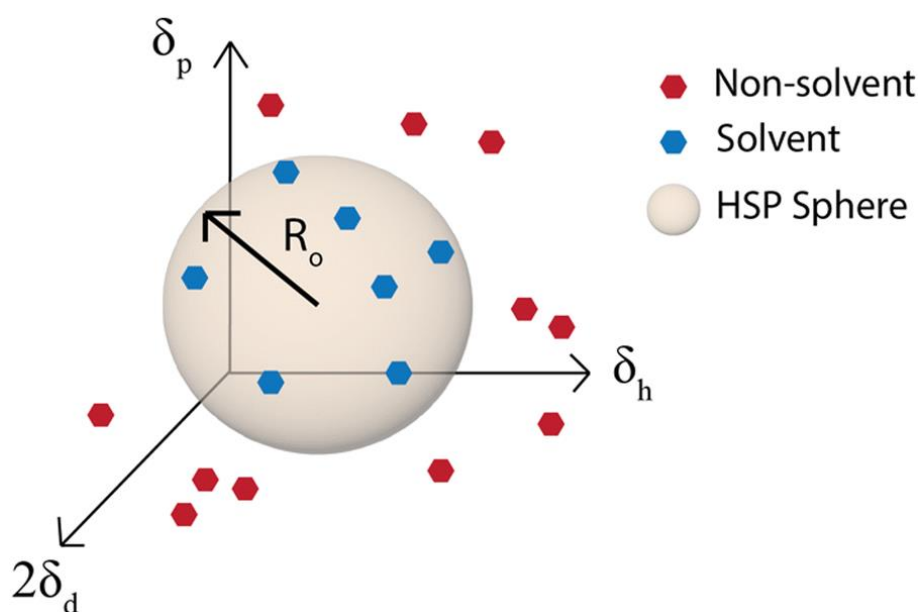


Figure 2.8. Illustration of the Hansen sphere in three-dimensional Hansen space for a specific polymer defined by polar δ_p , dispersive δ_d and hydrogen bonding δ_h interactions. R_0 denotes the interaction radius, defining the boundary of the Hansen sphere within which solvents are considered compatible [84].

$$R_a = \sqrt{4(\delta_{dp} - \delta_{ds})^2 + (\delta_{pp} - \delta_{ps})^2 + (\delta_{hp} - \delta_{hs})^2}. \quad (2.7)$$

For predicting the compatibility of a polymer and a solvent, one should consider the interaction radius R_0 along with the Hansen distance R_a . This comparison is referred to as the relative energy difference RED, which is the ratio of the Hansen distance to the interaction radius ($RED = R_a/R_0$). If $RED < 1$, the solvent lies in the Hansen sphere and is considered compatible, leading to dissolution, and in cases where $RED > 1$, the solvent lies outside the sphere and is considered poorly compatible [84, 85]. In general, a polymer is considered to be compatible with a solvent when the Hansen solubility parameters of the two species are similar [86]. This results in a favorable interaction and increased swelling of the polymer block when used in an SVA setup.

The strong chemical contrast between PS and PDMS results in different affinities for common organic solvents. Table 2.1 summarizes the Hansen solubility parameters for PS, PDMS, and the solvents used in this work. The individual solubility parameter values indicate differences in the polymer-solvent interaction. For example, toluene exhibits a dispersion-dominated interaction similar to PS. Similarly, n-heptane has a nonpolar character comparable to PDMS. In contrast, acetone possesses strong polar and hydrogen bonding contributions, indicating less compatibility with both polymer blocks. A similar trend is also reflected in the Hansen distances. Toluene exhibits comparable Hansen distances with both PS and PDMS, resulting in comparable swelling of both domains. Thus, toluene behaves as a non-selective (neutral) solvent. On the other hand, n-heptane has a significantly smaller Hansen distance with PDMS compared to PS. As a result, it has a stronger affinity for PDMS and swells it selectively. Acetone shows a comparatively large Hansen distance, especially with PDMS, implying weaker compatibility and limited swelling ability compared to toluene.

Table 2.1. Hansen solubility parameters (δ_d , δ_p , δ_h in $\text{MPa}^{1/2}$) and Hansen interaction distance (R_a) [85] between the solvents used in this work and PS and PDMS, respectively.

Solvent/Polymer	δ_d	δ_p	δ_h	R_{a-PS}	R_{a-PDMS}	Selectivity
Toluene	18.0	1.4	2.0	5.2	5.0	Neutral solvent
N-Heptane	15.3	0.0	0.0	8.7	4.2	PDMS selective solvent
Acetone	15.5	10.4	7.0	6.7	10.8	Non-solvent
PS	17.6	6.1	4.1			
PDMS	15.9	0.0	4.1			

Thus, the choice of solvent affects the effective volume fraction, domain orientation, and domain spacing in block copolymer thin films [2, 78]. The solvent should be selected such that either both PS and PDMS are swollen comparably (neutral swelling) or a controlled degree

of selective swelling is achieved. Mixing solvents in a specific ratio helps in tuning both the swelling behavior and the effective solvent selectivity for the system. For example, mixing a neutral solvent such as toluene with a selective solvent like n-heptane allows tuning of the relative swelling for the PS and PDMS domains [64]. To summarize, differences in polymer-solvent interaction influence the swelling behavior during the solvent vapor annealing, which can be used to steer the final morphology of the PS-*b*-PDMS block copolymers.

2.5 Directed self-assembly of block copolymers

The local positioning and long-range order of block copolymer (BCP) patterns can be controlled using various external fields and boundary conditions such as mechanical strain, electric fields, chemical or topographical pre-patterns [87–90]. The process of guiding the self-assembly of the block copolymer domains using such strategies is referred to as directed self-assembly (DSA). Block copolymers can spontaneously self-assemble upon annealing into periodic nanostructures; however, this often results in limited long-range order and defects. Here, the defects refer to deviations from the ideal periodic arrangement of nanodomains, such as dislocations, disclinations, and grain boundaries, which disrupt the long-range order [59]. Directed self-assembly techniques can be employed to overcome these limitations, thereby improving the long-range order and controlling the orientation of the polymer domains relative to the substrate. Most frequently used DSA techniques employ pre-patterned substrates to guide the self-assembly into well-ordered nanostructures with controlled orientation and placement [36, 37]. These approaches enable precise control over both orientation and ordering of the block copolymer domains, which is essential for nanolithographic applications.

By introducing guiding patterns, a physical or chemical constraint arises, and this directs the self-assembly of block copolymer domains. Within the prepatterned-based directed self-assembly, two primary approaches are distinguished: graphoepitaxy and chemoepitaxy [36]. In graphoepitaxy, topographical features such as trenches or grooves are fabricated on the substrate surface. This pre-patterned surface can confine the BCP thin film and guide the order and alignment of the polymer domains. In contrast, chemoepitaxy employs patterns of chemically modified and unmodified regions. In such cases, one of the polymer blocks preferentially interacts with the chemically modified regions, resulting in controlled alignment of polymer domains with respect to the underlying substrate. In DSA, the characteristic length scale of the guiding pattern is typically much larger than the natural domain spacing L_0 of the block copolymers.

In block copolymer lithography, topographical trenches are widely used for pattern rectification. When BCP films are confined in pre-patterned trenches, the trench geometry and the

polymer block interaction with the trench side walls govern the orientation of domains [37]. Long-range alignment of the cylindrical or lamellar domains along the trench direction defined by trench geometry can be achieved if the trench width is commensurate with the natural domain spacing of the block copolymer. Typically, well-ordered domains are achieved if the trench width W is equivalent to an integer multiple of the domain spacing, i.e., $W = nL_0$, where n is an integer [36]. In practice, only a limited range of integer multiples of n leads to well-ordered structures, as deviations from commensurability introduce defects. Such confinement improves the overall ordering of the nanostructures, while reducing the defect density [37].

A conceptual example of DSA using chemical and lithographical prepatterning is depicted

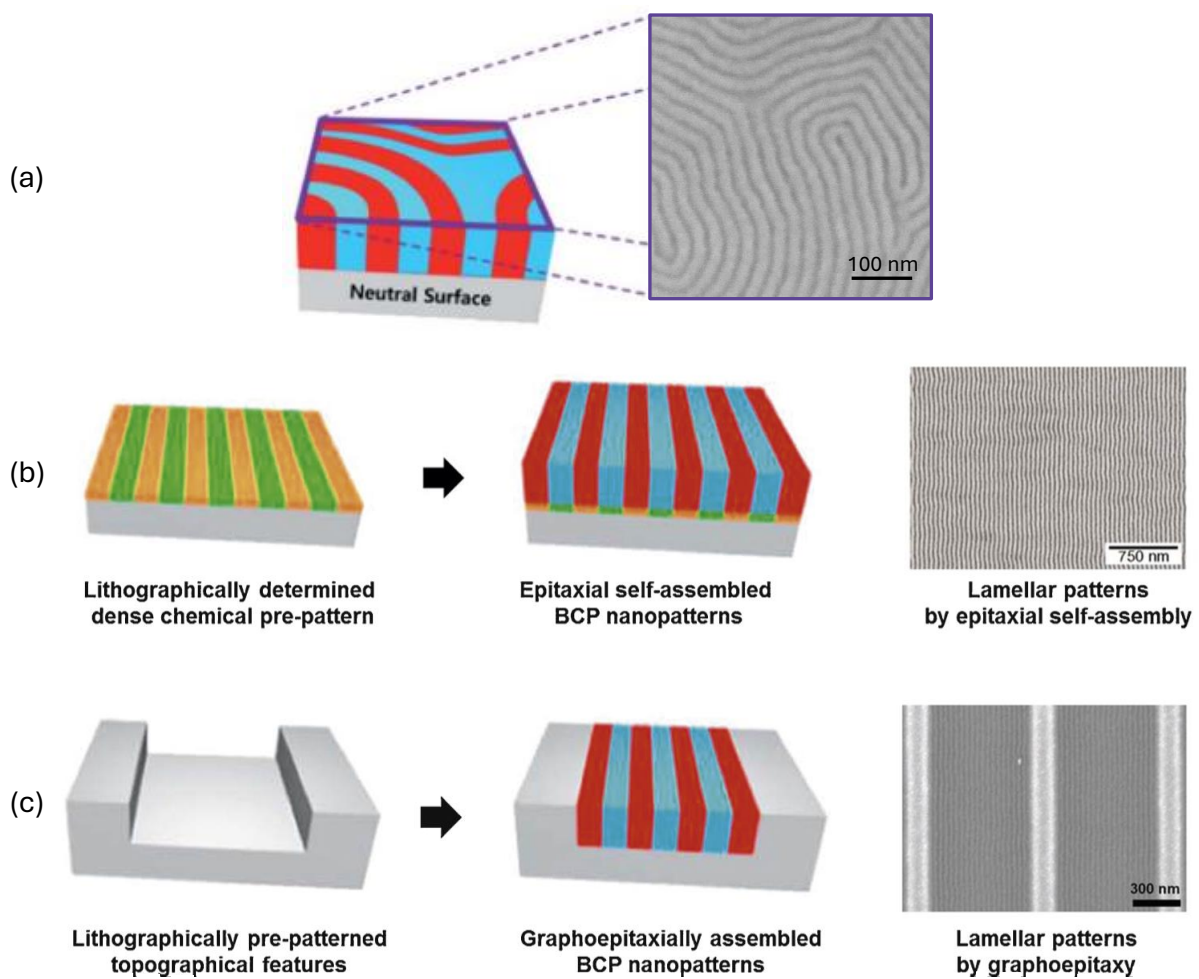


Figure 2.9. Conceptual illustration of directed self-assembly (DSA) using chemical and topographical guiding patterns. (a) A lamellar-forming block copolymer with fingerprint-like structures on a neutral nonpatterned substrate. (b) Guiding the polymer domains by a chemically prepatterened surface (chemoepitaxy). (c) Aligning the polymer domains in the prepatterened trenches created by conventional beam lithography (graphoepitaxy) [91].

in the Figure 2.9 [91]. Figure 2.9 (a) shows a sketch (left) and a scanning electron microscopy (SEM) image (right) of a lamella-forming block copolymer with a fingerprint-like structure. Firstly, it is modified by a chemical prepatter as illustrated in the sketch in Figure 2.9 (b) (left). The resulting structures after phase separation align straight as shown in the SEM image in Figure 2.9 (b) (right). Similarly, when pre-patterned with trenches by conventional lithography (left Figure 2.9 c), the lamellar block copolymer domains align straight along the side walls of the trenches, as illustrated in Figure 2.9 (c) (middle and right).

Directed self-assembly has gained significant attention in nanofabrication as it combines the high-resolution patterning capability of block copolymers with the position control ability of conventional lithographic patterning. Thus, it is considered a promising technique for next-generation lithography and nanodevice fabrication as it enables the fabrication of highly ordered nanopatterns over large-scale areas [37, 59]. In this work, graphoepitaxy was explored by fabricating trenches using electron beam lithography and subsequently combining them with BCP lithography to investigate the alignment of cylinder-forming PS-*b*-PDMS BCP.

2.6 Memristive devices and resistive switching mechanisms

A memristor is a two-terminal device whose resistance depends on the history of applied voltage or current, enabling it to store information. The memristor was theoretically predicted by Leon Chua [92] in 1971 and experimentally demonstrated later by Strukov *et al.* [93], and has since emerged as a promising class of devices for next-generation electronics. In practical devices, memristive behavior is commonly implemented using resistive random access memories (RRAMs). With the increasing demand for data storage, RRAMs gained significant interest due to their low power consumption, high endurance, high-speed switching, ease of fabrication, and due to in-memory computation capabilities [38, 94–96]. The fabrication of such a device is easy, as the basic structure consists of an oxide material inserted between two or more metallic layers which is commonly referred to as a metal-insulator-metal (MIM) structure [97].

A RRAM-based memristor operates based on resistive switching, where the device transitions between a high resistance state (HRS) and a low resistance state (LRS) under an applied electric field. The switching is typically governed by the formation of a conductive filament within an insulating matrix, driven by ionic migration or vacancy transport [98]. Two primary switching mechanisms relevant to this work are electrochemical metallization (ECM) and valence change memory (VCM) mechanism, as illustrated in Figure 2.10. The type of mechanism depends on the material system and electrode configuration.

Although the working mechanisms of both electrochemical metallization and the valence

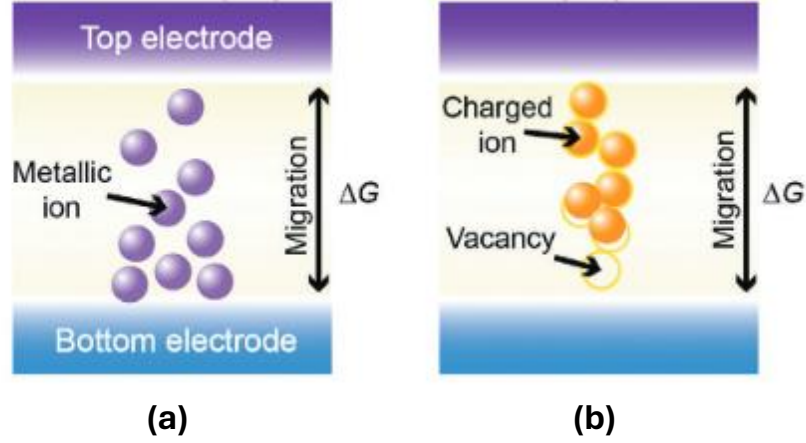


Figure 2.10. Schematic illustrating two different resistive switching behaviors, (a) electrochemical metallization mechanism (ECM) and (b) valence change memory (VCM) mechanism [98].

change memory mechanism are different, both switching processes rely on the formation and rupture of conductive filaments within the insulating layer. In ECM-based systems, an active metal electrode such as Ag or Cu undergoes oxidation, resulting in the migration of metal ions (Figure 2.10 a) through the dielectric layer under an applied electric field which then forms a metallic conductive filament. In the case of VCM-based systems, the conduction originates from the redistribution of oxygen vacancies under the application of an electric field. Here, the accumulation and migration of the vacancies (Figure 2.10 b) leads to the formation and rupture of the conductive filament. In both cases, switching behavior is governed by localized nanoscale processes, making the device highly sensitive to structural variations. These devices are promising for future non-volatile memory technologies, and their compatibility with the conventional CMOS fabrication process makes them attractive for large-scale integration. Based on these mechanisms, the resulting current–voltage (I–V) behavior is discussed in the following.

The characteristic I–V behavior of a memristor is shown schematically in Figure 2.11. The discussion below focuses on bipolar resistive switching, in which the set and reset transitions occur at opposite voltage polarities, since this is the dominant mode for the ECM and VCM systems relevant to this work. Starting at zero voltage in the high resistance state or off state, a positive voltage sweep produces a small current until V_{set} is reached. At V_{set} , a conductive filament forms abruptly and the device switches to the low resistance state or on state. The device remains in the LRS as the voltage is returned to zero, providing the non-volatile memory characteristic of the memristor. As the negative voltage reaches V_{reset} , the filament ruptures and the device returns to the HRS. The resulting hysteretic I–V loop passing through the origin is the defining signature of bipolar resistive switching, and the resistance state is retained as a

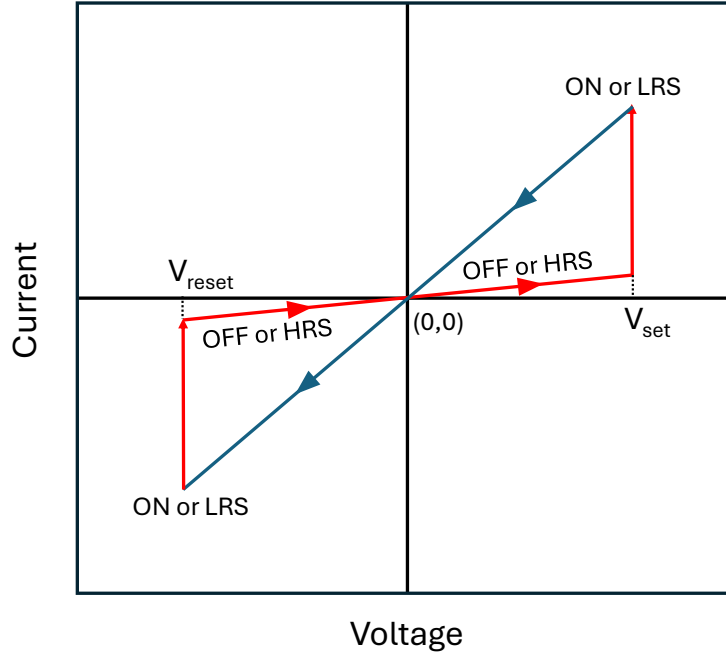


Figure 2.11. Schematic illustration of I–V curve for a bipolar memristor showing resistive switching between a high resistance state (HRS/OFF state) and a low resistance state (LRS/ON state). Increasing the applied voltage to the set voltage (V_{set}) causes the formation of filaments, and the device switches from HRS to LRS. During the reverse voltage sweep, the device remains in the LRS until the conductive filament ruptures at the reset voltage V_{reset} , causing the device to switch back to HRS.

memory even when no voltage is applied [99, 100].

Silicon dioxide (SiO_2)-based MIM systems have significant importance for memristor applications. One of the most widely used dielectric materials in semiconductor technology is SiO_2 due to its excellent insulating properties, chemical stability, and full compatibility with the CMOS fabrication process. When used in the MIM memristive system, SiO_2 serves as an excellent insulating material where switching occurs through the formation and rupture of filaments in the SiO_2 layer [101].

However, a major challenge in RRAM technology is the unpredictability of conductive filament formation. Additionally, the switching behavior is sensitive to local electric field distribution and nanoscale structural inhomogeneities within the active layer [102]. As a result, precise control of the nanoscale geometry and material distribution is essential in achieving uniform and reliable device performance. By nanopatterning the insulating material in a memristive device, precise and controlled formation of filaments can be achieved, thus forming a high-density memory device [103]. This is where block copolymer lithography becomes highly relevant in memristive applications, because controlled and ordered formation of nanostructures can be

achieved. Such nanopatterning is expected to influence filament formation across different switching mechanisms, since the geometric confinement of the active region affects the spatial nucleation of conductive filaments, while the underlying chemistry of their formation remains mechanism dependent.

3 Experimental Details

This chapter describes the materials used in this work and the experimental procedures employed. This includes sample preparation, solvent vapor annealing (SVA) processes to create periodic nanostructures, and the subsequent processing steps. In addition, the procedures for directed self-assembly of block copolymers, for transferring a monolayer of graphene, and for vibratory polishing of chromium are detailed.

3.1 Materials

Substrate used in this work were Czochralski grown silicon wafer with (100) orientation and the native oxide present at the surface. Two different PS-*b*-PDMS block copolymers and a PDMS homopolymer were used in this study. Their molecular mass, polystyrene fraction, and polydispersity index (PDI) are listed in Table 3.1. All polymers were purchased from Polymer Source Inc. (Canada). Analytical grade cyclohexane (99.5%, Carl Roth, Germany) was used for the preparation of polymer solutions. BCP films were prepared by spin coating PS-*b*-PDMS solution in cyclohexane onto the substrate surface. For PS-*b*-PDMS with a molecular weight of 16 kg/mol, a concentration of 0.5 wt% was used, whereas concentrations of 0.2 wt% and 0.5 wt% were used for PS-*b*-PDMS with a molecular weight of 21 kg/mol. The spin speeds of both BCP systems were calibrated by ellipsometry measurements and are provided in the supplementary information A.2.1.

For the creation of a neutral top-coat at the surface of BCP to air, polyvinyl alcohol (40% hydrolyzed) was purchased from Alfa Chemistry (USA). The PVA films were created by spin coating a 5 wt% PVA solution in a 1:1 water:methanol mixture at 2000 rpm, resulting in a PVA film thickness of 300 nm. To create a bottom coat, PDMS brush layers were created by spin coating 1.0 wt% PDMS in cyclohexane onto the substrate at 5000 rpm. The film was then annealed at 160 °C for 24 hours at a pressure of 10^{-6} mbar. During this step, the PDMS molecules near the surface graft to the substrate oxide layer, forming a polymer brush. The unbound PDMS molecules are removed by immersing the sample in cyclohexane for 30 minutes. For achieving homogeneous and thin polymer films, a Labspin6 spin coater (SÜSS Microtec, Germany) was

Table 3.1. Specification of block copolymers, PDMS brush, and PVA used in this work.

Polymer	Molecular mass (kg/mol)	Volume fraction of PS	PDI
PS- <i>b</i> -PDMS	16	0.68	1.05
PS- <i>b</i> -PDMS	21	0.72	1.03
PDMS brush	0.8	0	1.09

Material	Molecular mass (kg/mol)	Degree of hydrolysis (%)	Purity (%)
PVA	72	40	96

used. The rotation speed can be varied from 1 rpm to 8000 rpm in steps of 1 rpm.

For graphene transfer, CVD-grown atomic monolayer graphene on a copper foil of 18 μm thickness with 80 nm PMMA on top was purchased from Graphenea (Spain). Sodium persulfate and glacial acetic acid (Carl Roth, Germany) were used as an etchant for copper and PMMA, respectively. All other chemicals used in the work were purchased from local providers.

The BCP self-assembly process was initially performed on silicon (100) with a native oxide for optimizing the annealing parameters, resulting in well-ordered nanostructures. In addition, experiments were also performed on chromium, titanium, molybdenum, and ruthenium as substrates. All the mentioned metals were deposited on the silicon substrate by electron beam evaporation and were purchased from Kurt J. Lesker Company (USA). A Winter Vakuumtechnik 300 L electron beam evaporator was used to deposit all the metal films used in this work. The evaporation process was carried out with a base pressure of 1×10^{-7} mbar. Depending on the deposited material, the operational pressure varied between approximately 4×10^{-7} mbar and 8×10^{-7} mbar, while the substrate temperature ranged from 25 to 90 °C.

3.2 Block copolymer and top coat spin coating

The general experimental procedure of block copolymer lithography for surface nanopatterning is illustrated in Figure 3.1.

The lithography process begins with an ultrasonic cleaning of the substrate surface at a power of 100 W for 2 minutes at 40 °C in toluene and cyclohexane. Then, a BCP thin film is spin-coated onto the substrate surface at a controlled speed. Different spin speeds were used to obtain BCP films with varying thicknesses. In the next step, a PVA film of 300 nm was deposited onto the BCP thin film by spin coating. The sample at this stage is illustrated in Figure 3.1 (a). The sample is stored in a desiccator for one day to remove any residual moisture from the PVA thin film.

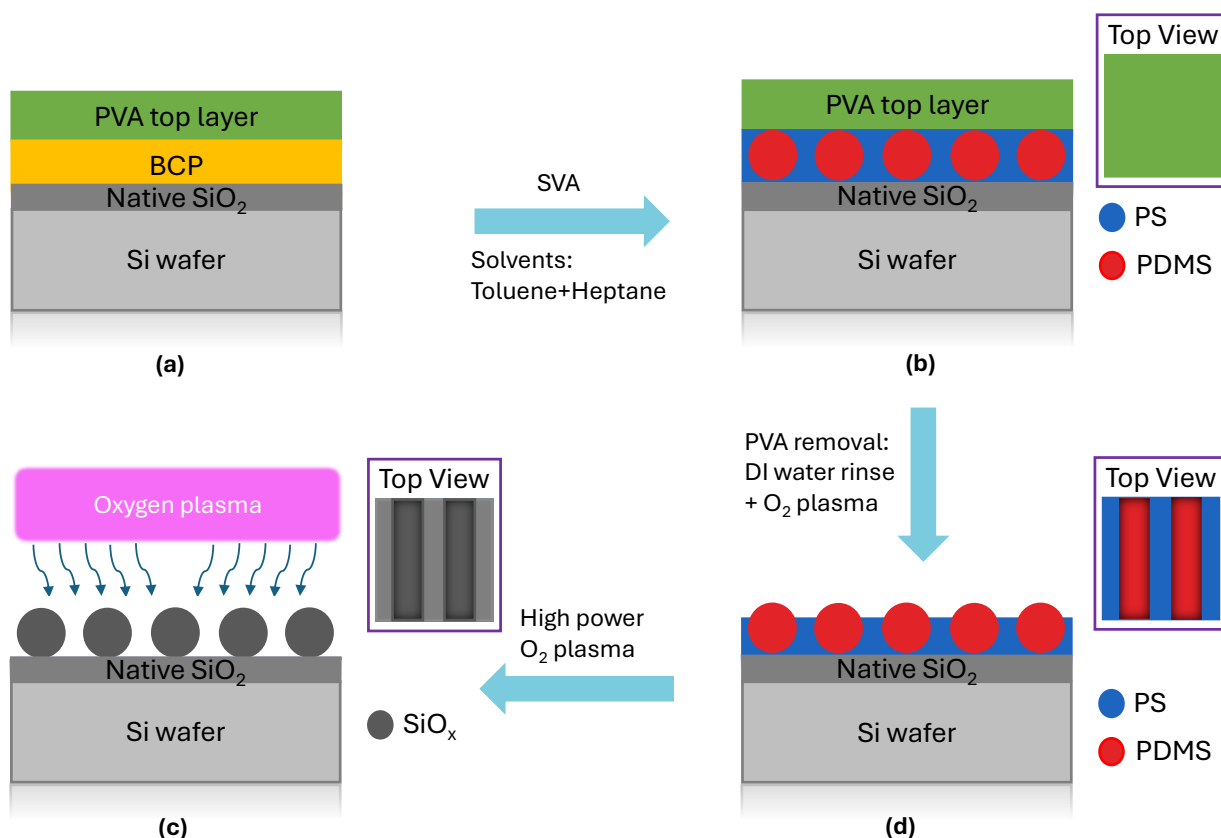


Figure 3.1. Steps in block copolymer lithography. (a) Deposition of block copolymer and PVA (for surface neutralization) film by spin coating, (b) Phase separation induced by solvent vapor annealing resulting in parallel oriented PDMS cylinders in a PS matrix, (c) Removal of PVA layer by DI water rinsing followed by a low-power oxygen plasma (plasma cleaning), (d) Removal of PS and conversion of PDMS to silicon oxide by high-power reactive ion etching, forming nanopatterned silicon oxide cylinders.

3.3 Solvent vapor annealing

Solvent vapor annealing was performed using different solvent vapors or solvent vapor mixtures, including a toluene:heptane mixture with a ratio of 5:1, prepared by mixing 25 mL of toluene with 5 mL of heptane, as well as pure acetone vapor. Process parameters such as annealing time, temperature, and solvent composition were varied to achieve well-ordered nanostructures. In this work, solvent vapor annealing was implemented in two different ways: static (Section 3.3.1) and dynamic (Section 3.3.2) SVA, which are explained previously in Section 2.3.

During the SVA, exposure to the solvent vapor causes the BCP thin film to swell. This increases the polymer chain mobility and facilitates microphase separation. The resulting film after annealing, i.e., after deswelling, contains nanophase-separated PS and PDMS. The BCP

film after nanophase separation with PDMS cylinders oriented parallel to the substrate surface within a PS matrix is depicted in the schematic in Figure 3.1 (b). The phase-separated BCP film is then stored in the desiccator under reduced pressure for one day, achieved using a prevacuum pump. This step is performed to remove any remaining solvents from the BCP film and the PVA. The PVA film is then removed by dissolving in DI water, and a low-power oxygen plasma treatment (plasma cleaning) is done to remove the remaining PVA, as shown in Figure 3.1 (c). Plasma cleaning (PC) was performed using a Tergeo Plasma Cleaner from PIE Scientific LLC (USA). This process uses 6 sccm of oxygen at 35 W RF power and a pressure of 220 mTorr. All the samples were treated for 2 minutes. During this step, the polystyrene matrix is also partially etched along with the residual PVA layer, thereby revealing the phase-separated nanostructures for further analysis.

The last step in the BCP lithography is the selective removal of PS, and this is achieved by a high-power oxygen reactive ion etching step. Reactive ion etching (RIE) processes were carried out in an Oxford Instruments Plasmalab 80Plus system (England). The high-power etching process was performed using oxygen plasma at 20 sccm, 80 W RF power, and 75 mTorr for 20 seconds. The plasma system can generate a maximum RF power of 600 W and operate at pressures ranging from 5–500 mTorr. The system is capable of handling wafers up to 200 mm. During the reactive ion etching, the PS block is removed, and the silicon-containing PDMS block is oxidized to silicon oxide as explained in Section 2.4. Thus, it forms an etch-resistant mask as shown in Figure 3.1 (d). The resulting nanopatterned silicon oxide can serve as a hard mask for further pattern transfer into the underlying substrate.

3.3.1 Static solvent vapor annealing

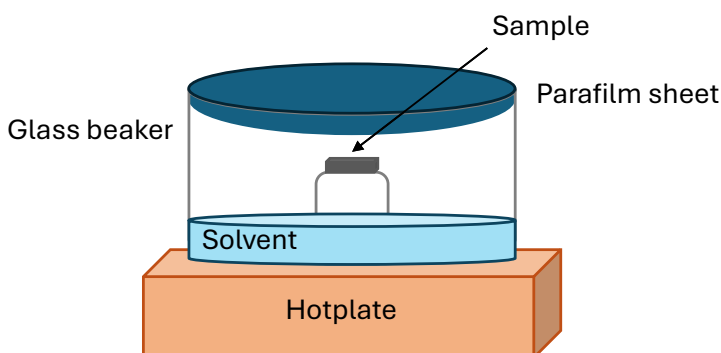


Figure 3.2. Schematic of static SVA setup used in this work.

A schematic of static SVA used in this work is depicted in Figure 3.2. The setup consists of

an annealing glass beaker filled with 30 mL of solvent, either a toluene:heptane mixture (5:1, prepared from 25 mL of toluene and 5 mL of heptane) or pure acetone. Prior to annealing, the beakers were preheated to 100 °C for 5 minutes to remove residual moisture. The samples are placed on another small beaker positioned upside down in the annealing beaker, as visible in Figure 3.2. The annealing beaker containing the solvent mixture and sample is sealed with four layers of Parafilm. The beaker is placed on a hotplate to adjust the annealing temperature. The annealing process is carried out with constant stirring of the solvent at 400 rpm using a magnetic stirrer for the whole annealing duration, which was varied from 15 minutes to 1 day. The termination of static SVA was done by removing the Parafilm and switching off the hotplate, allowing the sample to deswell.

3.3.2 Dynamic solvent vapor annealing

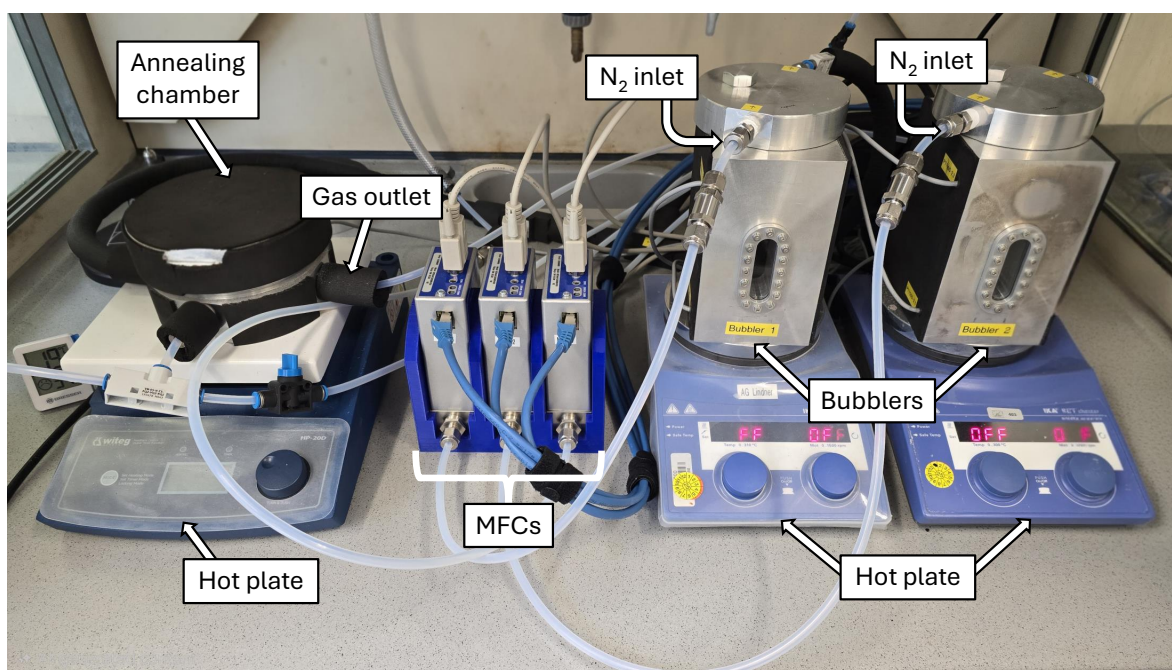


Figure 3.3. Photograph of self-built dynamic solvent vapor annealing setup.

Dynamic SVA allows control of the solvent flow in the annealing chamber as discussed in Section 2.3. A photograph of the self-built dynamic SVA setup is shown in Figure 3.3. The setup consists of an aluminum annealing chamber, two solvent reservoirs/bubblers for different solvents, and mass flow controllers (MFCs). Each bubbler is connected to a nitrogen gas line to induce bubbling of the solvent and transfer the solvent vapor to the annealing chamber. In addition, an extra nitrogen line allows to vary the vapor pressure during the swelling and

deswelling steps and to purge the annealing chamber prior to and after the annealing procedure.

In this study, a setup was developed equipped with built-in temperature sensors for the bubblers and annealing chamber, and with a microcontroller connected to a PC for controlling the whole setup via a LabVIEW-based program. The process starts by heating the annealing chamber and bubblers to the designated temperatures, followed by inserting the sample with or without the PVA top coat into the annealing chamber. The chamber is then closed and purged with 200 sccm nitrogen gas for 5 minutes to get rid of any air and moisture in the chamber. The solvent vapor mixture is then introduced to the annealing chamber by bubbling nitrogen gas through the solvent reservoir/bubblers. The annealing process is terminated by purging the annealing chamber with 10 sccm nitrogen gas for 10 minutes, enabling controlled solvent evaporation from the BCP thin film.

3.4 Graphene transfer

Graphene was transferred onto the silicon substrate to investigate the influence of an atomically thin conductive layer on the self-assembly of PS-*b*-PDMS block copolymers. Graphene transfer onto the silicon substrate was performed using a PMMA-assisted wet transfer method adapted from previously reported procedures [104, 105], with process parameters optimized for the present study. The process flow for transferring single atomic-layer graphene onto a substrate is depicted in Figure 3.4.

The purchased copper foil with graphene and PMMA on top was cut into 1 cm × 1 cm pieces using a cutting blade. The copper foil was flattened by pressing between two clean glass slides to remove any bends. To etch copper, 2 g of sodium persulfate was dissolved in 20 mL of DI water, and the copper foil was placed on the etchant surface. After 4 hours, the copper foil was dissolved, and the floating graphene supported by the PMMA film was scooped up using a silicon substrate and transferred to DI water to remove any residual etchant. Subsequently, it was transferred to the desired substrate as shown in Figure 3.4 (b). To improve graphene adhesion to the substrate, the sample was first heated to 40 °C for 30 minutes, followed by annealing at 140 °C for 1 hour at 10⁻³ mbar in a custom-built aluminum chamber heated using a hot plate. The PMMA was removed immediately after cooling down to room temperature by immersing the sample in an acetic acid bath for 3 hours at different temperatures. The sample was subsequently rinsed with acetone to remove acetic acid, and a monolayer of graphene on silicon was obtained as shown in Figure 3.4 (c). Finally, the sample was annealed at 140 °C for 2 hours at 10⁻³ mbar to remove any residual PMMA from the graphene.

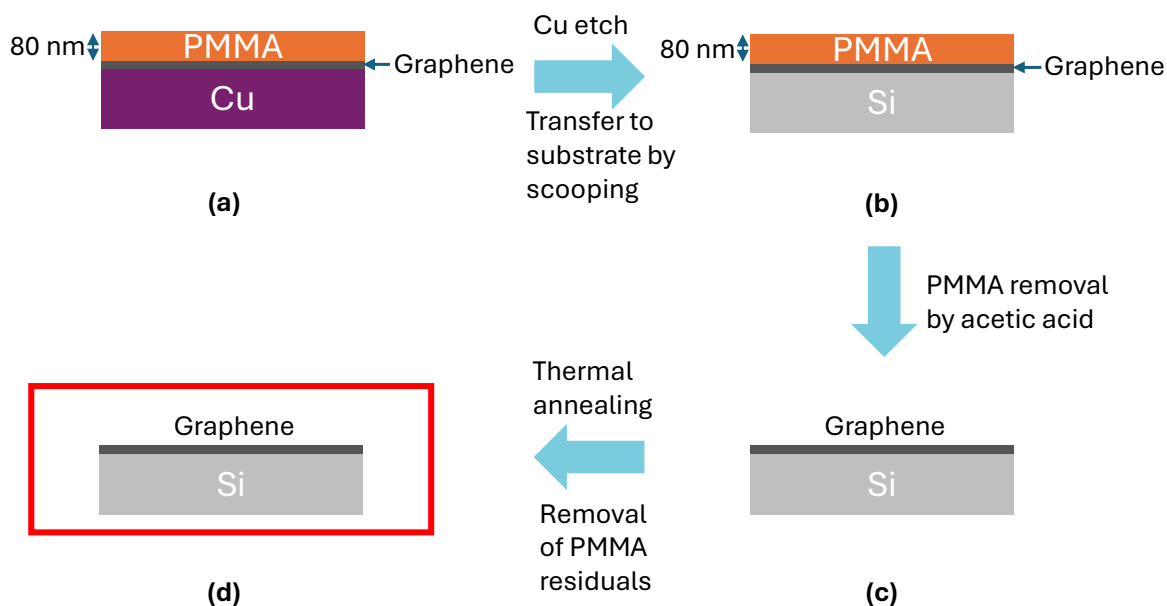


Figure 3.4. Schematic illustration of PMMA aided graphene transfer process (a) as received copper foil with graphene coated by PMMA support layer, (b) graphene/PMMA stack transferred to silicon substrate after copper etching, (c) graphene after PMMA removal by acetic acid rinsing, and (d) final monolayer graphene after annealing to remove PMMA residuals.

3.5 Fabrication of trenches for DSA

For the fabrication of rectangular trenches to guide the self-assembly of the block copolymers, electron beam lithography was utilized. The trench geometry was designed based on the natural domain spacing of the PS-*b*-PDMS BCP to promote the domain alignment within the trenches. The trench fabrication by electron beam lithography (EBL) was performed following the procedure described in [106].

The process begins with the deposition of a 100 nm thick silicon dioxide layer on a silicon substrate by PECVD, as shown in Figure 3.5 (a). This was carried out in an Oxford Plasmalab 80Plus (England) PECVD system using SiH_4 and N_2O as precursor gases, each at a flow rate of 400 sccm, with a substrate temperature of 300 °C, a chamber pressure of 1000 mTorr, and an RF power of 20 W, and for a process duration of 8 minutes 31 seconds. The PECVD parameters were selected according to an established in-house deposition protocol and subsequently optimized to achieve a silicon dioxide thickness of approximately 100 nm. The substrate was then spin-coated with the electron beam resist ZEP520A (Zeon Corporation, Japan). The resist was spin-coated at a speed of 5500 rpm to obtain a film thickness of approximately 310 nm [107], followed by a bake at 180 °C for 150 seconds on a hot plate (Figure 3.5 b). Patterning was performed with an acceleration voltage of 25 kV, and a 7.5 μm aperture with an exposure dose of 75 $\mu\text{C cm}^{-2}$ in a Raith Pioneer electron beam writer.

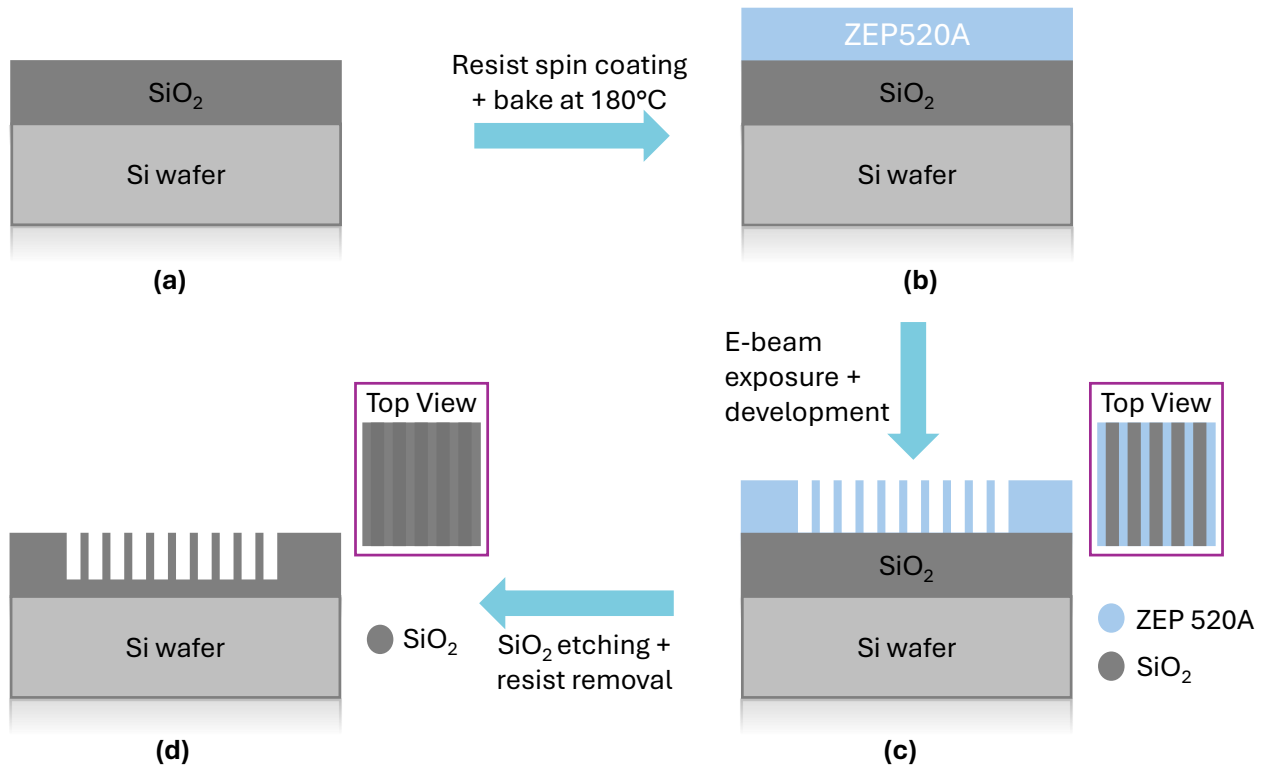


Figure 3.5. Schematic illustration of the fabrication steps for trenches produced by electron beam lithography to aid directed self-assembly. (a) Deposition of SiO₂ by PECVD, (b) Spin coating of resist ZEP520A followed by a baking process at 180 °C, (c) The resist after exposure and development in n-amyl acetate, and (d) The substrate surface post pattern transfer and resist removal.

The width W of the trenches was designed to be commensurate with the domain spacing ($W = nL_0$). Three trench geometries with different widths and inter-trench spacing were introduced to examine the influence on long-range ordering and defect density. For the PS-*b*-PDMS with a molecular weight of 16 kg/mol, two trench geometries were fabricated. The first geometry consisted of trenches with a width of 90 nm ($n=5$), where arrays of 10 trenches were patterned with a mesa width of 140 nm between adjacent trenches. The second geometry consisted of trenches with a width of 126 nm ($n=7$) and a mesa width of 200 nm. For the PS-*b*-PDMS with a molecular weight of 21 kg/mol, trenches with a width of 110 nm ($n=5$) and a mesa width of 130 nm were fabricated. In all three geometries, a 500 nm-wide spacer region was introduced after every set of 10 trenches for the resist stabilization during development.

The resist was then developed by immersing the sample in n-amyl acetate for 2 minutes, followed by rinsing in isopropyl alcohol and DI water. The patterns created after this step are depicted in Figure 3.5 (c). The patterned resist is then used as a mask to transfer the pattern to the PECVD-grown silicon dioxide by reactive ion etching. Reactive ion etching was carried out

using a CHF_3/Ar plasma in an Oxford Instruments Plasmalab 100 (England) system following an established in-house silicon dioxide etching recipe. The process was performed with a gas flow of 20 sccm for each gas, an RF power of 25 W, and a pressure of 30 mTorr. The etching time was adjusted to 7 minutes to achieve a trench depth of approximately 30 nm. The inductively coupled plasma (ICP) machine can operate with RF power up to 600 W and ICP source powers of up to 3000 W. The machine can operate at pressures ranging from 5–500 mTorr, and the system can handle wafers up to 200 mm.

Finally, the resist is removed by ultrasonically cleaning the sample in an acetone bath at 60 °C for 2 hours. Subsequently, BCP lithography was performed on the fabricated rectangular trenches on silicon dioxide (Figure 3.5 d) as discussed in Section 3.2.

3.6 Vibratory polishing of chromium

Vibratory polishing is a planarization technique that uses mechanical abrasion in combination with chemical reactions to remove metals from a thin film with extreme control. In this planarization process, the sample is subjected to a controlled vibratory motion in the presence of an abrasive slurry. As a result, the thin film is gradually thinned and polished at a controlled rate [108]. It utilizes the mechanical interaction between the abrasive particles and the sample surface, often assisted by chemical additives that facilitate material removal by softening or modifying the surface layer. For example, certain chemicals can interact with chromium, resulting in local softening at the near-surface, thereby increasing the polishing rate. Vibratory polishing is commonly used for removing surface oxides, improving corrosion resistance, deburring, and obtaining mirror-like finishes in metals [109]. This technique is also used for planarization of thin metallic films for controlled exposure of the underlying substrate.

In this work, vibratory polishing was investigated as a planarization strategy to fabricate antidots from the BCP template consisting of patterned silicon oxide cylinders (Section 5.3.1). The concept involved depositing chromium as a sacrificial layer onto a hexagonally arranged array of silicon oxide cylinders (oriented perpendicular to the substrate) by electron beam evaporation and subsequent planarization by polishing.

Vibratory polishing of chromium in this work was performed on Vibromet2 polisher from Buehler GmbH (Germany) with a fine polishing microcloth from the same vendor. Figure 3.6 shows the vibratory polishing machine with a polishing cloth fixed to the vibrating disc. The abrasive slurry was prepared by mixing colloidal silica suspension with deionized water in a 1:5 ratio to obtain a final silica concentration of approximately 8.3 wt%. The colloidal suspension used was Levasil CS50-34P, consisting of 55 nm SiO_2 particles produced by Obermeier GmbH (Germany), which has a pH range of 10–11. During the process, the sample experiences



Figure 3.6. Vibratory polishing machine with the vibrating stage and polishing cloth (left). The image on the right shows the polishing process, where the loaded sample with weights rotates in a SiO_2 colloidal suspension on the polishing cloth.

simultaneous vertical and torsional vibrations. A load of three stainless steel blocks weighing 20 g each was attached to the back side of the sample to ensure uniform contact between the sample and the polishing cloth. The amount of material removed depends on the load on the sample and the polishing time. The sample was polished for different durations to evaluate the polishing rate. After the required polishing time, the samples were cleaned by ultrasonication in acetone.

3.7 Characterization techniques

The structural, morphological, and chemical characterization of the samples was carried out using the techniques described below.

3.7.1 Ellipsometry

Film thicknesses of the polymer films were determined using an ellipsometer EL-X-02C (DRE-Dr. Riss Ellipsometerbau GmbH, Germany). A He-Ne laser with a wavelength of 632.8 nm and a measurement angle of 60° relative to the sample surface was used for the measurements. A layer system consisting of a silicon substrate, native oxide, and PS-b-PDMS film was assumed for the optical model with the Ellipsometer software, using optical data from [110–112]. The ellipsometry measurements probe a surface area on the order of a few mm^2 , providing an averaged film thickness over this region. A detailed description of the ellipsometer

can be found in [113].

3.7.2 Atomic force microscopy

Atomic force microscopy (AFM) measurements were performed using a Dimension Icon AFM (Bruker, Germany) to investigate the surface morphology of the samples. All the samples were measured in tapping mode with tips of 8 nm and 1 nm (ultra-sharp) radius. Both the tips had a resonance frequency of 160 kHz with a spring constant of 5 Nm^{-1} . The processing of the AFM data was carried out by Gwyddion (version 2.61) [114], free software for scanning probe microscopy techniques. A detailed description of AFM techniques is given in [115].

3.7.3 Scanning electron microscope

Scanning electron microscopy imaging [116] was performed using a Pioneer (Raith, Germany) microscope, with an in-lens detector. Imaging was typically carried out at an acceleration voltage of 7 kV and with an aperture of $30 \mu\text{m}$. Any deviation from these parameters is indicated where relevant. No conductive layer was deposited on the samples prior to imaging in order not to obstruct small features.

3.7.4 Transmission electron microscopy

Analytical transmission electron microscopy (TEM) was performed using a JEM ARM200F (Jeol, Japan) equipped with a cold field emission electron gun and a probe-side mounted ASCOR Cs-corrector (CEOS GmbH), allowing for the correction of geometric aberrations up to the 5th order in the scanning TEM mode [117]. All TEM images were captured at an acceleration voltage of 200 kV on a $4k \times 4k$ One-view camera from GATAN Inc. (USA). Fundamentals of TEM are described in [118].

3.7.5 Raman microscopy

Raman spectroscopy, as outlined in [119], was used to evaluate the structural quality and chemical characteristics of the transferred single-layer graphene. Measurements were performed using an InVia Renishaw Raman microscope (Renishaw, England) with a CCD detector, two lasers (532 nm and 785 nm) with corresponding gratings, and filter and mirror systems. A YAG-Laser (532 nm, 55 mW max. power) and a $50\times$ objective were used for all measurements, resulting in a lateral resolution (laser spot size) of approximately $0.76 \mu\text{m}$ and an axial

resolution below $1\ \mu\text{m}$. The laser power at the sample was measured using a calibrated photodiode power sensor (Thorlabs, Germany) and was $6.16\ \text{mW}$ [120]. A silicon wafer was used for internal calibration of the position of wave number $520.0\ \text{cm}^{-1}$ ($\pm 0.5\ \text{cm}^{-1}$).

3.7.6 DRIFT spectroscopy

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements [121] were performed using a Vertex 70 spectrometer (Bruker Corporation, Germany) equipped with a Praying MantisTM DRIFT spectroscopy setup (Harrick Scientific, USA), and a DTGS detector. The DRIFT technique can be used to obtain information about the structure and conformation of thin films, independent of any diffuse scattering within the layers. The measurements were performed with a spot size of approximately $2\ \text{mm}$. The spectra were recorded in the wavenumber range $600\text{--}4000\ \text{cm}^{-1}$ using 512 scans and a spectral resolution of $4\ \text{cm}^{-1}$. A silicon wafer was used as a reference.

3.7.7 Surface energy measurements

A drop shape analyzer DSA25E (KRÜSS GmbH, Germany) was utilized for the determination of the surface energy of different substrates. The surface energy was calculated using the OWRK method [122] with the contact angle data of three different test liquids dosed on the substrate surface. The test liquids were DI water, ethylene glycol, and diiodomethane, and their polar, dispersive, and total surface energies are presented in Table 3.2 [123]. The dosing volume of the test liquid was $5\ \mu\text{L}$ for all samples. The contact angle of each test liquid was measured on three separate spots on a $1 \times 1\ \text{cm}^2$ sample.

Table 3.2. Test liquids used in this work for drop shape analysis, with corresponding polar, dispersive, and total surface energy contributions [123].

Test liquid	Polar (mN m^{-1})	Disperse (mN m^{-1})	Total surface energy (mN m^{-1})
DI water	51.0	21.8	72.8
Ethylene glycol	16.8	30.9	47.7
Diiodomethane	0	50.8	50.8

4 Self-Assembly of PS-*b*-PDMS Thin Films via Solvent Vapor Annealing

In this chapter, the phase separation behavior of PS-*b*-PDMS block copolymer thin films with a molecular weight of 16 kg/mol, induced by solvent vapor annealing, is investigated. The influence of different process parameters on the formation and ordering of the nanostructures is systematically studied. Two different SVA techniques, namely static and dynamic solvent vapor annealing, are utilized to determine which SVA method is effective in producing the well-ordered nanostructures.

Initially, the experiments were performed on the static SVA setup because of its simpler configuration. In comparison to the dynamic SVA setup, the number of optimization parameters is limited, and the effect of individual parameters can be analyzed more easily. For this, the influence of thickness, temperature, annealing time, and solvent selection is investigated.

Dynamic SVA offers the advantage of being independent of ambient laboratory temperature and humidity conditions. Based on the optimized parameters obtained from static SVA, dynamic SVA is subsequently explored to further control the ordering of the block copolymer domains. In addition, the influence of substrate surface energy on the self-assembly behavior is investigated by conducting experiments on different substrates. Furthermore, the chemical and morphological changes that occurred in different steps of the BCP lithography process are also discussed. Finally, the PS-*b*-PDMS is utilized to explore the directed self-assembly of block copolymers.

4.1 PS-*b*-PDMS BCP phase separation by static SVA

To investigate the phase separation behavior of PS-*b*-PDMS thin films, static solvent vapor annealing was employed. Static SVA has a relatively simple experimental configuration (Section 2.3), allowing the effects of different parameters to be systematically studied. The objective is to determine suitable experimental parameters to produce uniformly ordered cylindrical structures throughout the silicon substrate surface, which is reproducible at the same time. In

the following subsections, the dependency of BCP film thickness, annealing temperature, annealing time, and annealing solvents on the resulting nanostructures is analyzed separately. For all the studies, samples after annealing were subjected to PVA removal by water rinsing, followed by plasma cleaning in oxygen plasma. Plasma cleaning removes PVA residues and partially etches PS, thereby enhancing the contrast between the nanostructures when the morphology is investigated using SEM.

4.1.1 Influence of film thickness

The nanostructures formed after phase separation depend on several parameters, as discussed in Section 2.2. Among these, film thickness plays a crucial role in determining the orientation and ordering of the block copolymer (BCP) domains. Thus, the influence of BCP film thickness on the resulting nanostructures is studied first. Since the film thickness (h) is closely related to the natural domain spacing of the polymer ($h \approx nL_0$, Section 2.2.1) in the case of lamella-forming polymers, it provides a useful guideline for selecting an initial thickness range. However, this approximation is primarily valid for parallel (lying) lamellae and may not apply to other morphologies or orientations. Therefore, initial experiments were conducted with BCP film thicknesses comparable to the natural domain spacing. The PS-*b*-PDMS used in this study has a natural domain spacing of approximately 18 nm [64, 124]. Accordingly, the BCP thin films with thicknesses ranging from 14 nm to 24 nm were investigated. The solvent for annealing was selected as a mixture of toluene and heptane with 5:1 volume ratio, as previous studies [64] report a comparable swelling of PS and PDMS with this solvent combination. Static solvent vapor annealing was performed as described in Section 3.3.1, while the annealing temperature, time, and solvent mixture were kept constant. These BCP thin films were annealed at 35 °C for 1 hour and subsequently characterized by scanning electron microscopy (SEM) after PVA removal.

Figure 4.1 shows top-view SEM images after static SVA of PS-*b*-PDMS thin film with different thicknesses. The thinnest BCP film with a thickness of 14 nm (Figure 4.1 a) reveals poorly phase-separated nanostructures without a preferred orientation. In the SEM images, the bright gray contrast corresponds to PDMS due to the silicon backbone and the dark area represents partially etched PS. The contrast arises from selective etching during oxygen plasma treatment, where the top PDMS domains are partially oxidized into a silica-like structure, appearing brighter, while the partially etched PS matrix appears darker, as commonly reported in the literature for PS-*b*-PDMS block copolymers [125]. A similar trend is visible for a 16 nm thick BCP film (Figure 4.1 b), where the contrast between PS and PDMS is a little more pronounced, but the structures are not properly oriented.

Increasing the thickness of the BCP film to 18 nm (Figure 4.1 c) shows in-plane cylindrical

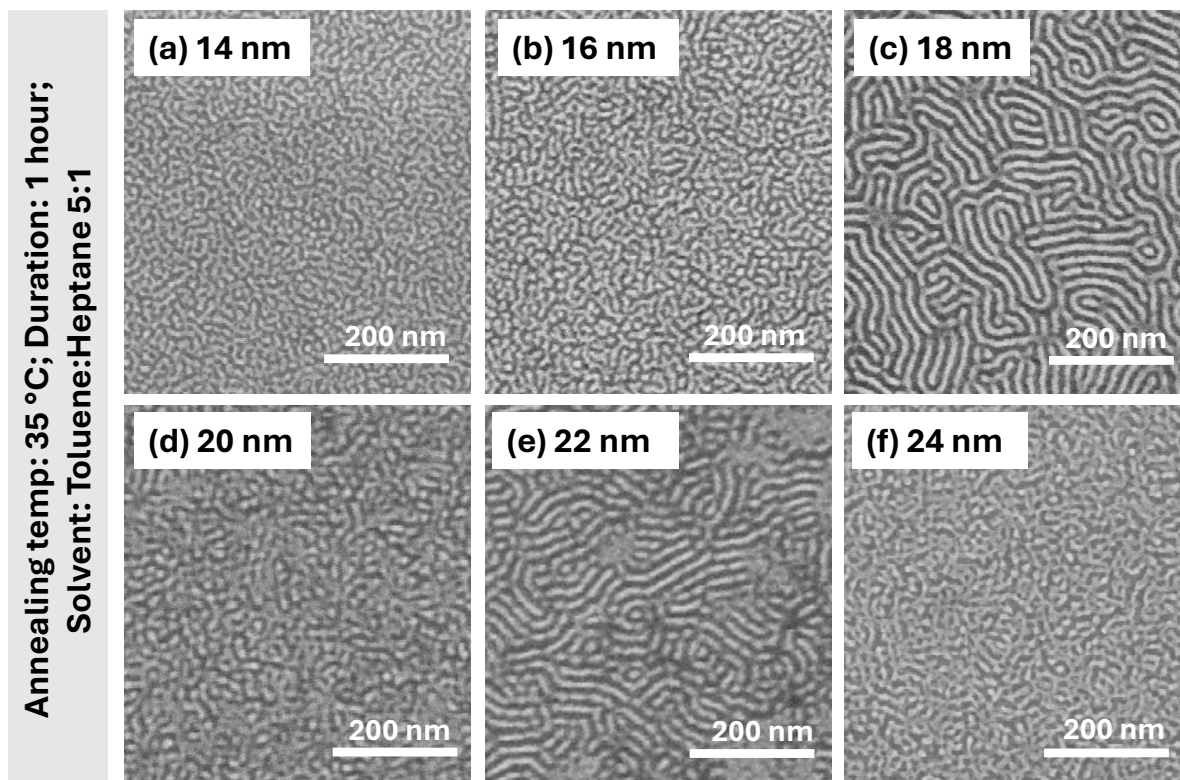


Figure 4.1. SEM top-view images of PS-*b*-PDMS BCP films with different thicknesses ranging from 14 nm to 24 nm. The static SVA is performed at a fixed temperature of 35 °C and a constant annealing time of 1 hour in a 5:1 toluene:heptane solvent mixture.

structures covering the substrate surface. The cylinders appear relatively uniform and exhibit improved domain continuity compared to the thinner films. For the 20 nm thick BCP film, the SEM image in Figure 4.1 (d) indicates a mixture of in-plane and out-of-plane cylinders which are poorly phase-separated. For the case of a 22 nm thick BCP film, Figure 4.1 (e) shows a similar morphology to 20 nm but with more in-plane cylinders. A cloud-like gray contrast on top of the structures is visible in Figure 4.1 (e). This is likely attributed to a PDMS wetting layer, as a high-power oxygen plasma afterwards was not successful in etching those structures, as it most likely converts the PDMS to SiO_x. The highest BCP thickness attempted was 24 nm (Figure 4.1 f), which also lead to poorly ordered and poorly phase-separated structures, as in the case of the thinnest film.

From the investigation for finding the optimum thickness for producing well-ordered cylindrical nanostructures, it is evident that a film thickness of 18 nm yields the most well-ordered structures. The measured average cylinder spacing of approximately 18 nm (see a detailed morphology investigation in Section 4.4.2) is consistent with the natural domain spacing (L_0) of PS-*b*-PDMS reported in the literature for perpendicular ordered cylinders [125]. However, a

direct commensurability relationship between film thickness and domain spacing, analogous to the $h \approx nL_0$ condition described for lamellar BCPs, cannot be established here, as the cylinders adopt a parallel rather than perpendicular orientation. The improved ordering at $h \approx L_0$ also reported in [35] suggests that geometric compatibility between the film thickness and the natural domain spacing plays a role in improving domain ordering, but the precise physical origin of this observation remains to be fully understood.

Although the PVA top coat was applied to modify the surface energy at the air interface and suppress preferential wetting of PDMS, perpendicular cylinder orientation was not observed. In films other than 18 nm, small isolated regions of PDMS segregation to the surface were occasionally detected (Figure 4.1 c). These features do not form a continuous wetting layer, but rather appear as localized inhomogeneities. This indicates that surface neutralization alone is not sufficient to ensure perpendicular alignment under the present conditions. The observed morphology might be attributed to the influence of various factors, such as annealing temperature and time, which might not be high or long enough to provide phase separation in all cases, as well as the substrate-polymer interactions. If the native oxide of the substrate preferentially interacts with the PS, parallel orientation will be favored, as observed for the 18 nm film in the present study. The well-ordered structures at this thickness suggest that both sufficient chain mobility and favorable thickness conditions are achieved, whereas films with thicknesses below or above 18 nm result in less ordered or mixed morphologies. In the following sections, the annealing parameters will be varied to study the influence on cylinder ordering and alignment. Based on the results, a film thickness of 18 nm was selected for subsequent experiments.

The parameter that strongly influences the swelling behavior of the polymer blocks and mobility of the polymer chains during SVA is temperature. A study was carried out by altering the annealing temperature with BCP thickness fixed at 18 nm to examine the influence on the ordering and alignment of the PS-*b*-PDMS nanostructures.

4.1.2 Influence of annealing temperature

To investigate the influence of annealing temperature on the phase separation behavior of PS-*b*-PDMS block copolymer thin films, static SVA was performed at three different temperatures, 25 °C, 35 °C, and 45 °C. The BCP film thickness of 18 nm, the annealing duration of 1 hour, and the toluene:heptane (5:1) solvent mixture were kept constant during these experiments. The nanostructures obtained from these experiments are shown in Figure 4.2.

The investigation began at the lowest achievable temperature under the given laboratory conditions. Figure 4.2 (a) shows the top-view SEM image of a polymer film annealed at 25 °C. The SEM image shows disordered structures with a mixture of partially formed cylindrical domains on the substrate. The poorly ordered and interrupted domains indicate insufficient poly-

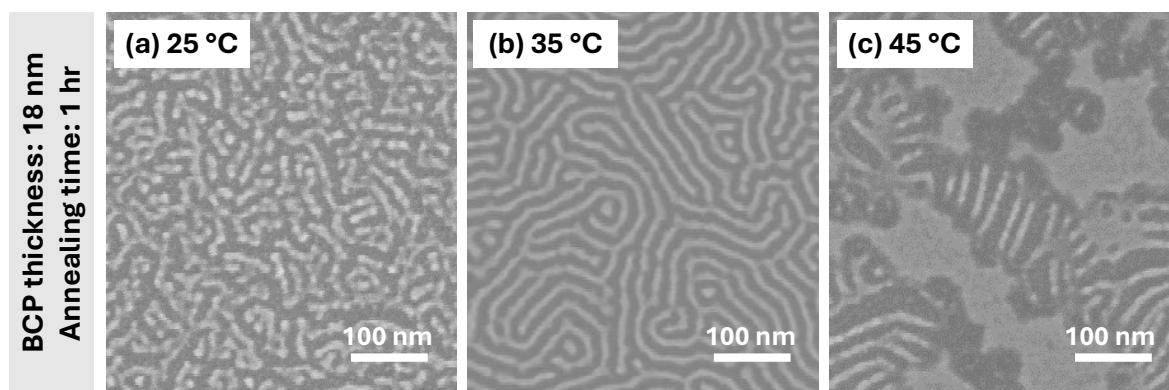


Figure 4.2. SEM top-view images of PS-*b*-PDMS BCP film annealed at different temperatures. The static SVA is carried out on an 18 nm thick film for 1 hour using a toluene:heptane (5:1) solvent mixture.

mer chain mobility for proper microphase separation. Thus, a higher temperature is required to enhance polymer chain mobility for proper phase separation. The SEM image of the sample annealed at 35 °C (Figure 4.2 b) reveals well-defined fingerprint-like cylindrical structures that are uniformly distributed across the substrate surface. The structure shows improved ordering and domain continuity compared to those obtained at 25 °C.

Upon increasing the temperature to 45 °C, partially ordered structures with island-like features are visible in the SEM image (Figure 4.2 c). This could be due to the excessive swelling of the BCP film due to the increased temperature during solvent vapor annealing. The SEM images reveal a combination of in-plane PDMS cylinders and island-like features, which are likely associated with PDMS-rich domains wetting the top surface.

To verify the nature of these island-like features, high-power oxygen plasma was used to etch the PS. If the islands consisted of PS or PVA residuals, these would be expected to be removed during the oxygen plasma process. However, the top-view SEM investigation did not show any changes in the island structures. Since PDMS gets converted to silicon oxide during this process, it exhibits a high resistance to etching. This observation suggests that the islands are unlikely to consist of PS, and are likely to be PDMS-rich regions. The BCP films were also annealed at higher temperatures (55 °C and 65 °C), and it was found that the dewetting happens at both higher temperatures as well (data not shown).

The formation of island-like features at higher temperatures can be attributed to increased solvent vapor pressure, which enhances film swelling and chain mobility. In particular, the low glass-transition temperature of the PDMS block facilitates its tendency to segregate toward the air interface in order to minimize surface energy, while also reducing the effectiveness of the PVA top coat under strongly swollen conditions. Thus, the formation of such island-like features indicates that high-temperature annealing leads to film instability and disrupts the

uniform ordering of the cylindrical domains in PS-*b*-PDMS thin film.

Investigation of the annealing temperature dependence revealed that lower annealing temperature led to improper phase separation, whereas annealing at 45 °C and above resulted in island formation between the nanostructures. Therefore, 35 °C is considered the optimal annealing temperature under the investigated conditions for creating well-ordered fingerprint-like structures. Based on the thickness and temperature optimization investigation, a film thickness of 18 nm annealed at 35 °C produced well-ordered fingerprint-like nanostructures. Thus, the next parameter to investigate and optimize is the annealing time.

4.1.3 Influence of annealing time

Annealing time plays a crucial role during solvent vapor annealing. It determines the duration over which the polymer chains can reorganize and reach an equilibrium swollen state. This section focuses on the influence of annealing time on the structures after phase separation by static SVA. Annealing thin films for shorter or longer time can have different influences on their structures. A shorter duration may not impart sufficient polymer chain mobility to swell the polymer film, whereas a prolonged duration causes excessive solvent absorption, resulting in thin film overswelling. Having found the optimal film thickness and temperature, these parameters were kept constant at 18 nm and 35 °C, respectively.

The BCP films were annealed for durations ranging from five minutes to one day and were analyzed by top-view SEM. Figure 4.3 (a) shows the top-view SEM image of the BCP film annealed for five minutes, revealing a coarse grainy structure throughout the sample surface. This indicates insufficient phase separation into polymer domains due to the very short annealing time. This annealing duration was insufficient to provide adequate chain mobility for poly-

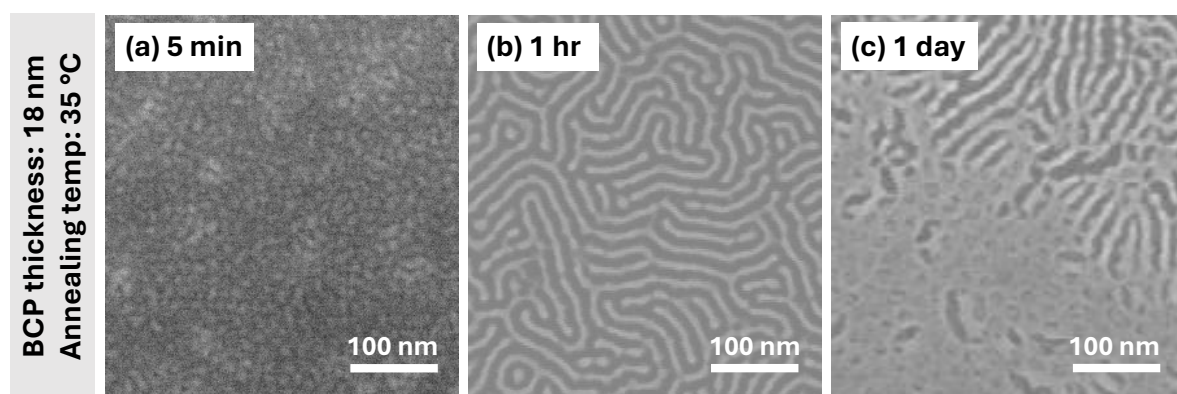


Figure 4.3. SEM top-view images of PS-*b*-PDMS BCP films with different annealing durations. The static SVA is performed on a 18 nm thick film at 35 °C using toluene:heptane (5:1) solvent mixture.

mer chain rearrangement. When the annealing time is increased to 1 hour, the SEM image (Figure 4.3 b) shows a properly phase-separated PS and PDMS domain. The in-plane PDMS cylinders are visible in bright gray in the SEM image, and the dark area corresponds to the PS. Fingerprint-like structures are uniformly arranged all over the substrate surface, indicating that sufficient time is provided for the polymer chains to reorganize. This observation is consistent with observations from the annealing temperature and thickness dependency studies (Section 4.1.2 and 4.1.1).

Upon increasing the annealing time to 1 day, the SEM image in Figure 4.3 (c) shows poorly ordered structures with significant distortions compared to the film annealed for 1 hour. Domain coarsening is visible in the SEM image, with the features appearing larger and less uniform in size at longer annealing times, suggesting that prolonged annealing leads to continued chain rearrangement and a deterioration of the initially well-defined morphology. The distorted structures observed on top of the cylindrical domains have a cloud-like appearance and are most likely polymer residues on top of PDMS cylinders consisting of thin PDMS-rich wetting layers. Their persistence after high-power oxygen plasma treatment suggests that they are not composed of PS or PVA residues, consistent with observations from the temperature dependency study.

Additional experiments at intermediate annealing times (2 hours, 4 hours, and 6 hours) show that the cloud-like structures appear from 2 hours onward. Since this behavior is not observed in the 1-hour annealed film, it develops as a consequence of prolonged annealing beyond the optimal condition. With prolonged annealing, the BCP film remains in a highly swollen state for an extended duration. Continued solvent uptake reduces the effective χN and increases polymer chain mobility in the solvent-rich film. If swelling exceeds a critical threshold, the thin film can transition into a disordered state, destabilizing the well-defined cylindrical morphology [64, 126].

Although a PVA top coat was applied to suppress preferential segregation of PDMS to the air interface, the longer annealing duration may allow partial migration of low-surface-energy PDMS blocks toward the surface. This leads to the accumulation of PDMS-rich regions at or near the surface, resulting in the observed cloud-like features. Surface segregation of the PS blocks with prolonged SVA duration has been reported for polystyrene-*b*-polylactide (PS-*b*-PLA) BCP [127] and is consistent with this interpretation.

This behavior appears to be less commonly reported for PS-*b*-PDMS under static SVA conditions and represents an empirical observation of the present study. Based on these observations, an annealing time of 1 hour was found to produce well-ordered fingerprint-like cylinders under the investigated conditions. Therefore, an annealing time of 1 hour was selected for subsequent experiments.

4.1.4 Influence of solvent selection on phase separation

Based on the static SVA optimization studies, a BCP film thickness of 18 nm, an annealing temperature of 35 °C, and an annealing duration of 1 hour were identified as the most suitable parameters for obtaining well-ordered fingerprint-like cylindrical structures using a toluene:heptane (5:1) solvent mixture. To investigate the role of solvent selectivity in PS-*b*-PDMS thin films, an additional solvent was employed. In this study, acetone was used for static SVA due to its different interactions with the PS and PDMS blocks, as discussed in Section 2.4.2. The selection of the solvent influences the swelling behavior of the polymer blocks, thereby affecting the resulting morphology. In addition, the solvent selectivity may also affect the orientation of cylindrical domains. Therefore, acetone was employed to examine whether it could promote the formation of perpendicular cylinders instead of fingerprint-like cylindrical structures observed with the toluene:heptane mixture. Acetone was chosen for this experiment because it is a non-selective solvent for both PS and PDMS compared to toluene and heptane, and has been reported to produce well-ordered structures [29, 30, 125].

Figure 4.4 shows top-view SEM images of PS-*b*-PDMS thin films annealed in acetone (a) and toluene:heptane (5:1) mixture (b). The nanostructures formed after phase separation reveal in-plane fingerprint-like structures similar to those observed for toluene and heptane solvent mixture, as visible in Figure 4.4 (b). However, the domain edges appear slightly rougher compared to structures obtained after annealing with toluene:heptane. In addition, SEM inspection across large sample areas revealed that the fingerprint structures formed with toluene:heptane appeared more continuous and less interrupted by defects. Additionally, a comparison of characteristic domain spacings for both samples shows similar L_0 values of 18 ± 1.2 nm for acetone

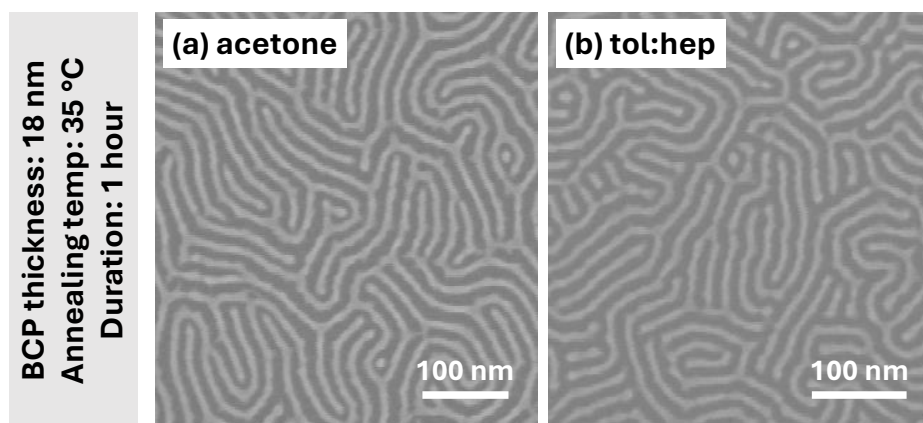


Figure 4.4. SEM top-view images of PS-*b*-PDMS BCP films annealed using (a) acetone and (b) toluene:heptane (5:1) mixture. Static SVA was performed on 18 nm thick films at 35 °C for 1 hour.

and 19 ± 1.0 nm toluene:heptane. The domain spacing was calculated from the radial distribution function of the FFT-processed SEM image. Details of the FFT-based analysis and domain spacing calculation are provided in the Supplementary Information (Section A.2.3).

Overall, the results indicate that the solvent selectivity does not significantly change the orientation of the cylindrical structures under the investigated conditions. For both solvent systems, the PS-*b*-PDMS thin films predominantly form fingerprint-like structures. Even after the optimization of the SVA parameters, the absence of perpendicular cylinders suggests that tuning these parameters is insufficient to overcome the preferential interaction between the polymer blocks and the substrate surface. Therefore, to modify the substrate-polymer interaction and promote perpendicular cylinder orientation, an additional study was conducted by altering the substrate surface energy with a PDMS brush layer.

4.1.5 Influence of substrate modification using a PDMS brush

In PS-*b*-PDMS BCP thin films deposited on a silicon substrate with a native oxide layer, the PS blocks typically exhibit a stronger interaction with the substrate. This promotes the parallel orientation of the PDMS cylinders relative to the substrate, most likely sandwiched between PS layers at the interfaces with the substrate and with the air, where PS was partially plasma-removed prior to SEM inspection. To modify the substrate-polymer interaction, a PDMS brush layer was employed to make it more attractive to the PDMS block.

To examine whether modifying the substrate surface results in an orientation change of the polymer domains, the silicon substrate with native oxide was grafted with a PDMS brush, as detailed in Section 2.4.1. PS-*b*-PDMS thin films with a thickness of 18 nm were then spin-coated onto the PDMS brush layer, followed by the PVA top coat. The PVA layer modifies the interfacial energy to air and suppresses preferential segregation of PDMS toward the free surface, thereby replacing the polymer-air interface with a polymer-PVA interface. The films were subsequently subjected to static SVA. The annealing was done using the previously optimized parameters, which resulted in well-ordered nanostructures, i.e., at 35 °C for 1 hour using the toluene:heptane (5:1) solvent mixture.

Figure 4.5 shows top-view SEM images of PS-*b*-PDMS thin films on substrates modified with a PDMS brush. Two different samples were prepared and annealed under identical conditions to check the reproducibility of the resulting structures. The two SEM images in Figure 4.5 (a) and (b) correspond to different regions of the same sample. A low-magnification SEM top-view image in Figure 4.5 (a) for sample 1 shows a mixed morphology consisting of dot-like features and partial horizontal cylindrical domains distributed across the surface. The higher magnification SEM image in Figure 4.5 (b) reveals the partial cylinder domains similar to the fingerprint-like structures observed previously without the PDMS brush layer.

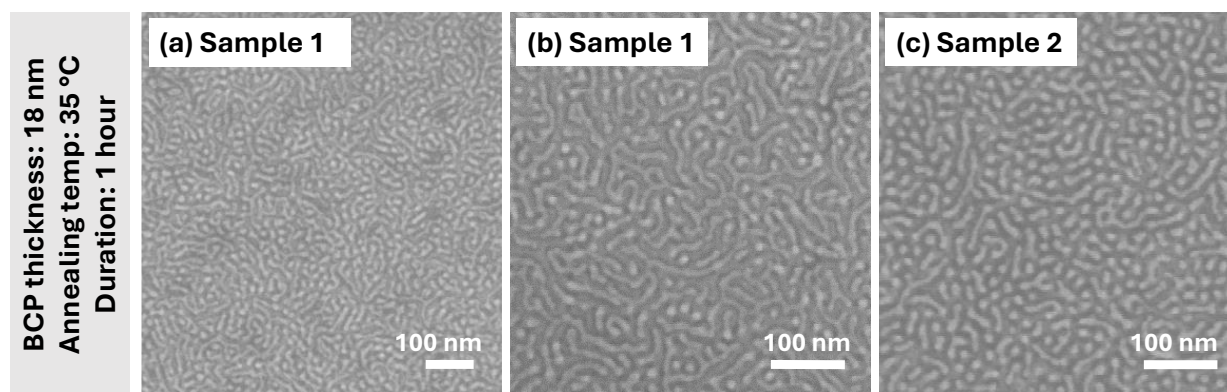


Figure 4.5. SEM top-view images of PS-*b*-PDMS thin films annealed with a PDMS brush layer grafted to a silicon substrate. (a) A low-magnification image showing the overview of the structures at the substrate for sample 1. (b) A high-magnification image of the nanostructures after SVA from sample 1. (c) A high-magnification image of the nanostructures after SVA from sample 2, processed under identical conditions to check reproducibility. Static SVA was performed separately on samples 1 and 2 with an 18 nm thick films at 35 °C for 1 hour with a PVA top coat.

The observed mixed morphology may result from the change in polymer-substrate interaction with the PDMS brush, and the presence of dot-like structures may indicate a tendency to form perpendicular cylindrical domains. However, a well-defined perpendicular cylinder morphology is not achieved under the investigated conditions. The third SEM image (Figure 4.5 c) was acquired from a different sample prepared under identical conditions. It shows a similar morphology with a mixture of dot-like features and parallel cylinder-like domains, indicating that the observed morphology is reproducible. This behavior suggests competing interfacial interactions between the substrate and the top interface.

In summary, the application of the PDMS brush layer resulted in a mixed morphology rather than fully perpendicular-oriented cylindrical domains. The introduction of the PDMS brush modifies the interfacial interactions and shifts the morphology to the expected domain direction. However, this modification alone is not sufficient to achieve perpendicular cylinder orientation, and the most homogeneous morphology observed is the in-plane cylindrical morphology achieved without a brush layer. These observations suggest that surface modification with the PDMS brush does not reliably promote well-ordered perpendicular structures in PS-*b*-PDMS thin films under the investigated annealing conditions. Further improvements in the domain morphology may be achieved by tuning the SVA parameters, such as annealing temperature or time. Alternatively, implementing a brush layer at the substrate, which is neutral to both PS and PDMS, could facilitate the formation of perpendicular cylindrical domains.

4.2 PS-*b*-PDMS phase separation by dynamic SVA

In addition to the extensive optimization of static solvent vapor annealing, which resulted in well-ordered fingerprint-like nanostructures, dynamic solvent vapor annealing was utilized to explore the domain order control as well as the possibility of influencing domain orientation. In dynamic SVA, controlled variation of the solvent vapor concentration during the swelling and deswelling stages enables continuous and precise tuning of the annealing conditions, allowing gradual adjustment of polymer chain mobility. Dynamic SVA has been reported to offer enhanced control over the domain orientation and improve long-range ordering in block copolymer thin films [72, 124].

The optimized parameters obtained from static SVA were used as a starting point to study phase separation. The experiments were carried out on PS-*b*-PDMS thin films with a thickness of 18 nm, coated with a 300 nm PVA top layer and without the use of a PDMS brush layer, at an annealing temperature of 35 °C. The SVA was performed using a toluene:heptane (5:1) solvent mixture, as this resulted in slightly better ordering of the nanostructures than with acetone as a solvent. Following the swelling step, the films were deswelled by purging with nitrogen at a flow rate of 10 sccm for 10 minutes. The influence of the dynamic SVA process on the resulting morphology and ordering of PS-*b*-PDMS nanostructures was systematically investigated.

4.2.1 Influence of solvent vapor flow rate

The most crucial parameter in a dynamic solvent vapor swelling process is the flow rate of the solvent vapor/carrier gas mixture. The flow rate determines the swelling behavior of the polymer film by controlling the rate of solvent absorption or desorption [64]. This directly influences the polymer chain mobility, which governs the morphology evolution of the phase-separated nanodomains. Therefore, the influence of the solvent/carrier gas flow rate is investigated for PS-*b*-PDMS thin films with a thickness of 18 nm. The films were annealed at 35 °C for 1 hour, with the solvent reservoirs (bubblers) maintained at the same temperature. After the swelling step, the films were deswelled by purging the chamber with nitrogen gas at a flow rate of 10 sccm for 10 minutes.

Dynamic SVA was performed on different samples with flow rates ranging from 25–400 sccm. The resulting morphologies are shown in Figure 4.6. At a low flow rate of 25 sccm (Figure 4.6 a), the nanostructures appear poorly phase-separated. The top-view SEM image reveals a grainy morphology with poorly-defined polymer domains without proper ordering. This indicates that the solvent concentration in the polymer film was too low to allow for adequate swelling of the polymer film, leading to insufficient polymer chain mobility.

Increasing the flow rate to 37 sccm, the SEM image in Figure 4.6 (b) reveals well-ordered

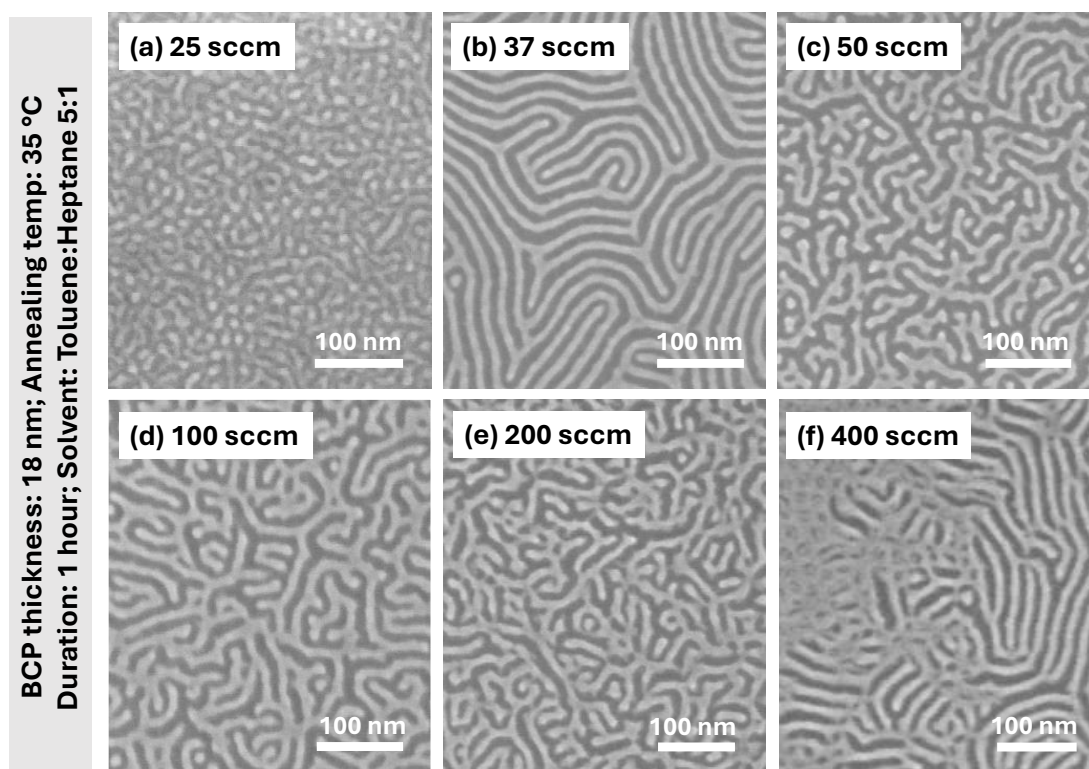


Figure 4.6. SEM top-view images of PS-*b*-PDMS thin films annealed in a dynamic solvent vapor annealing setup with different nitrogen carrier gas flow rates: (a) 25 sccm, (b) 37 sccm, (c) 50 sccm, (d) 100 sccm, (e) 200 sccm, and (f) 400 sccm. The dynamic SVA was performed on an 18 nm thick film at 35 °C for 1 hour using toluene:heptane (5:1) mixture.

fingerprint-like structures with long, continuous cylindrical domains. This indicates the solvent concentration in the PS-*b*-PDMS thin film was able to provide sufficient chain mobility for effective phase separation and domain ordering. At a flow rate of 50 sccm (Figure 4.6 c), the morphology transits to a distorted cylindrical domain. The cylindrical domain shows reduced domain continuity and increased domain spacing compared to those observed at a flow rate of 37 sccm. This increase in domain spacing is supported by the domain spacing evaluation, which showed an increase from 19 ± 2 nm to 23 ± 4 nm (see Supplementary information Section A.2.3). The transition of structures between 37 sccm and 50 sccm highlights a narrow window in the dynamic SVA process. At 37 sccm, the polymer domains attain sufficient chain mobility while having adequate time for domain reorganization, whereas at 50 sccm the increased solvent supply leads to over-swelling of the BCP film, resulting in poor ordering and increased domain spacing.

Further increasing the flow rate to 100 sccm (Figure 4.6 d), yields cylindrical domains with reduced long-range ordering. At the higher flow rates of 200 sccm (Figure 4.6 e) and 400 sccm (Figure 4.6 f), the nanostructures appear highly distorted with reduced domain definition. In

addition, segregation of polymer residuals on top of the cylinders was observed at the highest flow rate. This observation of PDMS segregation was similar to the ones from the static SVA, where the polymer film is over-swollen at the high temperature and long annealing time (Section 4.1.2 and 4.1.3). The behavior of deterioration in the morphology of nanostructures at a higher solvent flow rate is plausibly attributed to over-swelling at high flow rates. In an over-swollen state, the high solvent content reduces the effective segregation strength (χ_{eff}), which can drive the system across the order-disorder transition into a disordered swollen state [64, 72]. The subsequent rapid deswelling kinetically traps this disordered configuration, locking in non-uniform domains with increased disorder [72]. Direct measurement of the in-situ swelling would be needed to confirm this, but the proposed mechanism is consistent with the observed morphology evolution.

From these observations, it is evident that the solvent vapor flow rate during dynamic SVA plays a crucial role in producing well-ordered PS-*b*-PDMS nanostructures. A lower solvent flow rate was not able to induce phase separation due to insufficient swelling, whereas higher flow rates resulted in morphological instability. A flow rate of 37 sccm was successful in producing well-ordered fingerprint structures across large sample areas under the set conditions. This demonstrates that the flow rate is a highly sensitive parameter during dynamic SVA, and small variations in the solvent vapor flow rate can significantly influence the nanostructure morphology.

4.2.2 Influence of annealing time

After optimizing the solvent vapor flow rate during dynamic SVA, the influence of annealing duration was investigated to explore the possibilities of improving the order or changing the orientation. The dynamic SVA was carried out on PS-*b*-PDMS thin films with a thickness of 18 nm at 35 °C using a solvent/carrier flow rate of 37 sccm with a toluene:heptane (5:1) mixture. The annealing durations were varied from 20 minutes to 2 hours while the solvent reservoirs (bubblers) were maintained at the same temperature. Following this step, the polymer films were deswelled by purging with nitrogen gas at a flow rate of 10 sccm for 10 minutes, as described in the last Section 4.2.1. Top-view SEM images of the resulting structures after dynamic SVA are shown in Figure 4.7.

Figure 4.7 (a) shows the nanostructures after a short annealing time of 20 minutes. The polymer domains appear to be phase separated, exhibiting an irregular morphology. Dot-like features are visible in the SEM image and may be indicative of locally ordered perpendicular domains; however, a definitive assignment of standing cylindrical domains cannot be made based on top-view SEM alone.

Increasing the annealing time to 40 minutes (Figure 4.7 b) induced phase separation with

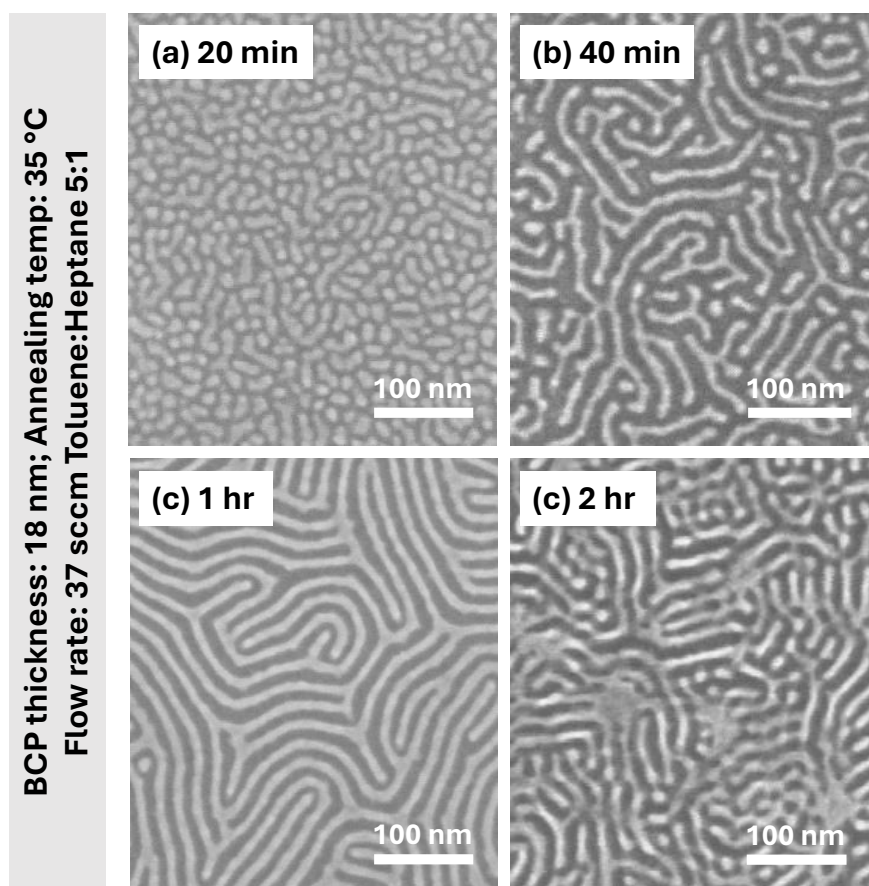


Figure 4.7. SEM top-view images of PS-*b*-PDMS thin films annealed in a dynamic SVA setup for different annealing durations, (a) 20 minutes, (b) 40 minutes, (c) 1 hour, and (d) 2 hours. The dynamic SVA was performed on an 18 nm thick film at 35 °C using 37 sccm of toluene:heptane (5:1) mixture.

parallel-oriented cylindrical structures, indicating that the system has begun reorganizing toward an in-plane orientation. However, the structures resulting include cylinders of small length resembling limited long-range order that coexist with significantly less dot-like features, suggesting that the reorientation from perpendicular to parallel domains is incomplete at this stage. At an annealing time of 1 hour (Figure 4.7 c), well-defined in-plane fingerprint-like cylindrical nanostructures are observed with significantly improved long-range order and domain continuity. This indicates that sufficient time is provided for the polymer domains to attain effective chain mobility and reorganize into energetically favorable conditions. As for the static SVA, the fingerprint pattern embedded between PS wetting layers seems to be a relatively stable low-energy configuration for 18 nm thick PS-*b*-PDMS films.

Further increase of the annealing time was done to check if the obtained nanostructures can be fine-tuned. The top-view SEM image of a sample annealed for 2 hours does not exhibit any significant improvement in domain ordering or alignment; instead, slight irregular-

ities start to appear between the in-plane cylindrical domains. The morphology corresponds to an incomplete transition toward a structure with residual polymer at the surface, similar to Figure 4.6 (f), 4.3 (c), 4.1 (e). This final state is energetically even more favourable but kinetically more difficult to reach, and is accessed only after passing through states as observed in Figure 4.6 (a) to (c). This suggests that prolonged annealing does not improve the domain ordering or alignment.

Overall, the study of annealing time dependency aided in optimizing the annealing time to achieve the best possible structure. Fingerprint structures are formed across a relatively broad window of annealing times, and an annealing time of 1 hour is sufficient to achieve well-ordered fingerprint structures. At shorter annealing times (20 minutes), the morphology is close to dot-like or perpendicular domains, while at longer annealing times the structures evolve towards in-plane cylinders. The observation of dot-like features at 20 minutes suggests that a more regular array of perpendicular cylinders may be accessible at shorter annealing times than were investigated here.

In conclusion, studies on dynamic solvent vapor annealing on PS-*b*-PDMS thin films revealed improved ordering of the nanostructures compared to the static SVA. In particular, solvent vapor flow is observed to critically influence the resulting structures, with a narrow window around 37 sccm yielding highly ordered in-plane fingerprint-like structures. Despite the improved ordering achieved through dynamic SVA, exclusively perpendicular cylindrical domains were not observed under any of the investigated conditions. Furthermore, the implementation of a PDMS brush layer was only able to achieve mixed structures with dot-like and cylindrical domains. These results indicate that, although the annealing parameters and surface energy influence the alignment of the nanostructures, they are not sufficiently tunable to overcome the intrinsic preferential interactions in this particular PS-*b*-PDMS (16 kg/mol) polymer film. Therefore, more advanced strategies, such as precise control of interfacial energies (application on different substrates) or directed self-assembly techniques, are explored to achieve perpendicular orientation of the polymer domains. This highlights the challenge of achieving perpendicular orientation in high- χ block copolymer systems such as PS-*b*-PDMS, where the strong segregation strength and interfacial interaction limit the control of domain orientation.

4.3 Self-assembly of PS-*b*-PDMS on different substrates

From the static and dynamic SVA studies, it was observed that neither the optimization of annealing parameters nor the neutralization layers was sufficient to achieve perpendicular cylindrical orientation of the nanostructures. This indicates that the substrate-polymer inter-

actions play a dominant role in determining the orientation of cylindrical domains. To further explore this effect, the PS-*b*-PDMS thin film was deposited on different substrate surfaces with varying surface energies. By modifying the substrate, the interfacial energy balance between the polymer blocks and substrate can be tuned, and this investigation aims to show whether altering the surface energy induces perpendicular orientation of cylindrical domains. Initially, the BCP lithography was performed on metallic substrates, namely chromium (Cr), titanium (Ti), molybdenum (Mo), and ruthenium (Ru). Among these, Ru is particularly relevant due to its widespread use as an electrode material in memristor structures owing to its chemical inertness, thermal stability, and good electrical conductivity [128, 129]. In such applications, Ru could serve as a bottom electrode if an appropriate BCP pattern can be fabricated.

Subsequently, graphene was selected as a substrate to examine the influence of a distinct surface chemistry on the resulting morphology. Block copolymer (BCP) lithography has been successfully implemented on graphene for applications including graphene nanoribbon fabrication [34] and pattern transfer to various substrates [35]. Therefore, understanding BCP self-assembly on graphene is crucial for enabling controlled nanoscale patterning in graphene-based technologies.

The experiments were performed using the optimized parameters obtained for annealing with the static SVA setup. An 18 nm thick BCP film with PVA top layer was annealed at 35 °C for 1 hour using a toluene:heptane (5:1) solvent mixture as described in Section 3.3.1. The resulting morphology was investigated by SEM after plasma cleaning to remove PVA residues and partially etch the PS block.

4.3.1 Metallic substrates

Metallic substrates provide a range of chemical interactions and surface energies that influence the preferential wetting behavior of the polymer blocks. To investigate the influence of surface properties, thin films of chromium, titanium, molybdenum, and ruthenium were deposited onto silicon substrates by electron beam evaporation. All metal films had a thickness of 30 nm and a root mean square (RMS) roughnesses in the angstrom range, enabling a consistent comparison of the resulting structures due to their smoothness. The AFM roughnesses were calculated from the AFM height images captured in tapping mode and are compiled in Table 4.1. This table also summarizes the surface energies and their dispersive and polar contributions for all metal films investigated. Prior to contact angle measurements and BCP deposition, all substrates were cleaned by ultrasonication in cyclohexane to ensure consistent surface conditions between surface energy characterization and thin film processing. Surface energies and their contributions were determined by contact angle measurements with three test liquids using OWRK method [122] as detailed in Section 3.7.7. The polar and dispersive surface energy

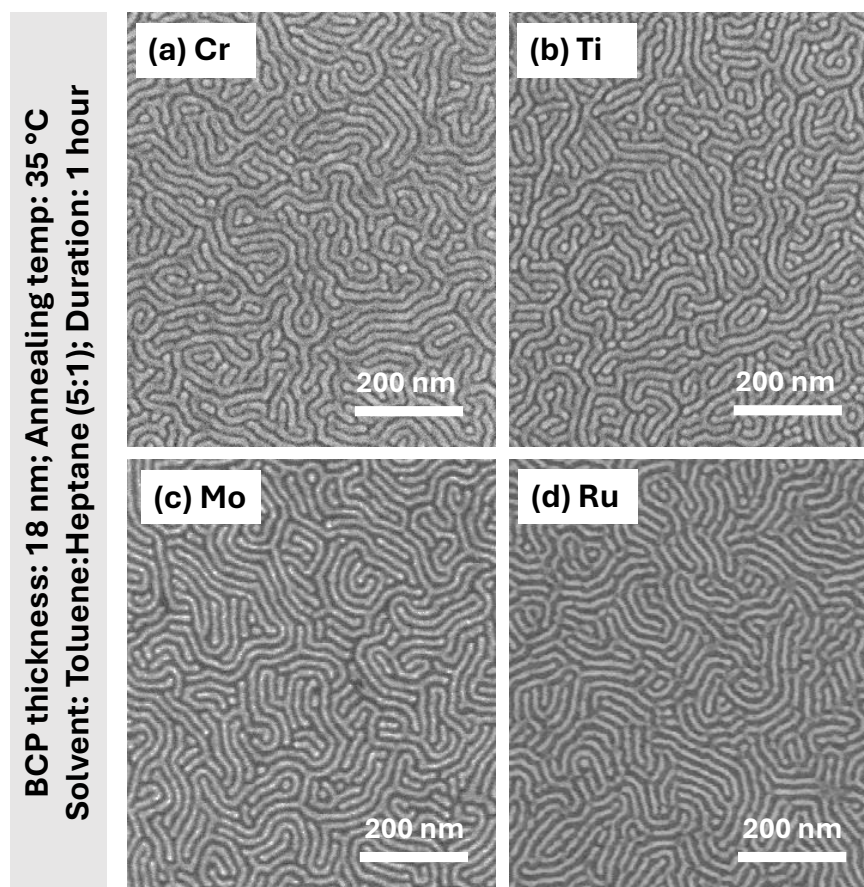


Figure 4.8. SEM top-view images of 18 nm thick PS-*b*-PDMS thin films on different metallic substrates of (a) chromium (Cr), (b) titanium (Ti), (c) molybdenum (Mo), and (d) ruthenium (Ru) after static SVA at 35 °C for 1 hour using a toluene:heptane (5:1) mixture. No brush layer was deposited prior to spin coating of BCP, and the static SVA was done with a PVA top coat. All metal films were 30 nm thick and prepared by electron beam evaporation.

components for each substrate provide insights into the interactions between each substrate and the polymer blocks. The BCP morphologies resulting after spin coating of 18 nm thick PS-*b*-PDMS and subsequent static SVA are shown in Figure 4.8.

A successful phase separation is observed on every substrate with in-plane fingerprint-like structures. This indicates that optimized annealing conditions established on a silicon substrate are also sufficient to induce microphase separation on the present metallic substrates. Nanostructures on all substrates exhibit similar morphologies and no significant difference is observed in the domain continuity or ordering.

The observed similarity in morphology can be explained by the comparable surface energies of the substrates. Table 4.1 shows that the total surface energies lie within the range of 39 mN m⁻¹ to 47 mN m⁻¹ with a noticeable difference in the polar and dispersive contributions. All investigated substrates are predominantly dispersive in nature, similar to polystyrene,

Table 4.1. Different substrate surfaces covered by their native oxides used in this study with their polar, dispersive, total surface energy contributions and RMS roughnesses. The surface energies are evaluated using the OWRK method based on contact angle measurements. RMS roughness of each substrate was evaluated from AFM height images.

Substrate	Polar	Disperse	Total surface energy (mN m ⁻¹)	RMS roughness (nm)
Silicon	11	34	45	0.2
Chromium	8	39	47	0.3
Titanium	3	36	39	0.4
Molybdenum	10	34	43	0.3
Ruthenium	2	38	40	0.3

resulting in preferential wetting of the substrate surface by the PS blocks. As a result, PS segregates to the substrate surface, forcing PDMS domains away from the substrate surface and promoting a parallel orientation of cylindrical domains. This is the primary reason for the in-plane fingerprint morphology on all the tested substrates. The polar contributions among the five substrates show small differences, with silicon and molybdenum indicating a higher value. These differences are relatively small and are therefore unlikely to significantly influence the domain continuity or ordering. Furthermore, exposure of the films to air prior to BCP spin coating results in the formation of native oxide layers on the surface. Consequently, the measured surface energies correspond to these oxide-covered surfaces rather than the pure metals.

Similar studies [58] on PS-*b*-PMMA BCPs have shown that controlling the substrate surface energy is crucial for achieving perpendicular domain orientation. In that work, SiO₂ substrates exhibited a high polar contribution (approximately 46%), which led to preferential wetting and parallel orientation of the domains. By introducing a random copolymer brush layer, the polar contribution was reduced to approximately 9%, resulting in a more neutral surface that enabled perpendicular orientation. In contrast, evaporated metal films such as gold or platinum exhibit predominantly dispersive surface character with very low polar contributions, allowing perpendicular orientation to be achieved without the need for a brush layer.

These observations highlight the importance of tuning the surface energy to control block copolymer morphology. In the present case, although all substrates exhibit predominantly dispersive surface character, the interfacial interactions are not sufficiently balanced to achieve neutral wetting conditions. As a result, oxide-covered metallic substrates preferentially interact with the PS block, leading to its segregation at the substrate interface and promoting parallel orientation of cylindrical domains.

In contrast to PS-*b*-PMMA BCPs, where reducing the polar contribution enables surface neutrality and perpendicular alignment, the present results indicate that a predominantly dispersive surface alone is insufficient to achieve perpendicular orientation in PS-*b*-PDMS thin

films. Therefore, introducing a neutral interfacial layer that provides balanced interactions for both PS and PDMS blocks could enable perpendicular orientation on these substrates.

4.3.2 Graphene substrates

The influence of substrate chemistry was also investigated by employing a monolayer of graphene as a substrate. Unlike the metallic substrates, graphene is chemically inert and atomically smooth, while also exhibiting excellent electrical conductivity. Graphene exhibits predominantly dispersive surface energy characteristics [130], similar to the investigated metallic substrates, leading to weak polar interactions at the substrate interface. Block copolymer lithography on graphene has attracted significant interest due to its potential applications in nanoelectronics, sensing, and membrane technologies [131, 132].

For preparation of the substrate, single-layer graphene was transferred onto a planar silicon substrate, as detailed in Section 3.4. The transferred graphene was characterized using AFM and Raman spectroscopy to analyze the morphology and quality of graphene after the transfer. The first part of this subsection focuses on evaluating the quality of the transferred graphene and optimizing the transfer process parameters. Subsequently, the nanostructures fabricated by BCP lithography on graphene as a substrate are discussed.

Raman spectroscopy was employed to check the structural quality of transferred graphene. In a typical Raman spectrum of single-layer graphene, three characteristic peaks are observed [133]. The G peak at 1580 cm^{-1} arises from in-plane vibrations of the sp^2 -bonded carbon atoms, indicating graphitic structure [133]. The 2D peak at 2680 cm^{-1} is a second-order overtone of different in-plane vibrations due to double phonon scattering [133]. Lastly, the D peak around 1355 cm^{-1} is associated with defect-induced scattering and indicates the presence of structural defects or disorder in the graphene lattice [133]. A low intensity or absence of the D peak confirms a high-quality graphene with minimal defects and is suitable for studying the self-assembly behavior of PS-*b*-PDMS thin film after solvent vapor annealing. This ensures that the nanostructures formed after SVA are influenced by the graphene-polymer interface rather than defects arising during the transfer process.

Figure 4.9 shows the Raman spectrum after the graphene transfer to a silicon substrate. All the characteristic peaks are clearly visible in the Raman spectrum after the transfer onto a silicon substrate with a native oxide layer. The sharp and intense 2D peak, along with an intensity ratio of the 2D peak to the G peak greater than 2 ($I_{2D}/I_G > 2$), confirms that the transferred graphene is single-layered [133, 134]. A low-intensity D peak is observed, indicating a low defect density in the graphene. The weak feature at approximately 2450 cm^{-1} is attributed to the G^* band, a two-phonon combination mode that is intrinsic to pristine graphene, and its presence does not indicate defects or contamination [133]. Thus, the transferred graphene can be considered to

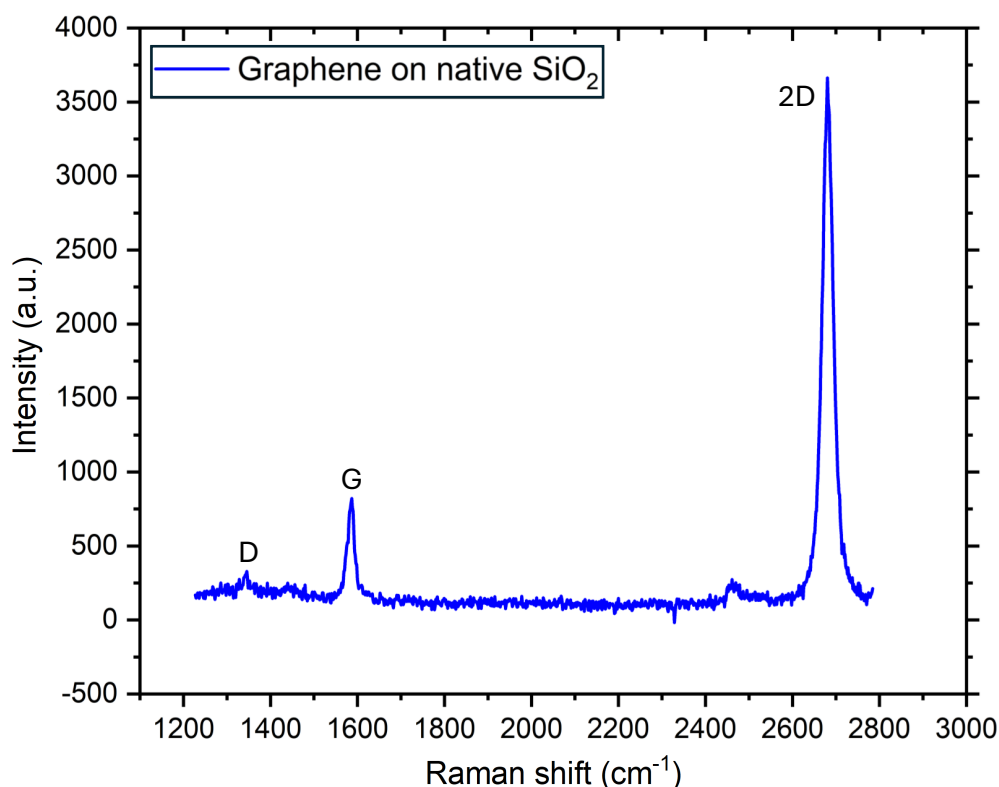


Figure 4.9. Raman spectra of graphene transferred to a silicon (100) substrate with a native oxide layer.

be of high quality, which serves as a reference for evaluating the graphene quality in subsequent optimization steps.

Before performing BCP self-assembly on the graphene substrate, it is crucial to make sure that the graphene surface is clean, i.e., free of any PMMA which is deposited by the manufacturer to protect the graphene. According to the literature [31], PMMA residuals tend to adhere to the graphene surface, and it is crucial to check the efficiency of the PMMA removal. To check this, the PMMA removal step using an acetic acid bath after graphene transfer was performed at different temperatures.

The samples were treated at 25 °C, 35 °C, and 45 °C for 2 hours and subsequently analyzed using Raman spectroscopy and AFM. Figure 4.10 shows the Raman spectra of transferred graphene treated with acetic acid at different temperatures. The Raman spectrum reveals that the sample treated at 25 °C (blue spectrum) exhibits a minimal D peak intensity and a higher I_{2D}/I_G ratio, 5.4, compared to 3.3 at 35 °C and 2.8 at 45 °C (see Table 4.2). This value is in good agreement with reported values for high-quality monolayer graphene (Table 4.2), confirming that the optimized transfer process produces a graphene substrate of quality comparable to the best results reported in the literature. This indicates a higher quality of graphene at the lower temperature treatment, and higher treatment temperatures might introduce additional

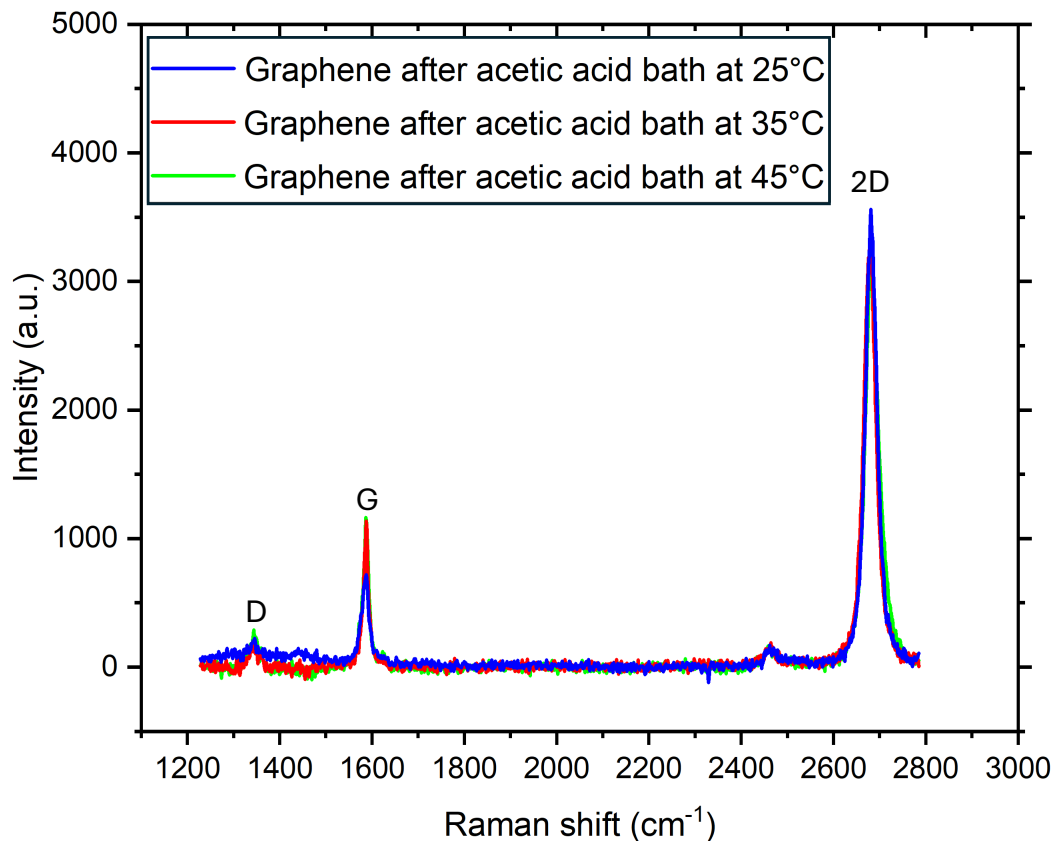


Figure 4.10. Raman spectra of graphene transferred to silicon (100) substrate with native oxide layer subjected to PMMA removal at 25 °C (blue), 35 °C (red), and 45 °C (green).

defects, reducing the structural quality of the graphene. Based on these observations, acetic acid treatment at 25 °C was adopted as the standard PMMA removal condition for all subsequent experiments.

Table 4.2. Comparison of measured I_{2D}/I_G ratio of the transferred graphene at different PMMA-removal temperatures with representative literature values for monolayer graphene obtained using different graphene sources and transfer methods.

Reference / Condition	Graphene origin	Transfer method	I_{2D}/I_G
<i>Literature</i>			
Ferrari et al. [134]	Bulk graphite	Mechanical exfoliation onto SiO ₂ /Si	≈ 4
Suk et al. [104]	CVD on Cu	PMMA wet transfer onto silicon nitride	≈ 5.4
Hong et al. [135]	CVD on Cu	Roll-to-roll dry transfer	> 3
<i>This work</i>			
PMMA removal at 25 °C	CVD on Cu	PMMA wet transfer onto SiO ₂ /Si	5.4
PMMA removal at 35 °C	CVD on Cu	PMMA wet transfer onto SiO ₂ /Si	3.3
PMMA removal at 45 °C	CVD on Cu	PMMA wet transfer onto SiO ₂ /Si	2.8

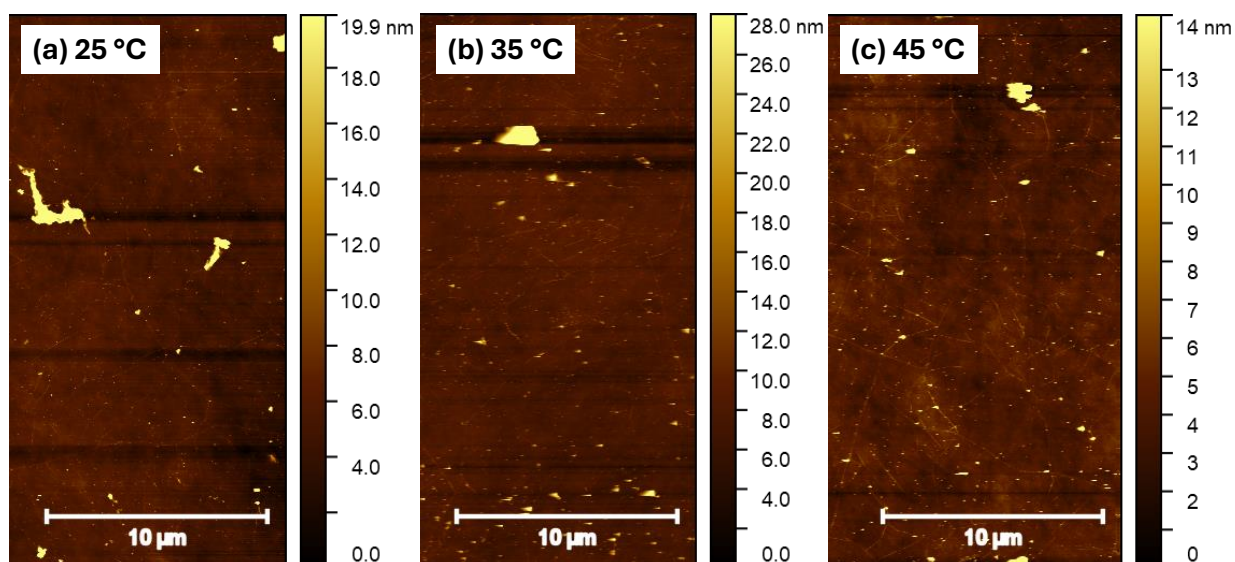


Figure 4.11. AFM height images of graphene transferred onto silicon substrates with a native oxide layer after PMMA removal in an acetic acid bath at (a) 25 °C, (b) 35 °C, and (c) 45 °C.

AFM analysis was performed to check the surface morphology of the transferred graphene. Figure 4.11 shows AFM height images of samples treated for PMMA removal at 25 °C, 35 °C, and 45 °C, respectively. In all the AFM height images, the bright gold features are observed. They represent residuals (likely PMMA) at the surface with a height ranging from 8–30 nm. The residuals exhibit a bimodal size distribution with smaller particles in the size range of 8–12 nm and the larger ones with sizes of approximately 30 nm. The RMS roughness of the transferred graphene was determined with a line scan diagonally along a 25×25 μm scan, free of larger residuals. The graphene subjected to PMMA removal at 45 °C (Figure 4.11 c) exhibits the highest roughness with a value of 0.8 nm compared to the other two samples. The graphene after PMMA removal at 25 °C (Figure 4.11 a) revealed the lowest RMS roughness of 0.42 nm, although a small amount of residual contamination is still present. Thus, PMMA removal at 25 °C is identified as the optimum condition, resulting in a good quality of the transferred graphene layer with minimal defects and lower surface roughness, comparable to the values obtained on the metallic substrates discussed in Section 4.3.1.

This optimization ensures that the graphene surface is relatively clean and smooth, which helps in the subsequent BCP thin film processing. PS-*b*-PDMS thin films were deposited onto transferred graphene and subjected to static SVA with the optimized parameters. The polymer thin film with a thickness of 18 nm with a PVA top layer was annealed at 35 °C for 1 hour using a 5:1 fraction of toluene:heptane mixture. A PDMS brush was not used as this study focused on the self-assembly behavior of PS-*b*-PDMS thin films on monolayer graphene. The resulting morphologies are shown in Figure 4.12.

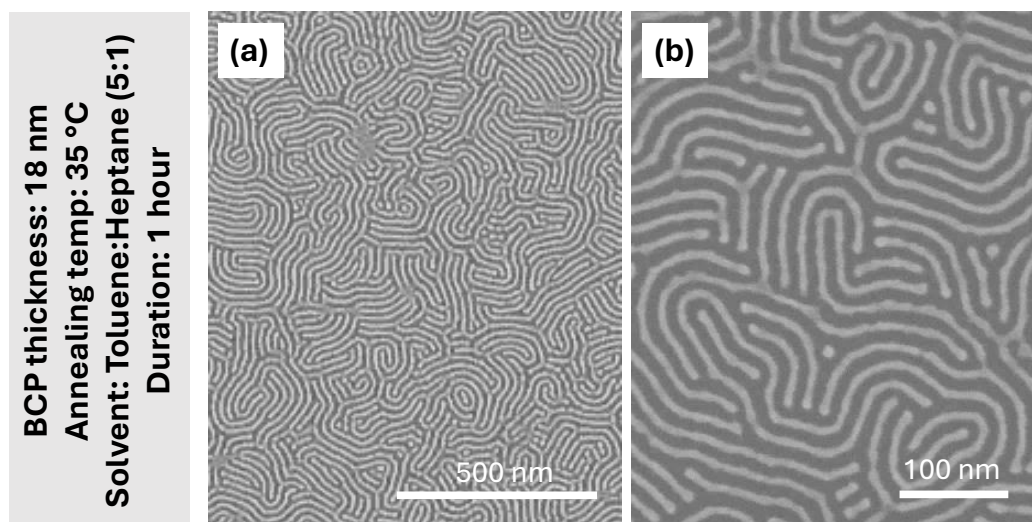


Figure 4.12. SEM top-view images of a PS-*b*-PDMS thin film on a monolayer graphene substrate. (a) Low magnification image revealing the nanostructures over a large surface area, and (b) a high-magnification image from the same sample showing smooth interfaces between PS and PDMS.

Figure 4.12 shows top-view SEM images of the nanostructures formed after SVA at two different magnifications. A successful phase separation is observed with nanostructures forming fingerprint-like cylinders aligned parallel to the substrate surface. The lower magnification image (Figure 4.12 a) confirms that the self-assembly behavior is consistent across the graphene surface. The high-magnification image (Figure 4.12 b) reveals well-ordered cylindrical domains with uniform spacing and smooth interfaces, with clear contrast between PS and PDMS. Quantitative analysis yielded a spacing of domain spacing of 19.8 ± 2.0 nm (see Supplementary Information, Section A.2.3). The calculated domain spacing is consistent with the values obtained from well-defined structures in Section 2.4.2, confirming that well-ordered nanostructures can also be achieved on graphene substrates.

The observed nanostructures appear similar to those obtained on silicon and metallic substrates, with cylindrical domains oriented parallel to the substrate surface. Perpendicular cylinders were not observed under the investigated conditions. This behavior can be attributed to the strong dispersive nature of the graphene [130], and is consistent with the observations on dispersive metallic substrates. Similar to metallic substrates, the dispersive surface attracts PS to the substrate surface, resulting in the PDMS domain being displaced away from the substrate surface. This results in the formation of cylinders oriented parallel to the substrate.

In summary, despite the significant difference in the chemical nature between graphene and metallic substrates, PS-*b*-PDMS thin films on graphene form well-defined, continuous fingerprint-like nanostructures over large areas. This indicates that the substrate chemistry

alone is insufficient to significantly influence the resulting structure after phase separation. The resulting morphology consists of parallel cylindrical domains with a characteristic spacing of $L_0 \approx 19$ nm, providing a uniform and reproducible nanoscale pattern.

These structures are directly suitable as templates for pattern transfer processes; in particular, they enable the fabrication of graphene nanoribbons (GNRs). Following the selective removal of the PS matrix and subsequent reactive ion etching, the oxidized PDMS cylinders serve as a hard mask that transfers the periodic line pattern into the graphene layer. While BCP-assisted routes to sub-10 nm GNRs have been demonstrated using graphoepitaxy to align the polymer cylinders [34, 136], the current study demonstrates that well-ordered cylinder patterns can be obtained directly on flat graphene without substrate pre-patterning.

With the measured pitch of $L_0 \approx 19$ nm and cylinder width of approximately 8 nm, this approach would yield graphene nanoribbons of approximately 8 nm width. This approach is well-suited to applications where the long-range alignment is not critical, for example, porous graphene templates for filtration or gas separation, where pore-size control and density are the key performance parameters. Such graphene membranes have been demonstrated using disordered pore arrays for both ionic filtration [137] and gas separation [138]. In addition, combining the above results with directed self-assembly approaches such as graphoepitaxy or chemoepitaxy could provide a route toward the fabrication of aligned GNRs. Overall, these results highlight the potential of block copolymer self-assembly on graphene for scalable nanopatterning and graphene-based nanodevice fabrication.

4.4 Conversion of PDMS to SiO_x by plasma oxidation

The PDMS cylinders formed by self-assembly are not directly suitable as an etch mask. To enable pattern transfer, the PS-*b*-PDMS film is therefore subjected to a two-step plasma treatment: a low-power oxygen plasma cleaning (PC) step which removes the PVA top coat residuals, followed by a high-power oxygen plasma treatment (80 W) that selectively removes the PS matrix while simultaneously converting the PDMS domains into silicon oxide (SiO_x), as detailed in Section 3.3. The conversion of PDMS into SiO_x is a key advantage of the PS-*b*-PDMS BCP, enabling direct pattern transfer into the substrate without requiring an additional hard-mask fabrication step. This section investigates the conversion process from three perspectives. First, the changes in chemical composition before and after plasma treatment are characterized (Section 4.4.1), to verify that PDMS is indeed converted to SiO_x . The morphological evolution is then compared before and after plasma treatment (Section 4.4.2), since the plasma etching process can change the shape and dimensions of the features. Finally, the resulting SiO_x nanostructures are investigated in detail (Section 4.4.3) to characterize the final

mask geometry available for pattern transfer. Together, these investigations provide insight into the formation mechanism and structural characteristics of the oxidized nanostructures.

4.4.1 Changes in chemical composition

In block copolymer lithography, following the formation of well-ordered nanostructures, the next step involves the selective removal of one polymer block to create a lithography mask. In PS-*b*-PDMS, this is achieved by the two-step plasma process discussed above. As we will see in Section 4.4.2, the SEM top-view images alone do not clearly confirm the complete removal of the PS matrix by the high-power plasma treatment. Therefore, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was employed after oxygen plasma treatment as this technique is capable of detecting specific chemical bonds in ultra-thin organic films. The initial experiments were performed on a pure PDMS film, spin-coated onto the silicon substrate to optimize the plasma process. The PDMS film used was the same as the brush layer (3.1) used for the surface modification study. A 17 nm thick film was spin-coated from a solution of 1.0 wt% PDMS in cyclohexane onto the silicon substrate at 5000 rpm. As in BCP lithography, a two-step plasma treatment was performed to verify the complete conversion of PDMS to SiO_x. Once the plasma process was optimized, it was applied to the BCP thin films after SVA.

Figure 4.13 shows the DRIFT spectra of a pristine 17 nm thick PDMS film on a silicon wafer (green spectrum). Characteristic peaks are observed and ascribed to C-H stretch in CH₃ at 2961 cm⁻¹, symmetric bending of CH₃ in Si-CH₃ at 1257 cm⁻¹, Si-O-Si stretch at 1089 cm⁻¹ and 1022 cm⁻¹, and a combined CH₃ rocking and Si-C stretching at 798 cm⁻¹ [139]. All these characteristic peaks are clearly visible in the spectrum for pristine PDMS (Figure 4.13). After a single high-power oxygen plasma step for 20 seconds (red spectrum), the overall intensity decreases, consistent with partial physical etching and densification of the film. While the overall intensity decreases, the reduction in carbon-related peaks at 2962 cm⁻¹ (CH stretching) and 798 cm⁻¹ (CH₃ rocking and Si-C stretching) is particularly pronounced, indicating preferential degradation of organic groups, although not complete removal.

Upon low-power plasma cleaning with subsequent high-power plasma etching for the conversion of PDMS, a significant change is observed in the spectrum (blue spectrum). All the CH/CH₃ related peaks at 2962 cm⁻¹ and 798 cm⁻¹ disappear, implying substantial removal of carbon-containing groups. The Si-O-Si contribution merges into one dominant peak at 1180 cm⁻¹ with a broad shoulder on the right, which indicates the conversion of PDMS to SiO_x [140].

To establish a reference for the silica-like phase formed during plasma treatment of PDMS-based films, DRIFT measurements were also carried out on an 8 nm thick silicon oxide film by electron beam evaporation. The film was deposited from SiO₂ pellets at an operating pressure of

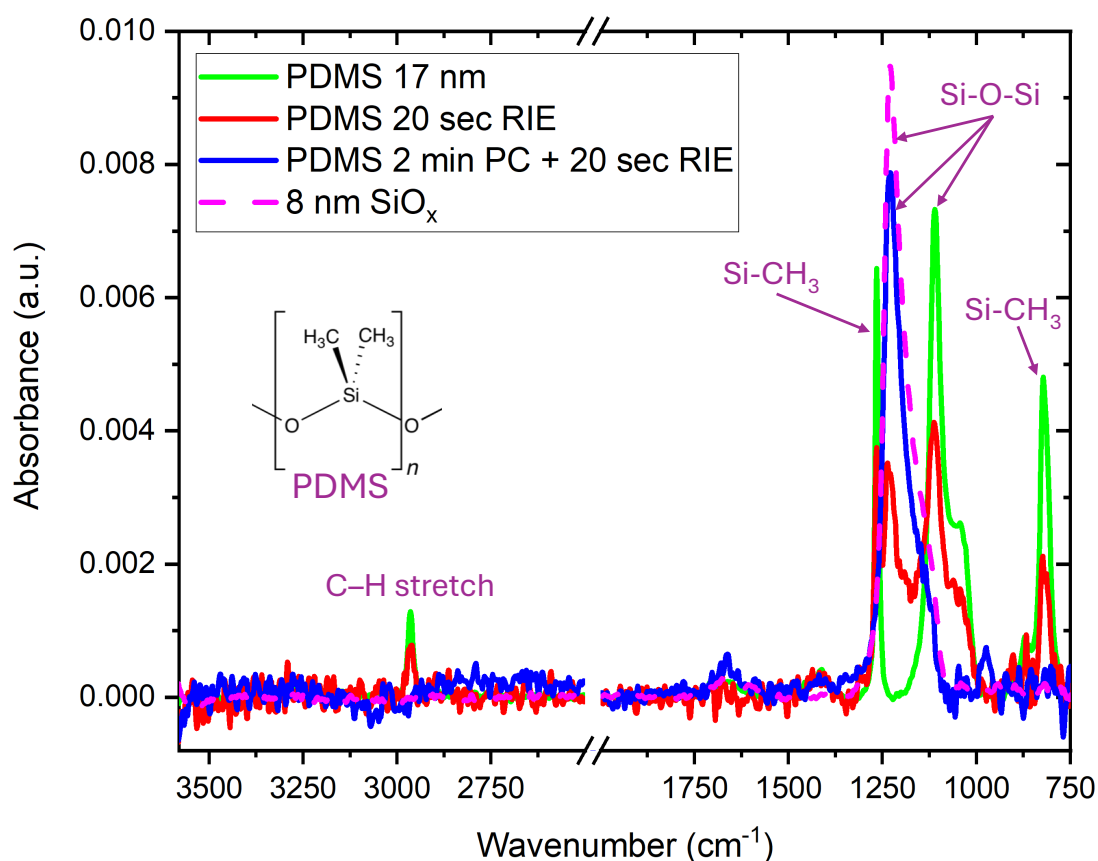


Figure 4.13. DRIFT spectra for a spin-coated 17 nm pristine PDMS film, after high-power oxygen plasma etching (red), after a low-and high-power oxygen plasma etching (blue), and an 8 nm thick silicon oxide reference film deposited by electron beam evaporation (magenta dashed line). PC denotes the low-power plasma cleaning step, while RIE refers to the high-power oxygen plasma treatment.

5×10^{-7} mbar and a deposition rate of $1 \text{ \AA/s}$, conditions known to produce a near-stoichiometric silicon oxide film, although the exact stoichiometry was not directly verified. Figure 4.13 also includes the DRIFT spectrum of an 8 nm SiO_x reference film deposited on a silicon substrate (magenta dashed line). The spectrum shows a single dominant Si-O-Si peak at 1180 cm^{-1} and closely resembles the spectrum of two-step plasma-etched PDMS thin film, indicating successful conversion of PDMS into silicon oxide SiO_x during oxygen plasma treatment. Quantitative confirmation of the stoichiometry, including the O/Si atomic ratio and the distribution of Si bonding states, would require complementary techniques such as XPS, which lies beyond the scope of the present work but represents a useful direction for future characterization.

The same two-step plasma procedure was subsequently applied to the phase-separated PS-*b*-PDMS nanostructures to etch the PS and convert the PDMS to silicon oxide. The plasma-processed film is subjected to DRIFT measurements to investigate the removal of PS and the

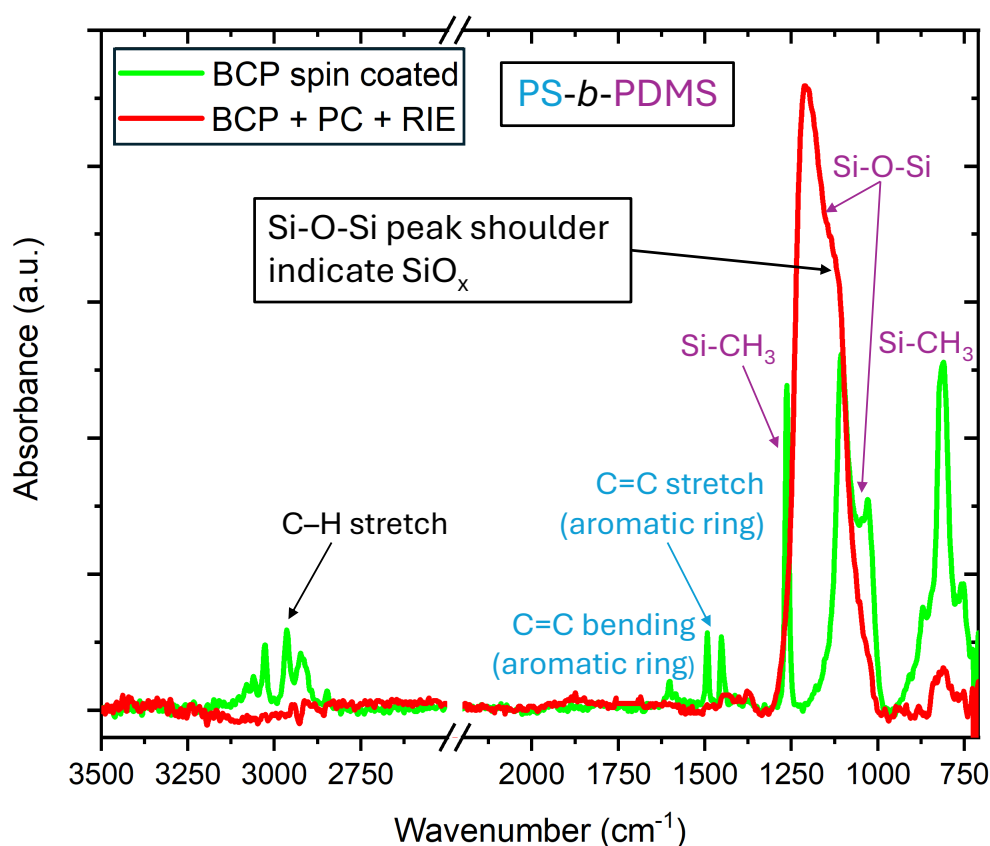


Figure 4.14. DRIFT spectra of spin-coated PS-*b*-PDMS BCP film (green) and a two-step oxygen plasma-treated film (red). PC and RIE correspond to plasma cleaning and reactive ion etching.

conversion of PDMS to SiO_x . Figure 4.14 depicts the DRIFT spectra for a spin-coated BCP film (green spectrum) and a two-step plasma-treated film (red spectrum). In the case of a spin-coated BCP film (green spectrum), characteristic peaks from both PS (indicated in cyan) and PDMS (indicated in purple) are visible. In the case of PS [141], peaks from vibrations (Figure 2.7) of the aromatic rings are visible as C=C stretching at 1494 cm^{-1} and 1452 cm^{-1} , and C=C bending at 1602 cm^{-1} . For PDMS, intense peaks associated with Si-C stretching/Si-CH₃ rocking and Si-CH₃ bending are observed at 798 cm^{-1} and 1259 cm^{-1} , respectively. A strong Si-O-Si contribution is visible from the PDMS at 1018 cm^{-1} . Additionally, the C-H stretching is visible at 2962 cm^{-1} , which is a combined contribution from both PS and PDMS.

After the two-step plasma etching (red spectrum), a significant change in the spectrum is observed. The aromatic ring contribution from the PS and the C-H stretching disappear, indicating that this step effectively removes the PS matrix. A broad dominant Si-O-Si peak appears at 1180 cm^{-1} with a shoulder on the right side, indicating the formation of SiO_x . Although the red spectrum closely resembles both the two-stage etched PDMS film and the electron beam evaporated SiO_x reference, a small residual Si-C/Si-CH₃ peak at 798 cm^{-1} is still visible. The cor-

responding Si-CH₃ symmetric bending mode at 1257 cm⁻¹ cannot be independently resolved, as it overlaps within the broadened Si-O-Si stretching band. The persistence of the peak at 798 cm⁻¹ indicates substantial but incomplete removal of carbon-containing side groups, suggesting the formation of a silica-like network containing a small fraction of residual Si-C bonds rather than fully stoichiometric SiO₂. Direct quantification of the carbon content would require complementary techniques such as XPS, which was not performed in this work. Such measurements have been reported in previous studies on plasma-oxidized PDMS to identify a heterogeneous distribution of fully oxidized, partially oxidized, and PDMS-like environments [142]. The retention of a small carbon content is not necessarily detrimental for the intended application as a hard mask, as PS-*b*-PDMS-derived SiOC layers have been reported to exhibit high thermal and mechanical stability, supporting their suitability as etch-resistant masks for pattern transfer [143].

4.4.2 Morphological comparison before and after plasma treatment

The chemical changes during the plasma process for hard mask creation are well understood; however, understanding the corresponding morphological changes during these processes is equally important for practical applications. To investigate these changes, a comparative study using SEM and AFM was carried out. The nanostructures were fabricated by static SVA using the previously optimized annealing parameters detailed above.

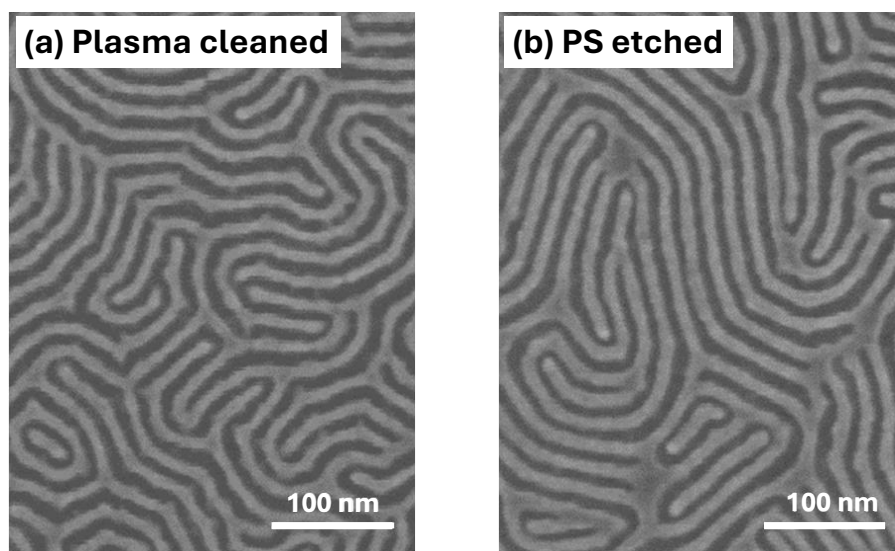


Figure 4.15. SEM top-view images of the phase-separated PS-*b*-PDMS film, (a) after low-power plasma cleaning and (b) after additional high-power PS etching.

A top-view SEM investigation of PS-*b*-PDMS thin films subjected to two-stage etching is shown in Figure 4.15. In the top-view SEM images, the brighter gray regions correspond to PDMS/SiO_x cylinders, the darker regions between the cylinders correspond to the former PS regions. In Figure 4.15 (a), these regions are only partially etched by the low-power plasma cleaning step. The structures appear well-ordered with a parallel orientation to the substrate, however the interfaces appear relatively rough and not strictly well-defined due to partial removal of the PS matrix compared to the structures obtained after the complete two-step plasma etching (Figure 4.15 b). After the two-step plasma etching (Figure 4.15 b), the SiO_x cylinders (bright gray) exhibit sharper features with a smoother interface and enhanced contrast compared to the PDMS cylinders (Figure 4.15 a).

A comparison of size distributions has been done from the SEM top-view image of the same sample before and after PS etching, as shown in Figure 4.16. Using Digital Micrograph software [144], the size distributions were estimated from the SEM images based on image contrast thresholding and are shown in Figure 4.16 (b) and (d). Line profiles were taken across the

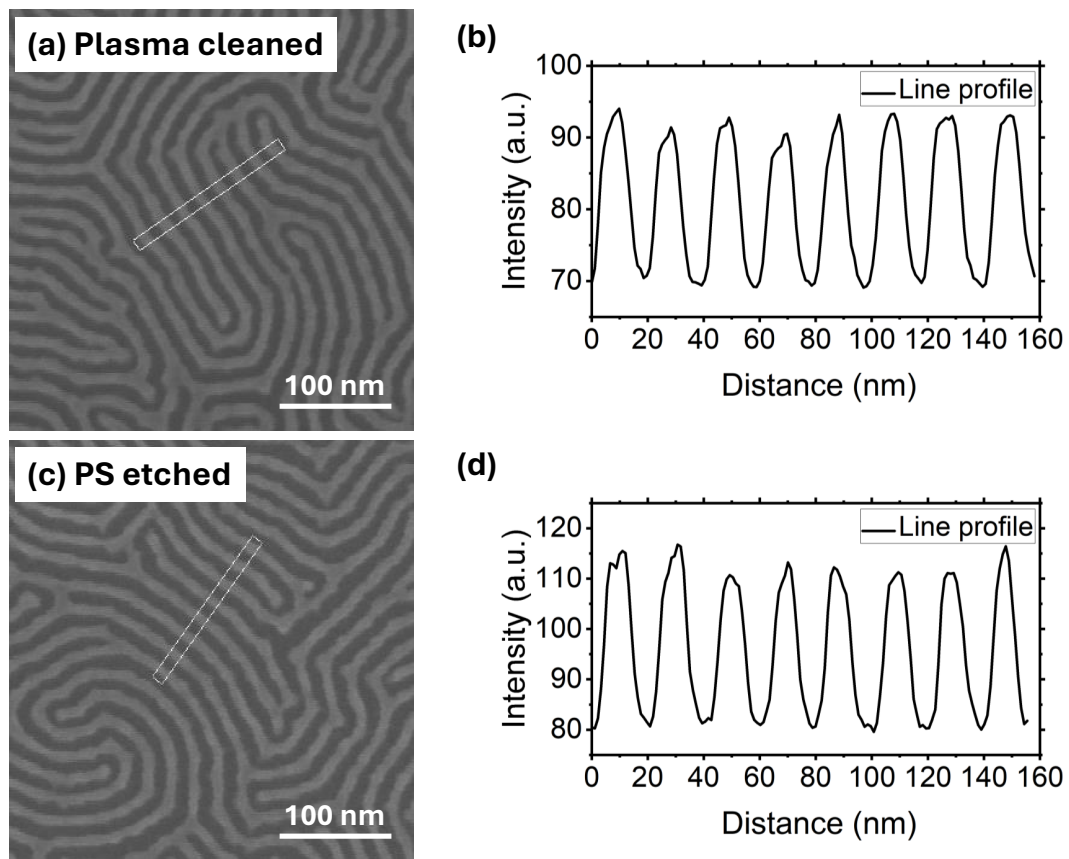


Figure 4.16. SEM top-view image of the phase-separated PS-*b*-PDMS film, (a) after low-power plasma cleaning and respective line profile (b), (c) after PS etching by additional high-power oxygen plasma and corresponding line profile (d) for morphology characterization.

cylindrical domains to determine the domain spacing and width. The extracted values represent average domain spacings and width obtained from the highlighted line profile and are subject to uncertainties arising from SEM resolution and image processing.

The feature size of the cylinders was estimated from the full width at half maximum (FWHM) of Gaussian-fitted peaks, while the domain spacing was determined from peak-to-peak distances of the line profile using OriginLab Origin [145], which enables robust multi-peak fitting and quantitative extraction of peak parameters. Gaussian fitting was preferred over direct measurements from the raw line profiles because the domain edges in the SEM images are not sharply defined and are affected by noise. This makes direct determination of the feature boundaries unreliable; therefore, peak fitting was employed to obtain a more consistent and reproducible estimation of the domain width. In addition, the line profiles were extracted over a finite width of 10 nm rather than from a single-pixel line, effectively averaging the intensity across the domain width of the selected profile region. This approach reduces noise and local intensity fluctuations and improves the reliability of the extracted peak parameters.

The average domain spacing of the selected cylinders was found to be 19.0 ± 0.4 nm after plasma cleaning and 19.8 ± 0.8 nm after high-power oxygen plasma process, indicating that the characteristic periodicity remains essentially unchanged. The average domain width of these cylinders decreased from 8.5 ± 0.7 nm to 8.1 ± 0.5 nm after the high-power plasma process. This indicates that the plasma cleaning and subsequent selective etching preserve the morphology of nanostructures. The reported values represent averages obtained from multiple fitted peaks, while the associated standard deviations arise from variations in the local domain dimensions, pixel resolution of SEM images, and uncertainties in the contrast-based edge definition during line profile analysis. It should be noted that this analysis is based on SEM top-view image contrast and may therefore be less accurate than techniques such as AFM or TEM.

AFM investigations were performed on the annealed PS-*b*-PDMS film subjected to a one-step and two-step plasma process. Figure 4.17 shows the top-view AFM height images of annealed thin films after low-power plasma cleaning and after the additional high-power oxygen plasma treatment. After plasma cleaning with low-power oxygen plasma (Figure 4.17 a), the bright regions correspond to in-plane PDMS domains, while the darker regions correspond to partially etched PS. The AFM height image reveals rough cylindrical domains as observed in the SEM investigation (Figure 4.16). The line profile (Figure 4.17 b) extracted from the height image shows that the cylinders have a pitch of 18.0 ± 1.6 nm. The average depth of trenches between the PDMS cylinders amounts to 4.5 ± 0.5 nm according to AFM data.

After the second plasma step, etching with a high-power oxygen plasma (Figure 4.17 c), the structures appear slightly narrower with smooth shapes, as observed in the AFM height image. The line profile (Figure 4.17 d) of the structure shows cylindrical domains with a pitch of 18.2 ± 1.4 nm similar to those after plasma cleaning, whereas the depth between the SiO_x

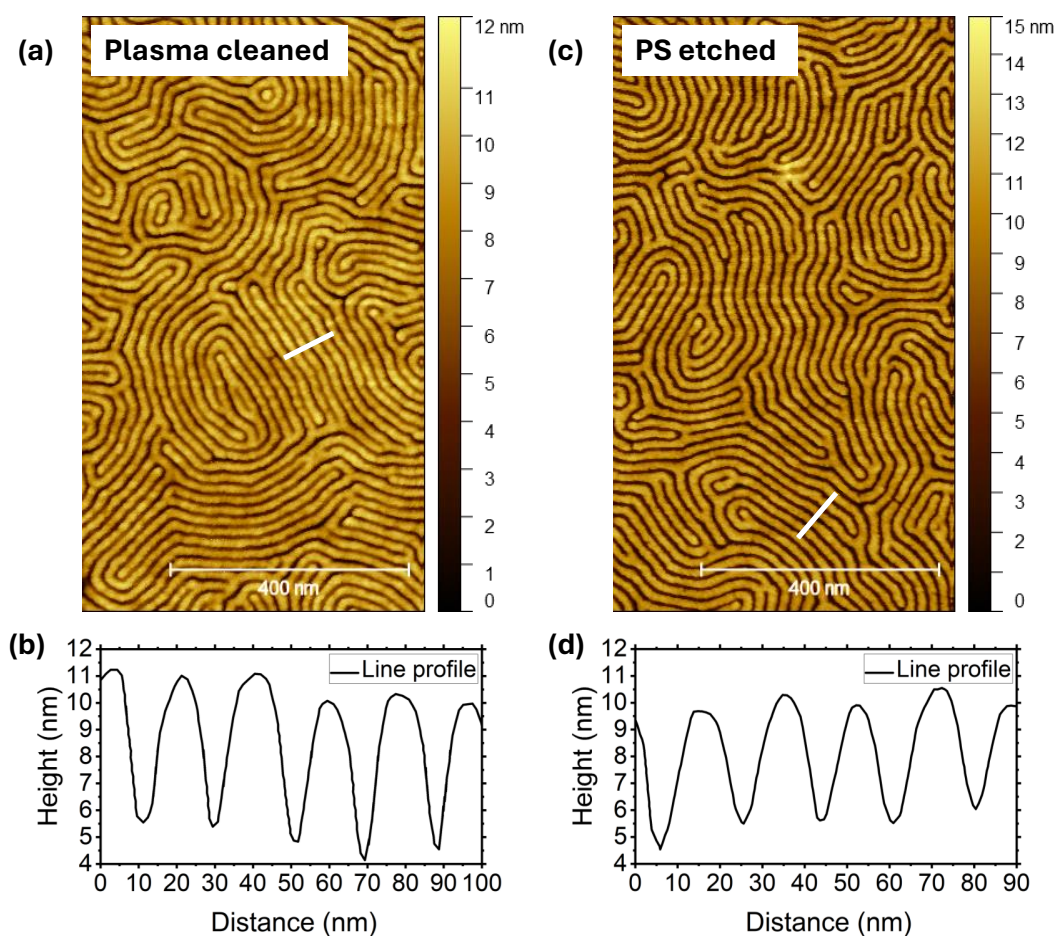


Figure 4.17. AFM height images of the phase-separated PS-*b*-PDMS film, (a) after low-power plasma cleaning, (c) after PS etching (two-step oxygen plasma), and their corresponding line profiles (b,d), respectively.

cylinders increases to 6.8 ± 0.7 nm. This indicates a progress in the removal of the PS matrix. These observations are consistent with the chemistry analysis by DRIFT spectroscopy (Section 4.4.1). The measured trench depth after high-power plasma etching (6.8 ± 0.7 nm) is considered reasonably reliable, particularly due to the use of an ultra-sharp AFM tip (≈ 1 nm), which minimizes tip convolution. However, the observed value is lower than the nominal cylinder diameter (≈ 8 nm), which is attributed not to measurement artifacts but to material changes during plasma processing. The conversion of PDMS to SiO_x is accompanied by densification and volume shrinkage, leading to a reduction in the dimensions [142]. This interpretation is supported by cross-sectional TEM analysis (see Section 4.4.3), which reveals feature heights of approximately 6 nm.

While the SEM highlights the interfacial definition and improvements in lateral contrast between domains, AFM measurements reveal a substantial increase in the height between the cylinders. Together, these results confirm that the morphology and periodicity of the nanos-

structures are preserved during the two-stage plasma processing. Therefore, the resulting SiO_2 nanostructures may serve as a reliable hard mask for subsequent lithographic pattern transfer.

4.4.3 TEM investigation of SiO_x nanostructures

Transmission electron microscopy (TEM) was employed to further investigate the morphology and spatial arrangement of cylindrical SiO_x nanostructures on the substrate surface. Unlike AFM and SEM, which provide surface and topographical information, cross-sectional TEM enables visualization of the nanostructures and the complete layer structure in side-view at high resolution.

Cross-section TEM analysis was performed to investigate the accurate dimensions of the nanostructures after the two-stage plasma process. The sample examined (18 nm thick PS-*b*-PDMS film with 300 nm PVA top coat) was annealed under optimized conditions (35 °C for 1 hour using a toluene:heptane (5:1) mixture), which resulted in well-ordered in-plane fingerprint-like structures. This analysis aids in determining the accurate dimensions of the nanostructures and the behavior of SiO_x cylindrical domains on the substrate interface after a two-stage plasma process. The TEM analysis also allows verification of the complete removal of PS and verification of the presence of any residual wetting layer on the substrate interface.

Cross-section TEM samples were prepared after depositing a chromium protective layer and an adhesive layer at the top surface. By this, the morphology of the surface can be imaged while avoiding contrast problems with the glue used in conventional cross-section preparation. The samples were then analyzed in bright-field TEM, and the resulting images are shown in Figure 4.18. In the low-magnification image in Figure 4.18 (a), the silicon substrate is visible at the bottom, followed by a thin layer of native silicon oxide. On top of this layer, three dome-

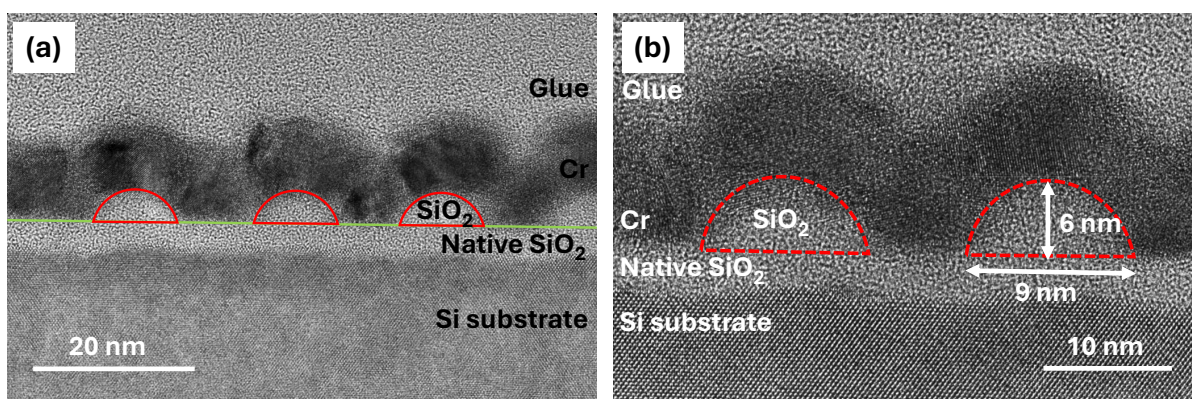


Figure 4.18. Cross-section bright-field TEM images of the phase-separated PS-*b*-PDMS film subjected to two-stage etching (a) Low-magnification TEM image indicating the nanostructures, and (b) High-resolution TEM image for feature size evaluation.

like, half-cylindrical structures spaced apart from each other are observed, corresponding to oxidized PDMS (SiO_x). Chromium is observed between these half-cylinders, confirming that the PS matrix is removed during the plasma process.

To resolve the structural changes distinctly, the sample was further investigated at high resolution. Figure 4.18 (b) shows a TEM image of the sample acquired at high resolution. The image reveals that the domain exhibits a dome-like or half-cylindrical SiO_x nanostructure on the native oxide. The average width and height of these structures were determined from measurements of five individual cylinders and found to be approximately 9.0 ± 0.6 nm and 6.0 ± 0.4 nm, respectively. The width and domain spacing of these SiO_x nanostructures are consistent, within experimental uncertainty, with values obtained from the AFM and SEM investigations as compiled in Table 4.3. This confirms that the overall pattern is preserved during the plasma process. The observed dome-like morphology of the SiO_x nanostructures was not evident from the top-view investigations. This highlights the importance of cross-sectional TEM in resolving the internal structural features at atomic resolution that are not accessible through other surface characterization techniques.

Table 4.3. Comparison of structural parameters obtained from SEM, AFM, and TEM analysis.

Technique	Pitch (nm)	Width (nm)	Height (nm)
SEM	19.8 ± 0.8	8.1 ± 0.5	–
AFM	18.2 ± 1.4	8.6 ± 1.4	6.8 ± 0.7
TEM	18.5 ± 0.8	9.0 ± 0.6	6.0 ± 0.4

The formation of dome-like morphology can be understood by considering the evolution of block copolymer during each process step, as schematically illustrated in Figure 4.19 (a-d). Initially, before annealing (Figure 4.19 a), the PS-*b*-PDMS film is in a disordered or weakly phase-separated state. Upon solvent vapor annealing, microphase separation leads to the formation of ordered PDMS cylindrical domains within the PS matrix. However, previous investigations indicate non-neutral interfacial interactions, and a PS wetting layer is likely present at the substrate interface, creating a PS-rich interfacial layer and forcing the PDMS domains away from the substrate. As a result, the cylindrical PDMS domains are not symmetrically positioned across the film thickness as illustrated in Figure 4.19 (b). Such effects of non-neutral interfacial interactions and preferential wetting on the morphology and vertical arrangement of domains in block copolymer thin films have been widely reported [72, 146, 147]. At this stage, the PDMS domains remain embedded within the PS matrix and are not exposed at the film surface, which is consistent with the absence of resolvable nanostructures in both SEM and AFM measurements before plasma cleaning. After the plasma cleaning (Figure 4.19 c), the PS matrix is removed partially, enabling characterization of structures using SEM and AFM.

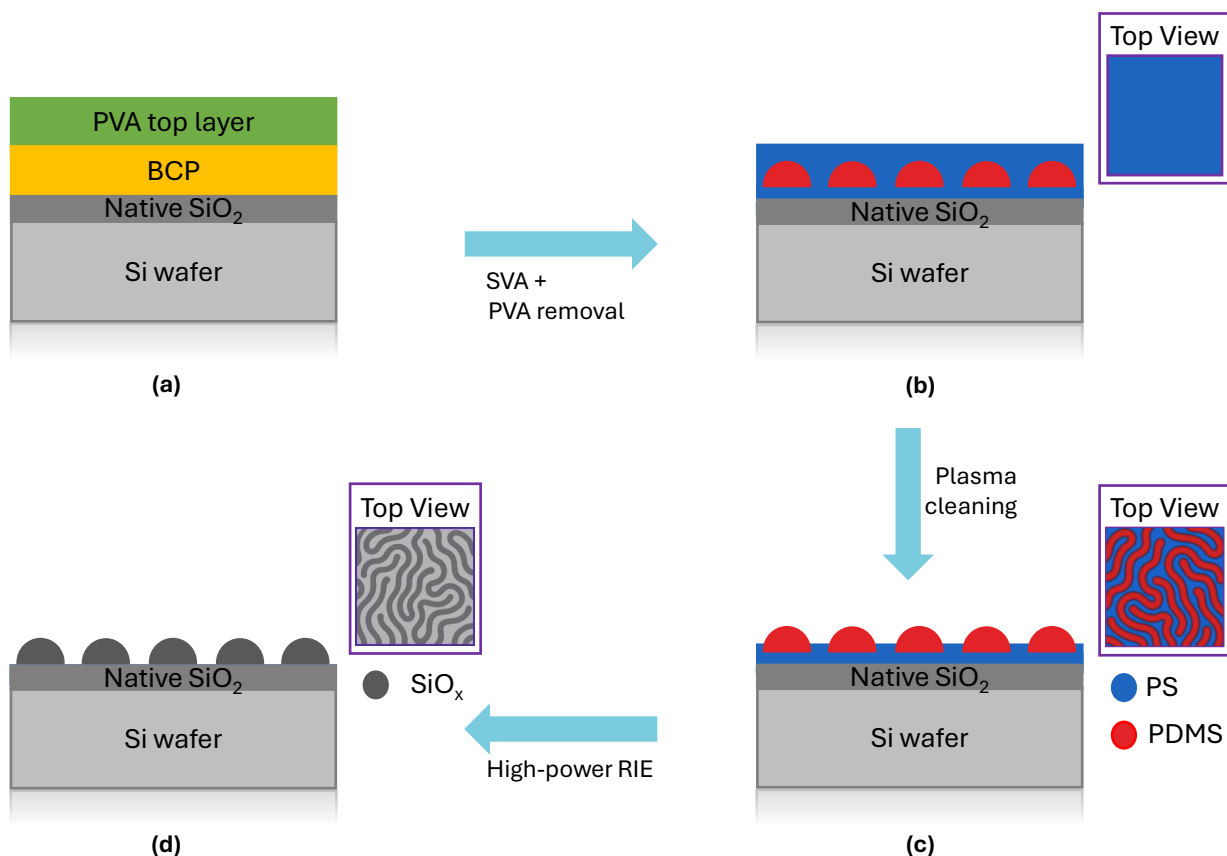


Figure 4.19. Schematic illustration of the mechanism leading to the formation of half-cylindrical or dome-like structures: (a) initial PS-*b*-PDMS film before annealing, (b) asymmetric PDMS domain distribution due to a PS wetting layer at the substrate after SVA, (c) partial PS removal after plasma cleaning, and (d) formation of dome-like structures after two-step plasma etching.

During the subsequent two-stage oxygen plasma treatment, the PS matrix is selectively removed while converting the PDMS domains to SiO_x . Since the PDMS cylinders are embedded in the PS matrix and are asymmetrically positioned across the film thickness, the domains do not form fully symmetric cylindrical domains. The resulting SiO_x structures appear as dome-like or half-cylindrical structures rather than a fully circular cross-section as shown in Figure 4.19 (d). In addition, plasma oxidation leads to the removal of carbon atoms from the PDMS, resulting in densification of PDMS along with loss of mechanical support, and this likely contributes to a reduction in the apparent height of these nanostructures [142].

The conversion of PDMS to SiO_x during oxygen plasma treatment results in significant volume shrinkage. Based on density and molar mass considerations, the final SiO_2 volume is approximately 36% of the initial PDMS volume, corresponding to a shrinkage of about 64%. Although the plasma-treated PDMS is commonly approximated as SiO_2 , it is more commonly described as silicon oxide (SiO_x), as complete oxidation may not be achieved under the ap-

plied conditions. In our study, the presence of residual carbon species, as evidenced by DRIFT spectroscopy, can lead to the formation of a carbon-containing SiO_x network (Section 4.4.1). While this may slightly modify the exact density and thus the magnitude of volume reduction, the overall effect remains a substantial shrinkage due to densification of the Si–O framework. This reduction in volume also contributes to the observed changes in domain morphology after plasma processing. Similar behavior, where oxidized PDMS structures exhibit reduced height compared to their lateral dimension after plasma treatment, has also been reported in the literature [148, 149].

To verify this hypothesis, future investigations could include a TEM analysis after annealing. If the half-cylinders are observed again, this could be due to the asymmetric domain orientation of the wetting layer. On the other hand, if fully circular cylindrical domains are observed after annealing, the plasma process plays a role in the deformation of the SiO_x cylinders. Despite the observed morphological changes of the SiO_x nanostructures, it still won't affect the pattern transfer unless silicon oxide etching takes place in such a subsequent process step.

Thus, the TEM investigations reveal that the feature sizes, domain width (9 nm) and spacing (18 nm) are consistent with previous SEM/AFM investigations. The analysis also supports the assumption that two-step etching was successful in the complete removal of PS, in agreement with the DRIFT analysis. Thus, the TEM studies employed aided in providing crucial insights about the morphologies of the nanostructured SiO_x .

4.5 Directed self-assembly of cylinder structures

From the static and dynamic solvent vapor annealing studies on PS-*b*-PDMS thin films, in-plane fingerprint-like cylindrical nanostructures were obtained under optimized conditions. However, these structures did not exhibit long-range order, as cylindrical domains were oriented randomly and lacked any preferred direction. To address this, the directed self-assembly (DSA) technique was employed to investigate whether the polymer domains can be guided to align in a particular direction. DSA utilizes external guiding patterns (such as trenches or grooves) to control the position and order of the block copolymer domains, in contrast to the conventional self-assembly. Therefore, this section focuses on the analysis of the effect of directed self-assembly of PS-*b*-PDMS thin films.

For this, a 100 nm thick SiO_2 layer was deposited by plasma-enhanced chemical vapor deposition (PECVD) on a silicon wafer. Trenches with a depth of 30 nm and length of $1\mu\text{m}$ were fabricated in the PECVD-grown SiO_2 using electron beam lithography, as detailed in Section 3.5. The trench width was designed to be commensurate with the domain spacing as discussed in Section 2.5. Two trench geometries were used with nominal widths of 90 nm ($5L_0$) and 126 nm

($7L_0$), and corresponding mesa widths of 140 nm and 200 nm, respectively. To stabilize the resist during development, a 500 nm wide spacer region was introduced after every 10 trenches. For each geometry, 50 trenches were fabricated.

The choice of these dimensions over narrower trenches was due to two reasons. First, from a fabrication perspective, the electron beam lithography process used in this work has an effective spot size of approximately 40 nm, which limits the reliable definition of very narrow features. Trenches with widths comparable to only a few domain spacings would therefore approach the resolution limit and be more susceptible to edge roughness and pattern transfer imperfections. Secondly, literature reports on PS-*b*-PDMS directed self-assembly demonstrate that multiple cylindrical domains, in some cases exceeding ten, can be accommodated within trench geometries [150, 151].

The trench depth was selected to ensure effective confinement of the polymer film during solvent vapor annealing. Although the exact swelling ratio was not directly quantified in this study, literature reports indicate that swelling ratios above ≈ 1.8 correspond to a critical regime where structural disordering can occur [64]. Therefore, the processing conditions were chosen to remain below this critical swelling limit. Based on the initial film thickness of 18 nm and the expected moderate swelling under the employed annealing conditions, a trench depth of 30 nm provides sufficient vertical space to accommodate the swollen film while maintaining confinement within the trench geometry.

The resist after e-beam exposure was characterized using SEM and AFM to verify the resulting pattern, as shown in Figure 4.20. The SEM analysis (Figure 4.20 a) indicates well-defined patterned trenches with smooth edges, confirming successful pattern creation. The AFM height image (Figure 4.20 b) shows the trenches and the spacer with distinct edges. A line scan was extracted from the AFM height image to evaluate the feature dimensions. The line profile confirms that the width of the fabricated trenches and spacer dimensions are consistent with the designed pre-pattern dimensions. However, the AFM line profile reveals a V-shaped trench bottom rather than a flat plateau. Given the trench width above 100 nm and the AFM tip radius of approximately 8 nm, the tip should be able to access and resolve any flat bottom region within the trench. While tip convolution may influence the apparent shape near the sidewalls, it is unlikely to account for the overall V-shaped profile across the trench. The absence of a clear plateau in the measured profile therefore suggests that the trench bottom is inherently sloped, most likely arising during the development of narrow resist features.

The patterned resist was subsequently used as an etch mask to transfer the pattern into the underlying SiO₂ layer. The resulting substrate after etching and resist removal was analyzed by SEM to check the quality of the pre-pattern, as this directly influences the directed self-assembly of the polymer domains. The top-view SEM image in Figure 4.21 reveals the trenches in the SiO₂ layer for a wider trench geometry. A low-magnification image (Figure 4.21 a) provides an

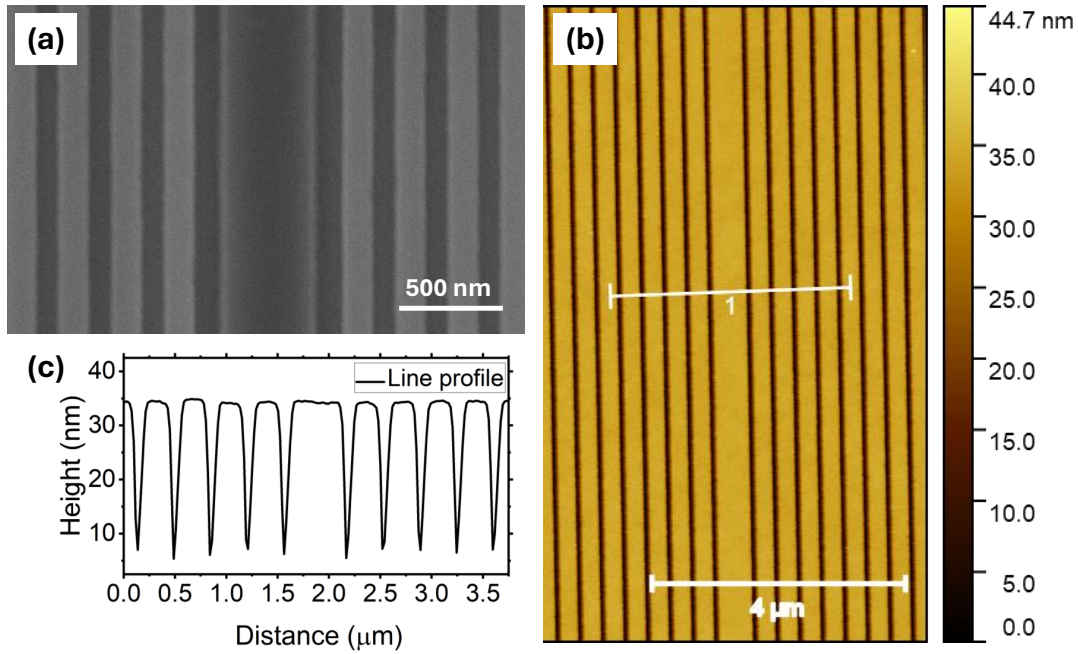


Figure 4.20. Electron beam lithography mask. The photoresist after exposure and development was characterized by (a) a top-view SEM image of the narrower trench geometry and (b) AFM height image of the wider trench geometry, with corresponding line profile (c) to verify the quality of the patterned features in the resist.

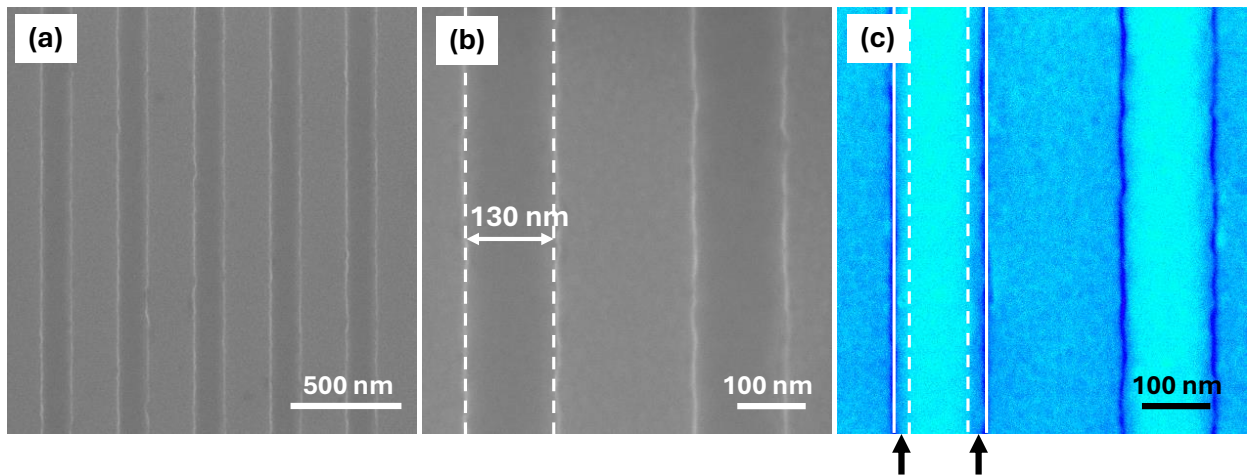


Figure 4.21. Top-view SEM images of trenches on a SiO_2 layer for the wider trench geometry: (a) low magnification showing an overview of trenches, (b) high-magnification to verify the trench width, and (c) False-color representation of the SEM image used to enhance intensity variations near the trench edges. The white solid lines indicate the trench boundaries, while the dashed lines highlight regions exhibiting a gradual contrast variation adjacent to the sidewalls, suggesting slight sidewall tapering.

overview of the trench array, while a high-magnification image (Figure 4.21 b) was acquired to evaluate the width of the fabricated trenches and the roughness at the line edges. Both trench geometries were characterized. The narrower trenches, with a nominal design width of 90 nm ($5L_0$), exhibit an average width of 100 ± 10 nm, while the wider trenches, with a nominal design width of 126 nm ($7L_0$), exhibit an average width of 130 ± 6 nm. The measured values are slightly larger than the designed dimensions, reflecting the variations introduced during lithography and pattern transfer.

The SiO_2 etching was carried out using a standard plasma etch recipe (Section 3.5) optimized for oxide pattern transfer, which is generally designed to provide anisotropic etching with controlled etch rates. The etch depth was estimated based on the known etch rate of the process; however, no cross-sectional characterization (e.g., AFM or SEM) was performed to directly assess the trench bottom profile or sidewall angle. Although the trenches are clearly resolved in top-view SEM, slight edge roughness is observed, and the exact degree of sidewall verticality and bottom flatness cannot be conclusively determined. A slight contrast variation near the trench edges is visible in the high-magnification image (Figure 4.21 b). To better visualize this, a false-color representation (using ImageJ [152]) of the SEM image is shown in Figure 4.21 (c). The white solid lines mark the trench boundaries, while the dashed lines indicate regions adjacent to the sidewalls where a gradual contrast variation is observed. Although SEM provides only surface-sensitive contrast, the presence of this intensity gradient suggests slight sidewall tapering. However, a quantitative assessment of the sidewall angle or trench bottom profile is not possible based on this analysis.

BCP lithography was performed on the patterned substrate using nominally 18 nm thick PS-*b*-PDMS thin films and the optimized annealing conditions. Prior to annealing, a 300 nm thick PVA layer was spin-coated onto the BCP film, and no brush layer was used. The directed self-assembly was first investigated on the narrower trench geometry (≈ 100 nm trench width). The resulting structures were analyzed by top-view SEM as shown in Figure 4.22. Two distinct types of structural orientation were observed throughout the sample. In one type (Figure 4.22 a), the polymer domains appear to be predominantly confined within the trenches without proper order. The mesa region between the trenches does not show clear nanostructure formation, although slight contrast variations are observed, likely arising from a possible presence of an ultra-thin residual film. Inside the trenches, most cylinders are aligned perpendicularly to the trench direction with only one PDMS line along the edges on each side of the trench, and with different widths. Such arrangements can be interpreted as a sign that the commensurability condition was not fulfilled well enough.

The other type of region, displayed in Figure 4.22 (b), shows a different morphology. Here, the polymer domains are no longer confined within the trenches but partially extend to the mesa regions. Within some trenches, a better ordering of PDMS domains is observed, suggesting

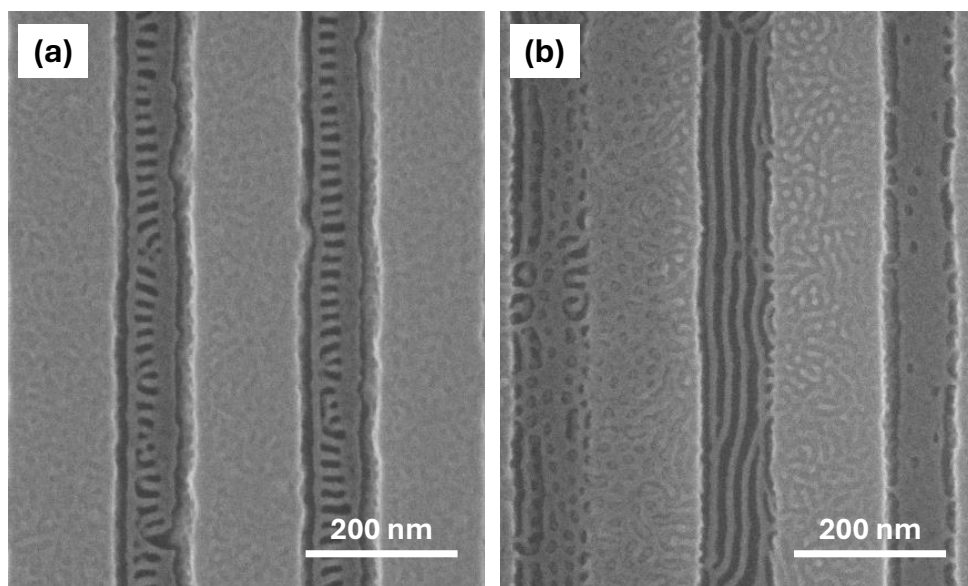


Figure 4.22. Top-view SEM images of the PS-*b*-PDMS thin films on the patterned SiO₂ substrate after static SVA for the narrower trench geometry (≈ 100 nm trench width), acquired from different regions of the sample. (a) Disordered structures confined within the trenches. (b) Mixed morphology of polymer domains with partial in-plane cylinder morphology in the trenches and dot-like features on the spacer region.

improved alignment compared to the previously discussed region. Another crucial finding here is the formation of dot-like structures on the mesa regions, resembling perpendicular oriented cylinders. A transition in morphology across the patterned region is observed in Figure 4.22 (b), suggesting a variation in local film thickness. While the exact origin of this variation cannot be conclusively determined, it may arise from spin-coating non-uniformities. Since the imaged region is located near the center of the sample, the contribution from macroscopic edge effects is expected to be limited.

The variation in morphology in two different regions highlights the sensitivity of the BCP system to local film thickness, wetting conditions, and confinement. In addition, the absence of well-aligned cylindrical domains in the trenches is influenced by the geometrical condition of the guiding patterns. Although the trench widths were designed to be commensurate with the natural domain spacing (90 nm for 5L₀), the experimentally measured widths deviate from this nominal value due to lithography and etching effects. This deviation from the ideal commensurate condition can contribute to imperfect ordering and alignment within the trenches. As observed in Figure 4.21, the trench sidewalls exhibit slight irregularities, and a contrast variation near the trench edges suggests the presence of sidewall tapering. This non-uniformity introduces local variations in the confinement, which disrupt the uniform propagation of polymer domains in the trench direction. In directed self-assembly, well-defined sidewall chemistry and

topography are essential for effective guidance of the polymer domains [153]. Furthermore, the absence of a neutral layer at the substrate interface may cause preferential wetting of the trench bottom, further preventing the system from reorganizing into well-ordered structures. Therefore, factors such as local film thickness variations, sidewall irregularities/tapering, and the absence of a neutral layer likely contribute to the limited domain alignment in the present DSA experiments.

To further investigate the influence of trench geometry on domain orientation, the wider trench geometry (≈ 130 nm trench width corresponding to $7L_0$, with a mesa width of 200 nm between the trenches) was also examined. This was done to examine whether the trench width has an effect on the arrangement and alignment of the cylinders relative to the trench axis. The PS-*b*-PDMS thin films were annealed similarly to those in the previous study and the resulting structures are shown in Figure 4.23.

In comparison to the morphology of structures in the narrower trenches, Figure 4.23 (a) shows significant change in the domain ordering within the wider trenches. The nanostructures in the trench exhibit continuous and ordered fingerprint-like cylindrical domains. The mesa regions between the trenches show a combination of fingerprint-like and dot-like features. This behavior suggests that on the mesa, the system is in a transitional state where neither in-plane nor perpendicular orientation is fully stabilized. The ordering within the trenches is influenced by the ordering on the mesas (Figure 4.23 a), indicating that the increased trench width reduces

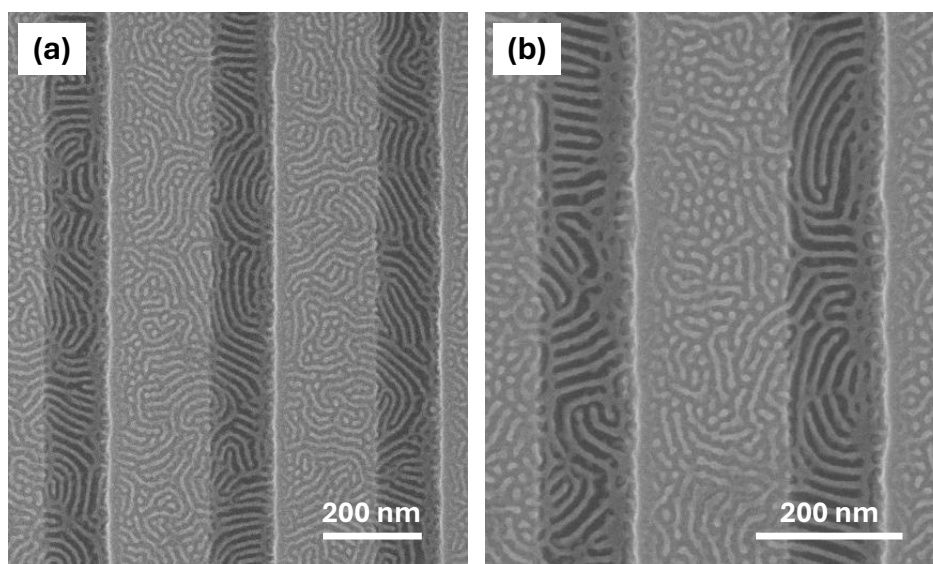


Figure 4.23. Top-view SEM images of a PS-*b*-PDMS thin film on the patterned SiO₂ substrate with increased trench width (130 nm) after static SVA, acquired at (a) low-magnification and (b) high-magnification. Ordering of a fingerprint-like structure is visible in the trenches, whereas the spacer regions exhibit a mixed morphology of fingerprint-like and dot-like structures.

the confinement effects in the polymer domains, allowing them to reorganize independently.

In this section, the directed self-assembly of PS-*b*-PDMS thin films was investigated by implementing a prepatterned SiO₂ substrate with trenches. Despite achieving ordered in-plane fingerprint-like nanostructures under the optimized conditions on a planar substrate, the nanostructures on a prepatterned substrate did not align successfully in the trench direction. For the narrower trenches, the polymers exhibited mixed morphologies consisting of both parallel and perpendicular. Upon increasing the trench width, the confinement imposed by the sidewalls is reduced, as one would expect. This suggests that deviations from ideal commensurability, sidewall irregularities, and interfacial effects continue to limit the establishment of well-aligned structures. Therefore, additional experiments with narrower trenches and widths matching more exactly the commensurability criterion are necessary to achieve effective directed self-assembly.

4.6 Summary

In this study, the self-assembly behavior of cylinder-forming PS-*b*-PDMS (16 kg/mol) thin films was investigated. The aim was to induce phase separation in polymer thin films and identify the optimal parameters for the formation of ordered nanostructures. Two different strategies were implemented: static and dynamic solvent vapor annealing (SVA) to create phase-separated nanodomains.

The static annealing setup provided few controllable parameters, where the influence of BCP film thickness, temperature, annealing duration, and solvent selectivity was analyzed. It was found that a BCP film thickness of 18 nm, matching the natural domain spacing, produced the best structures. The temperature and time dependency studies show that higher temperatures or longer annealing times result in preferential wetting of the PDMS domain to the surface due to over-swelling, although a neutral PVA top coat was implemented in all the experiments. Annealing at 35 °C for 1 hour resulted in well-ordered in-plane fingerprint-like structures. The changes were not drastic in the solvent selectivity study; both toluene:heptane (5:1) mixture and acetone produced similar in-plane cylindrical structures.

To overcome the interfacial interactions, hindering the formation of perpendicular cylinders, a PDMS brush layer was deposited at the silicon surface. The nanostructures after the phase separation showed a mixed morphology consisting of fingerprint-like and dot-like structures, where the dot-like structure resembles perpendicularly oriented cylinders. Thus, the use of a PDMS brush layer was insufficient to provide a surface favoring perpendicular orientation.

Dynamic solvent vapor annealing provided improved control over the swelling behavior as the solvent flow was precisely controlled using mass flow controllers. Out of different flow rates,

a narrow window (25–50 sccm) of solvent flow resulted in a significant change in structure morphology, where 37 sccm produced well-ordered fingerprint-like structures with long-range order. The annealing duration showed a similar trend to the time-dependent study performed in the static SVA setup, where 1 hour of annealing resulted in better-ordered nanostructures.

Self-assembly behavior of PS-*b*-PDMS thin films was conducted on different substrates consisting of different metallic films (Cr, Ti, Mo, and Ru) with their native oxides on top and graphene. The study aimed to verify whether the different substrate energies influence the cylindrical domain orientation. The nanostructures on the metallic substrates exhibited similar in-plane structures due to their predominantly dispersive fraction of the surface free energy. To investigate the behavior of nanostructures on graphene, a transfer protocol was developed by combining and adapting established methods from the literature, with additional optimization to achieve improved surface coverage and reduced residual contamination. This resulted in transferring a monolayer of graphene with an RMS roughness of 0.42 nm with full coverage on the substrate. SVA of PS-*b*-PDMS thin films on graphene resulted in well-ordered fingerprint-like structures. This highlights the advantage of the PS-*b*-PDMS system, which is capable of forming well-ordered nanostructures on different substrates, enabling its potential use in diverse applications.

The crucial step in the BCP lithography, selective removal of one of the polymer blocks, here the PS and conversion of PDMS to SiO_x, was also investigated. A two-step plasma process of the PS-*b*-PDMS thin films was characterized by DRIFT spectroscopy for chemical analysis and AFM, SEM, and TEM for the morphology. The DRIFT spectrum after two-step plasma processing revealed a dominant Si-O-Si peak characteristic of SiO_x, and the PS characteristic peaks vanished, which indicates complete PS removal and successful conversion of PDMS to SiO_x. Subsequently, AFM and SEM investigations were carried out to evaluate the feature sizes and domain spacing in top view. The cylinders had a width of approximately 8 nm with a domain spacing of 18 nm. This was verified by a cross-sectional TEM investigation, where the cylinder geometry is observed to be dome-like, likely resulting from the asymmetric domain positioning due to preferential wetting and plasma-induced densification.

Finally, directed self-assembly (DSA) was investigated. For this, trenches were fabricated on a PECVD-grown SiO₂ by e-beam lithography. Two different trench widths were examined. The nanostructures in the narrower (100 nm) trenches showed a mixed behavior. In wider trenches (130 nm), the in-plane cylindrical nanodomains were mostly confined in the trenches, although not aligned in the trench direction.

To conclude, the studied PS-*b*-PDMS system serves as a promising platform for nanopatterning across various substrates. The optimized parameters enable reproducible formation of ordered in-plane fingerprint structures, although achieving perpendicular alignment remains a key challenge.

5 Perpendicular Cylinder Formation and Pattern Inversion

The results presented in Chapter 4 demonstrate that the 16 kg/mol PS-*b*-PDMS BCP forms in-plane cylindrical morphologies, despite extensive optimization of solvent annealing conditions. This behavior is ascribed to interfacial interactions and preferential wetting effects that hinder the formation of perpendicular-oriented cylinders, thereby limiting the effectiveness of the directed self-assembly strategies under geometrical confinement.

To address this limitation, an alternative PS-*b*-PDMS block copolymer with slightly higher molecular weight (21 kg/mol) is investigated in this chapter. Table 5.1 summarizes the volume fraction of polystyrene f_{PS} , Flory-Huggins interaction parameter χ , degree of polymerization (N), and segregation strength χN for both polymers. The volume fractions of PS are estimated using densities of 1.02 g/cm³ for PS and 0.97 g/cm³ for PDMS [154]. The degree of polymerization is calculated from the molecular weights of the respective blocks, and the interaction parameter is evaluated at the annealing temperature (35 °C) according to [149].

Table 5.1. Volume fraction of polystyrene(f_{PS}), degree of polymerization (N), Flory-Huggins interaction parameter (χ), and resulting segregation strength (χN) of PS-*b*-PDMS systems at the annealing temperature (35 °C).

PS- <i>b</i> -PDMS (kg/mol)	f_{PS}	χ (35 °C)	N	Segregation strength χN
11- <i>b</i> -5	0.68	0.184	173	31.8
15.5- <i>b</i> -5.5	0.72	0.184	223	41.0

As shown in Table 5.1, both polymers exhibit similar volume fractions, indicating that they belong in the same cylindrical morphology regime of the phase diagram (Figure 2.2). However, the BCP investigated in this chapter with a higher molecular weight shows a significantly larger degree of polymerization, leading to an increase in segregation strength (χN). Since the interaction parameter (χ) remains identical for both systems at a given temperature, this increase arises from the higher N . The resulting stronger segregation enhances microphase separation, improves domain definition, thereby facilitating the formation of more uniformly

perpendicular cylindrical domains under suitable processing conditions [155]. The formation of perpendicular cylindrical domains is important for nanopatterning applications, as it can be directly utilized or further processed into functional architectures. The higher molecular weight polymer is subjected to static solvent vapor annealing using the previously optimized conditions from the last chapter as a starting point. Subsequently, the response of the polymer to topographical confinement is analyzed using prepatterned trench structures.

Furthermore, this chapter explores pattern inversion strategies to transform cylindrical domains into antidot-like nanostructures. For this, two approaches were employed: pattern inversion using a sacrificial layer combined with vibratory polishing, and selective-swelling-based inversion using dynamic solvent vapor annealing. The two approaches are investigated to evaluate their effectiveness and limitations.

Finally, the potential relevance of these antidot nanostructures for a memristive architecture is discussed. Although the full device fabrication is beyond the scope of this work, the results presented here demonstrate the feasibility of employing block copolymer lithography as a scalable route towards the fabrication of high-resolution nanostructures for future electronic applications.

5.1 Formation of perpendicular cylinder structures

The self-assembly behavior of 21 kg/mol PS-*b*-PDMS thin films was investigated by subjecting them to static solvent vapor annealing (SVA). Since the annealing conditions were optimized in Chapter 4, where clear phase separation was achieved in 16 kg/mol PS-*b*-PDMS thin films, similar annealing conditions were initially adopted. The natural domain spacing (L_0) of the 16 kg/mol PS-*b*-PDMS was determined to be approximately 18 nm, as discussed in Chapter 4. Based on strong segregation scaling $L_0 \propto N^{2/3}$ [156], the higher molecular weight polymer is expected to exhibit an increased domain spacing of approximately 21–22 nm. Accordingly, thin films of PS-*b*-PDMS with a thickness close to the L_0 were prepared on silicon substrates and annealed at 35 °C for 1 hour. Although this thickness- L_0 relationship is most strictly defined for lamellar morphologies, it also serves as a useful guideline for improving ordering in cylindrical systems. In previous studies conducted by J. Freibel [157], solvent vapor annealing of this polymer using a toluene:heptane mixture (5:1) did not yield fully ordered cylindrical morphologies. Therefore, acetone was employed as an alternative solvent. All samples were annealed with a PVA top coat to neutralize the top interface, without a brush layer on the substrate.

Figure 5.1 shows the top-view SEM images of PS-*b*-PDMS thin films with varying thicknesses after static SVA. The brighter domains correspond to PDMS, while the darker regions repre-

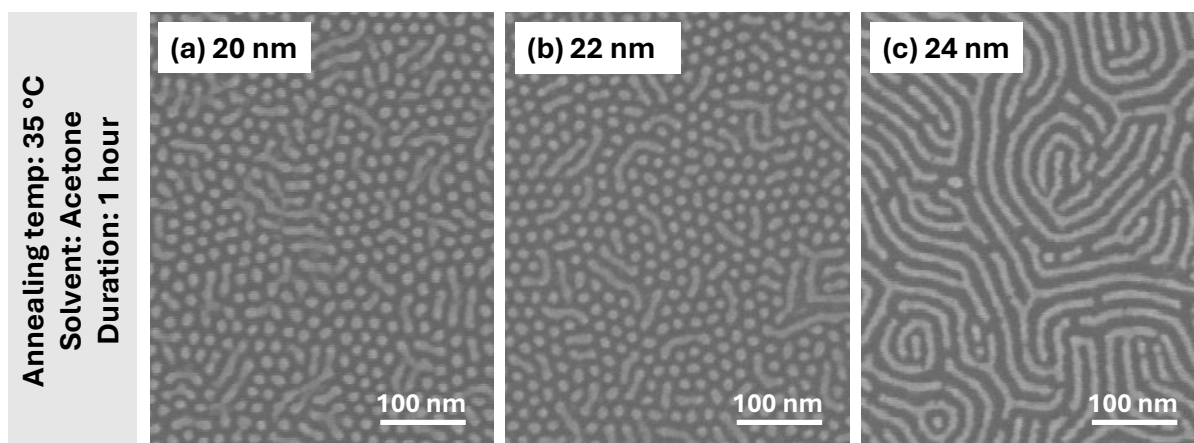


Figure 5.1. Top-view SEM images of the PS-*b*-PDMS thin films with thicknesses in the range of the natural domain spacing. The static SVA was performed by maintaining the temperature at 35 °C for 1 hour in acetone. SEM images were recorded after plasma cleaning in an oxygen plasma (details in Section 3.3) to remove PVA residuals and PS partially.

sent partially etched PS. A 20 nm thick film (Figure 5.1 a) reveals a mixed morphology across the substrate, consisting mostly of dot-like structures resembling a perpendicular cylinder, and some domains oriented parallel to the substrate. In the case of a 22 nm thick film (Figure 5.1 b), a similar morphology is observed, although the dot-like structures are dominant. To quantitatively support this observation, the areal density of dot-like domains was evaluated using image analysis. The dot density for the 20 nm film was found to be approximately 7.7×10^2 dots/ μm^2 whereas a significantly higher density of approximately 1.35×10^3 dots/ μm^2 was obtained for the 22 nm film. This confirms that perpendicular cylindrical domains are more prevalent at 22 nm compared to 20 nm.

Figure 5.1 (c) shows the nanostructure obtained for a thickness of 24 nm. A drastic change is observed in the orientation of the cylindrical nanodomains, dominated by in-plane cylindrical domains with only a negligible density of dot-like structures ($\approx 2.7 \times 10^1$ dots/ μm^2). Details of the image analysis procedure and parameter selection are provided in the Supplementary Information (Section A.2.3).

These observations indicates that the orientation of the cylindrical domains changes with increasing film thickness. Overall, the domains exhibit a relatively uniform size and spacing, consistent with the intrinsic periodicity of the block copolymer system. Compared to the 16 kg/mol block copolymer, the structures exhibit high contrast and show a clear thickness-dependent morphological variation, indicating a greater sensitivity of the 21 kg/mol polymer to confinement effects. The domain spacing obtained from FFT analysis of the 22 nm thick film was 20 ± 2 nm, which is consistent with the expected scaling behavior ($L_0 \propto N^{2/3}$), predicting values in the range of 21–22 nm. The small deviation lies within the uncertainty of the measure-

ment, primarily arising from peak broadening in the FFT analysis. Additionally, independent measurements reported a value of 20.7 ± 1.6 nm [158], further supporting the reliability of the extracted domain spacing. Although the 20 nm or 22 nm thick films are commensurate with L_0 , the presence of in-plane cylinders indicates that the perpendicular orientation is not fully stabilized under these conditions. This indicates that interfacial interactions and preferential wetting still have some influence over the geometric confinement effects.

Based on these results, the film thickness was reduced systematically below the natural domain spacing, L_0 , to investigate the role of geometric confinement on cylinder orientation. The motive behind this strategy is to examine if geometric confinement restrains the formation of in-plane cylindrical domains and promotes perpendicular orientation. Thus, PS-*b*-PDMS thin films were prepared at sub- L_0 thickness and subjected to static SVA under the same conditions.

Figure 5.2 shows the annealed thin films with thicknesses of 8 nm, 10 nm, and 13 nm. The thinnest film (Figure 5.2 a) exhibits a mixed morphology with irregularly lying cylinders (worm-like features) and a few dot-like structures. Increasing the thickness to 10 nm (Figure 5.2 b) leads to an improvement in the structural orientation. There are still some worm-like features, although the dot-like features are dominant throughout the sample. At 13 nm (Figure 5.2 c), the substrate is fully covered with uniformly arranged dot-like structures. The domain diameter was determined to be 11.4 ± 1.5 nm from particle analysis. The domain spacing (pitch) was extracted using FFT analysis, yielding a value of 19.2 ± 0.5 nm. This is slightly smaller than the 20.7 ± 1.6 nm obtained at $h \approx L_0$ [158]. The small reduction may also reflect a lower edge sharpness of the cylindrical domains or a lower SEM contrast in the thinner film. Further

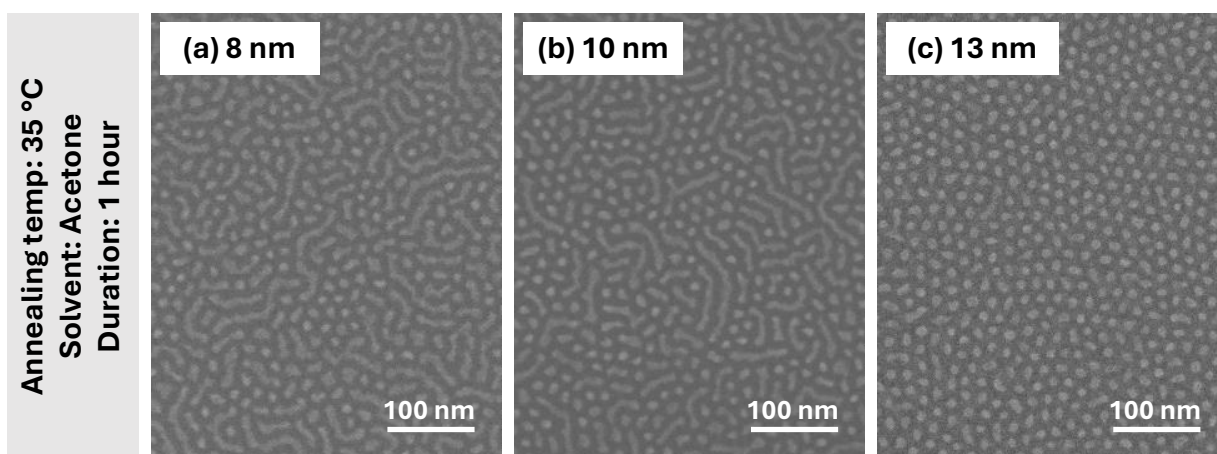


Figure 5.2. Top-view SEM images of PS-*b*-PDMS thin films with thicknesses below the natural domain spacing L_0 . The static SVA was performed by maintaining the temperature at 35 °C for 1 hour in acetone. SEM images were recorded after plasma cleaning in an oxygen plasma (details in Section 3.3) to remove PVA residuals and PS partially.

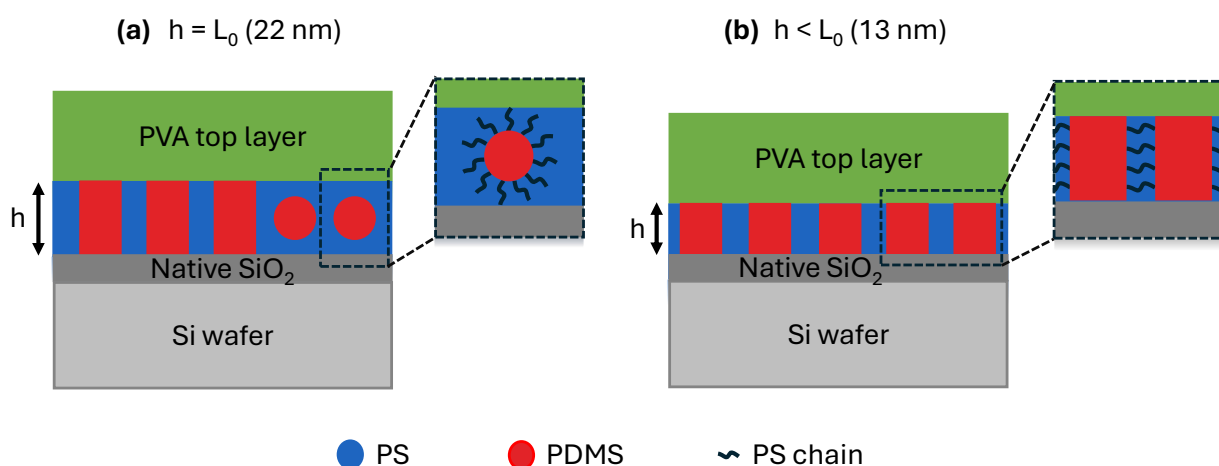


Figure 5.3. Schematic illustration of the cylinder orientation in PS-*b*-PDMS thin films at two thickness regimes. (a) At a thickness commensurate with the natural domain spacing, $h \approx L_0$ (22 nm), the film accommodates a mixture of parallel and perpendicular cylindrical domains. (b) At sub- L_0 thickness, $h < L_0$ (13 nm), the available film thickness no longer permits the parallel arrangement, and perpendicular cylindrical domains become the dominant morphology, with cylinder height adapting to the film thickness.

details of the analysis methods are provided in the Supplementary Information (Section A.2.3 and A.2.3).

For all sub- L_0 thicknesses, the SEM contrast of the nanodomains is lower than at $h \approx L_0$, attributed to the reduced height of the PDMS/SiO_x features in the thinner films, which lowers the topographic signal-to-noise ratio in SEM. A possible explanation for the observed thickness-dependent morphology is illustrated schematically in Figure 5.3.

At a thickness comparable to the natural domain spacing ($h \approx L_0$; Figure 5.3 a), the SEM investigation shows a mixture of perpendicular and parallel cylindrical domains. In the parallel configuration, the in-plane PDMS cylinder is sandwiched between PS wetting layers at the substrate and the PVA top coat interface. The PS chains extend radially from the PDMS cylinder toward the substrate and top interface. A similar wetting-layer arrangement was previously identified for the 16 kg/mol PS-*b*-PDMS thin films studied in Chapter 4 (see Section 4.4.3).

When the film thickness is reduced below L_0 , the available vertical space is no longer sufficient to accommodate the full parallel arrangement with PS chains extending to the PVA top layer. Maintaining the parallel configuration would therefore require the PS chains to be compressed substantially below their natural extension, forcing them into a strained state and incurring an elastic free-energy penalty.

In contrast, the perpendicular configuration avoids this strain. The PDMS cylinders span vertically from the substrate to the PVA top coat, and the PS chains extend laterally between cylinders (Figure 5.3 b). The inter-cylinder spacing of L_0 provides sufficient room for the PS

chains to adopt their natural conformations. The perpendicular orientation is therefore the more energetically favored under sub- L_0 confinement, consistent with the experimentally observed transition to a fully perpendicular cylindrical morphology at 13 nm.

The chain conformation argument given above applies when the film thickness is below L_0 , but still larger than the polymer chain dimensions. The morphology observed in the 8 nm and 10 nm thick films requires a different consideration. The unperturbed end-to-end distance of the 21 kg/mol PS-*b*-PDMS chain is $R \approx 9.6$ nm (see Supplementary Information, Section A.2.2), which represents the typical spatial distance between the chain ends. At film thicknesses comparable to or smaller than R , both the parallel and perpendicular cylinder configurations involve significant chain stretching or compression along the constrained direction, and the chain-conformation argument no longer applies.

In this regime, the bulk cylindrical morphology is no longer the stable configuration. Self-Consistent Field Theory (SCFT) calculations [159] of diblock copolymers confined in thin films show that multiple morphologies, including parallel and perpendicular cylinders, perforated lamellae, and hybrid configurations, become possible in this thickness range. The equilibrium structure is strongly influenced by film thickness, volume fraction, and interfacial energies [159]. Experimentally, cylinder-forming BCP thin films are known to exhibit thickness-dependent surface reconstructions, with disordered or hybrid morphologies stabilized at film thicknesses comparable to or smaller than the microdomain size [160]. Similarly, ultraconfined BCP films exhibit extreme morphological sensitivity to small variations in film thickness under selective substrate conditions [161].

The morphology trend observed here is consistent with this framework: at 8 nm ($h < R$), the morphology consists of short, irregular features with significant local disorder. At 10 nm ($h \approx R$), predominantly dot-like features with some irregular features are observed. At 13 nm ($h > R$), the confinement argument described above applies and well-defined perpendicular cylinders form. This interpretation should be regarded as a plausible explanation; the morphology in the strongly confined regime depends on multiple coupled factors, including the film thickness, chain conformation, interfacial energetics, and the kinetics of microdomain ordering during SVA.

Overall, these results contrast with the observation in Chapter 4, where matching block copolymer thickness to the natural domain spacing promoted improved ordering but did not overcome the strong interfacial interactions that stabilize the parallel cylinders. In the present system, the combination of increased molecular weight and reduced film thickness promotes perpendicular cylindrical domains. These observations indicate that sub- L_0 film thickness plays a crucial role in overcoming preferential wetting effects and stabilizing perpendicular cylindrical domains under the investigated annealing conditions. This highlights that thickness reduction effectively enables perpendicular orientation in the current high- χ PS-*b*-PDMS system.

5.2 Directed self-assembly of cylinder structures

As the formation of perpendicular-oriented cylindrical structures was achieved, their behavior under directed self-assembly (DSA) was investigated to evaluate the applicability of the perpendicular cylinder-forming BCP. A prepatterned substrate with trench widths of 110 nm, mesa width of 130 nm, and a depth of 30 nm was employed. These geometrical parameters slightly differ from those of the topographical trench structures described in Section 4.5. The trench width of 110 nm corresponds to approximately five times the natural periodicity of the block copolymer ($L_0 \approx 21\text{--}22\text{ nm}$), indicating near-commensurate confinement conditions that are expected to facilitate ordered domain packing within the trenches. For both PS-*b*-PDMS polymers (16 kg/mol and 21 kg/mol), trench geometries were designed to satisfy commensurability with L_0 . This enables a qualitative comparison with the 16 kg/mol PS-*b*-PDMS, where confinement was insufficient to induce alignment of the domains in trench direction. BCP films of 13 nm thickness, which on planar substrates yielded perpendicular cylinders, were annealed under identical conditions (35 °C in acetone for 1 hour), on the patterned substrate.

Figure 5.4 shows the morphology of self-assembled PS-*b*-PDMS thin films on the patterned SiO₂ substrate. Compared to the results presented in Section 4.5, an overall improvement in

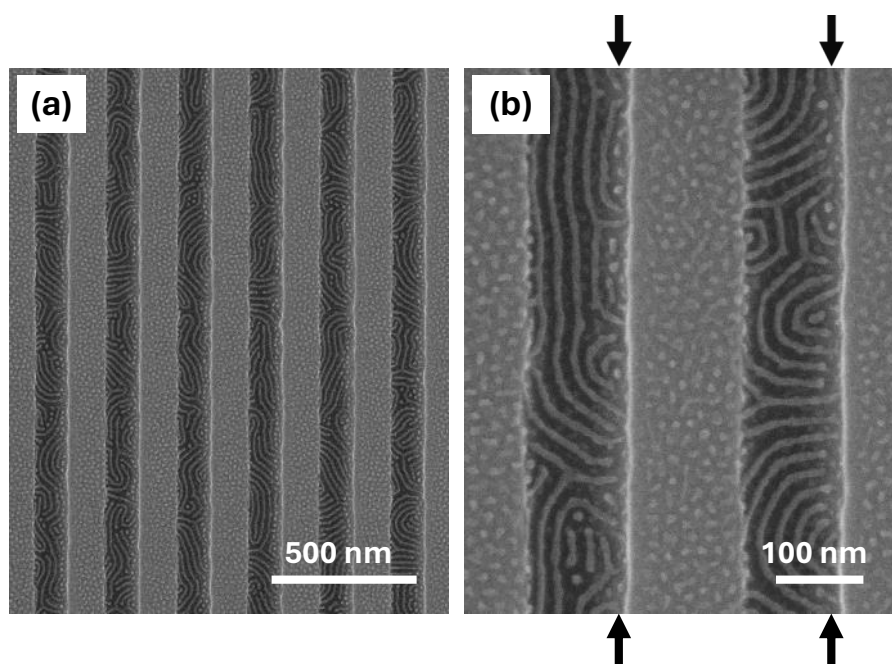


Figure 5.4. Top-view SEM images of the PS-*b*-PDMS thin films on a patterned SiO₂ substrate after static SVA followed by plasma cleaning. (a) Low-magnification image revealing trench confinement and (b) Higher-magnification view showing the domain morphology. Black arrows highlight localized regions within the trench where dot-like domains appear, suggesting local variations in confinement conditions.

structural ordering and uniformity is observed. Especially, the uniformity of the nanostructures is much improved compared to the previous polymer. The top-view SEM image at low magnification (Figure 5.4 a) exhibits an overview of the morphology on the patterned area, clearly showing trench confinement and uniformity of nanostructures.

Figure 5.4 (b) shows a high-magnification image revealing the domain morphology. The trench regions are predominantly covered with in-plane cylindrical domains, while the mesa regions consist of dot-like structures. However, these in-plane cylindrical domains do not exhibit long-range alignment along the trench direction; instead, a fingerprint-like morphology is observed, indicating limited guidance by the trench geometry. In addition, the presence of localized dot-like structures is observed within certain regions of the trench, particularly on the right-hand side, as highlighted by black arrows in Figure 5.4 (b). The observed asymmetry in domain orientation across the trench cannot be fully explained by geometric confinement alone. In particular, vertically oriented cylinders are observed on one side of the trench, while the opposite side exhibits reduced vertical alignment.

This behavior can be attributed to sidewall tapering, which was previously identified in Section 4.5. The presence of a non-vertical sidewall introduces a lateral gradient in the effective film thickness across the trench. As a result, regions near the tapered sidewall, where the effective film thickness is reduced, favor perpendicular cylinder formation, whereas regions deviating from the optimal thickness promote in-plane orientation or mixed morphologies.

This interpretation is further supported by the contrast variations in the SEM image (Figure 5.4 b), where bright regions near one sidewall correlate with areas exhibiting perpendicular-oriented cylinders. These observations suggest that, in addition to commensurability, subtle variations in trench geometry, such as sidewall tapering, play a critical role in determining local domain orientation.

The variation in morphology between the trench and the mesa regions can be attributed to BCP film thickness differences. The mesa regions likely retain a film thickness in the sub- L_0 regime and favor perpendicular orientation, whereas trenches with a thickness deviating from sub- L_0 result in a mixed morphology consisting of in-plane and perpendicular domains. This observation is consistent with the results from the thickness analysis discussed in Figure 5.2.

The coexistence of parallel and perpendicular domains, along with the absence of long-range alignment along the trench direction, suggests that the applied geometric confinement is insufficient to promote uniform domain orientation in the trenches. Several factors can influence this behavior. The most likely contributing factor is the sidewall tapering of the trenches, which gives rise to a non-uniform effective confinement geometry across the trench width and a locally disrupted alignment of the cylinders, particularly visible in the tapered regions. The dominance of interfacial interactions due to the absence of a neutral layer at the substrate and side walls is a further contributing factor influencing the domain configuration, particularly

under confinement.

These results highlight that achieving uniform graphoepitaxial alignment requires careful control of multiple parameters simultaneously: the trench geometry (smooth vertical sidewalls, well-defined trench width commensurate with nL_0), the film thickness, and the interfacial interactions at the substrate, sidewalls, and top interface. Optimising these parameters individually and in combination is a direction for future work.

5.3 Pattern inversion approaches

As the formation of perpendicular cylindrical domains and their conversion into SiO_x has been successfully achieved, these structures can serve as templates for nanopatterning. However, for many applications, including high-density nanoscale arrays, an antidot-like patterned mask instead of a dot-patterned mask would be preferable as exemplarily described in Section 5.4. Therefore, to enable broader applicability of the PS-*b*-PDMS block copolymers, pattern inversion from filled vertical SiO_x cylinders into empty cylinders in a SiO_x would be desirable, and needs to be investigated for translating self-assembled morphologies into functional architectures.

In this study, two different strategies were adopted to convert the dot-like morphology into antidot-like structures. The first approach involves the use of a sacrificial chromium film, which is partially removed in a controlled manner by vibration polishing. The second approach is completely different and utilizes selective swelling-driven inversion in which dynamic solvent vapor annealing (SVA) is used to induce reorganization of polymer domains to create antidot-like structures after phase separation. Both methods were systematically investigated and are discussed in the following subsections. Among these techniques, the solvent-based swelling technique is particularly attractive due to its ability to modify the nanoscale morphology without inducing mechanical damage.

5.3.1 Inversion using a sacrificial film and selective etching

The process flow of pattern inversion is schematically illustrated in Figure 5.5. The process starts by spin coating PS-*b*-PDMS (21 kg/mol) thin films with a thickness of 13 nm onto PECVD-grown SiO_2 (100 nm) films on silicon substrates. The thin film is subsequently coated with a PVA top layer and annealed using static SVA with annealing conditions (see Section 5.1) to obtain perpendicular cylindrical structures. These perpendicular PDMS domains are converted into SiO_x while the PS matrix is removed by plasma etching (as outlined in Section 4.4.2). This completes the first step in the inversion process, as shown in Figure 5.5 (a).

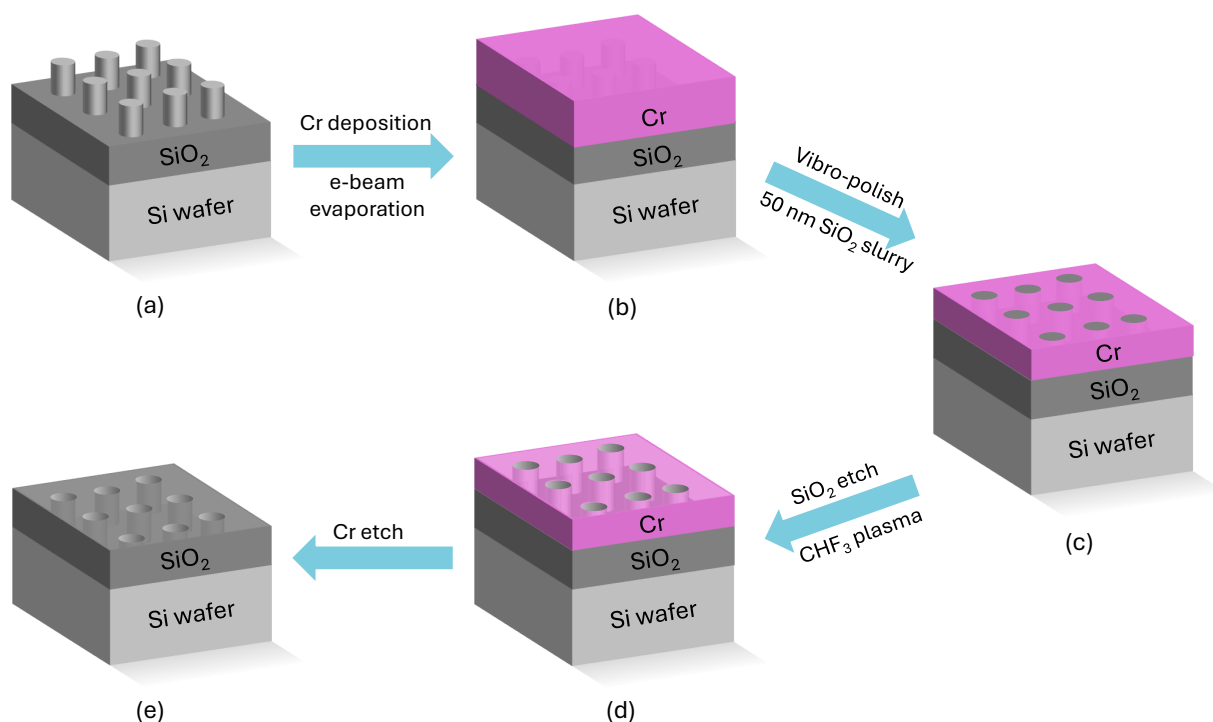


Figure 5.5. Schematic illustration of the pattern inversion process. A tilted view of the layer system is included to distinguish between cylinder/dot-like and final pore/antidot geometries.

On this nanopatterned SiO₂ surface consisting of vertical cylinders, a 30 nm thick chromium layer is deposited by electron beam evaporation, to ensure complete coverage of the pillar tops (Figure 5.5 b). The sample is then subjected to vibratory polishing for controlled chromium removal using a 50 nm SiO₂ abrasive slurry as mentioned in Section 3.6. The thin film is polished until the pillar tops are exposed, as shown in Figure 5.5 (c). This allows to etch the exposed SiO_x pillars selectively, while the chromium layer then acts as a hard mask. The anisotropic SiO_x etching is then performed to transfer the hole pattern into PECVD-grown SiO₂ film (Figure 5.5 d). Post etching to the required depth, the chromium can be selectively etched, resulting in a patterned silicon dioxide thin film with hexagonally arranged pores/antidots as illustrated in Figure 5.5 (e).

The chromium planarization step is crucial, since the SiO_x pillars need to be exposed but must not be removed completely. Vibration polishing is chosen as a material removal technique because mechanical lapping is also used in semiconductor technology for planarization steps [162]. Therefore, the first objective was to evaluate whether chromium can be polished at a controlled rate, so that it can be used in the inversion process. For this purpose, thin films of chromium (50 nm) were deposited on a planar silicon substrate. These test samples were subjected to vibropolishing for different durations with a load of 60 g as detailed in Section 3.6. The polished samples were analyzed by cross-section SEM using a sputter-deposited carbon

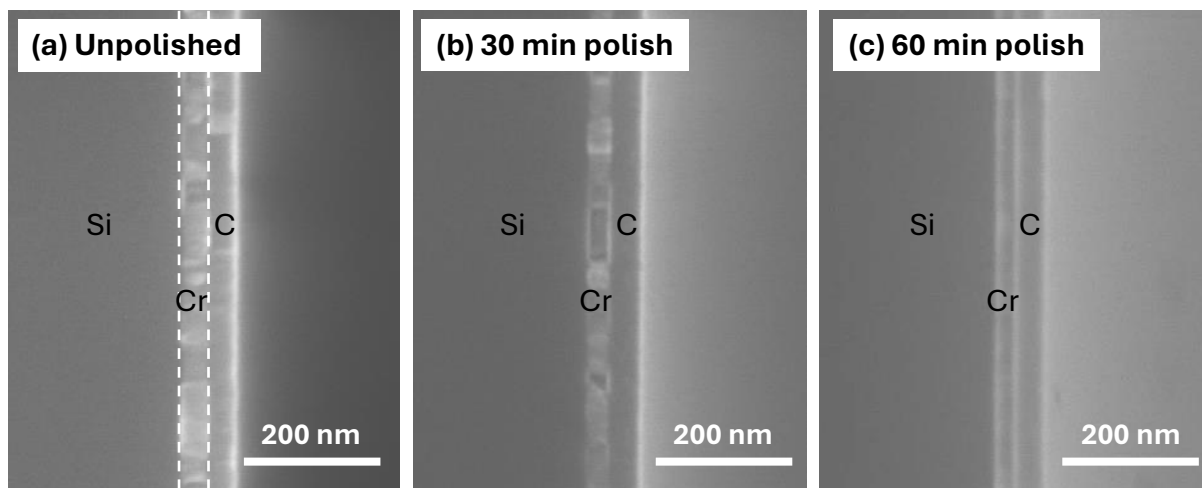


Figure 5.6. Cross-sectional SEM images showing the thickness of chromium films on bare silicon substrates: (a) unpolished sample, (b) after 30 minutes of vibratory polishing, and (c) after 60 minutes of vibratory polishing.

layer on top of the polished chromium film to enhance the image contrast. Figure 5.6 shows cross-section SEM image of chromium films before and after polishing.

Figure 5.6 (a) shows a cross-section SEM image for an unpolished chromium film. The leftmost region corresponds to the silicon wafer, followed by the chromium layer and a carbon layer on the right. The cross-section SEM images for all other samples in this study exhibit a similar layer configuration. The thickness evaluation for all the cross-section samples is done using DigitalMicrograph software [144] by measuring a line profile across the three different layers. The chromium film after 30 minutes and 60 minutes of polishing shows a decrease in

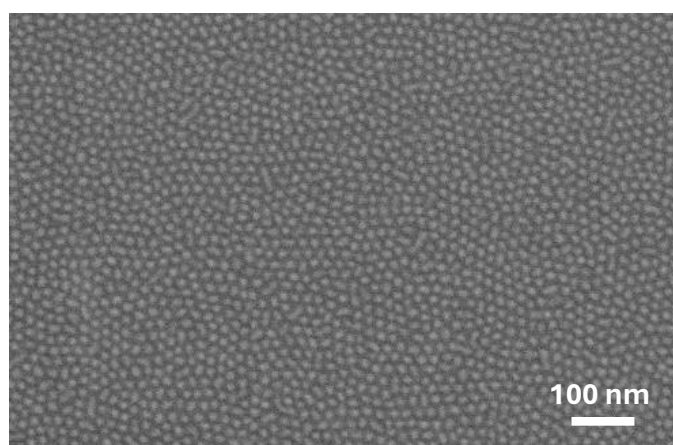


Figure 5.7. Top-view SEM image of a PS-*b*-PDMS thin film on the PECVD-grown SiO₂ (100 nm) substrate after static SVA. SEM images were recorded after plasma cleaning in an oxygen plasma (details in Section 3.3) to remove PVA residuals and PS partially.

film thickness. A polishing rate of 17 ± 1 nm/hour was determined from the thickness evaluation, which is slow enough to stop the process at a suitable chromium film thickness.

For the inversion process, 13 nm thick films of PS-*b*-PDMS on PECVD-grown SiO₂ films 100 nm were annealed to form perpendicular cylindrical domains. The top-view SEM image in Figure 5.7 shows perpendicularly oriented PDMS cylinders hexagonally arranged in a partially etched PS matrix (after plasma cleaning). The morphology is consistent with the structures on native SiO₂. The height of the PDMS-derived SiO_x cylinders after the two-step plasma process is expected to be approximately 8 nm, as indicated by previous investigations on the same polymer [158]. After the two-step oxygen plasma process, the sample was subjected to chromium deposition (nominal thickness of 30 nm) and subsequent vibropolishing. As the deposition is performed on a nanopatterned surface of SiO_x pillars, local variations in thickness are expected due to conformal coverage. The samples are subjected to vibratory polishing for different durations and analyzed by cross-section SEM for thickness evaluation.

Figure 5.8 summarizes the evolution of chromium film thickness as a function of vibropolishing time for patterned samples. An initial decrease in film thickness is observed from 10 minutes to 20 minutes with a linear trend. The cross-section SEM image of 20 minutes polished sample (Figure 5.8 a) shows a decrease in thickness to 21 nm. In this time range, chromium was removed at a rate of 60 nm/hour, indicating a controlled and effective removal during the early stages of vibropolishing.

However, beyond 20 minutes, no significant reduction in chromium thickness is observed even with an extended polishing time of 90 minutes, as shown in Figures 5.8 (b) and (c). The thickness reduction drops to around 1 nm/hour, and a continuous chromium layer is still present even after 90 minutes of polishing time. With the remaining 20 nm chromium thickness, the pillar tops cannot be exposed, given the SiO_x cylinder height of ≈ 8 nm. As a result, subsequent etching of the SiO_x pillars for pattern inversion is not feasible. Additionally, SEM and AFM analysis after 90 minutes of polishing showed a flat surface without any nanopatterns.

The observed behavior can be attributed to the influence of surface topography on the polishing process. Since the topography is initially conformal, the rougher surface promotes effective material removal at a high rate due to locally high pressure. As the polishing progresses, the surface becomes more planarized, reducing these variations and limiting further material removal. Unlike on a planar substrate Si/SiO₂/Cr, local shielding effects may persist in the patterned system due to the underlying topography. As a result, the surface becomes less accessible to the abrasive particles, resulting in a self-limiting polishing behavior.

Based on the initial design, approximately 22 nm of chromium is required to be removed from the deposited 30 nm of chromium to expose the underlying SiO_x pillars (≈ 8 nm). Although vibratory polishing results in a reduction of thickness, the limitation beyond 20 nm prevented the exposure of the pillar top.

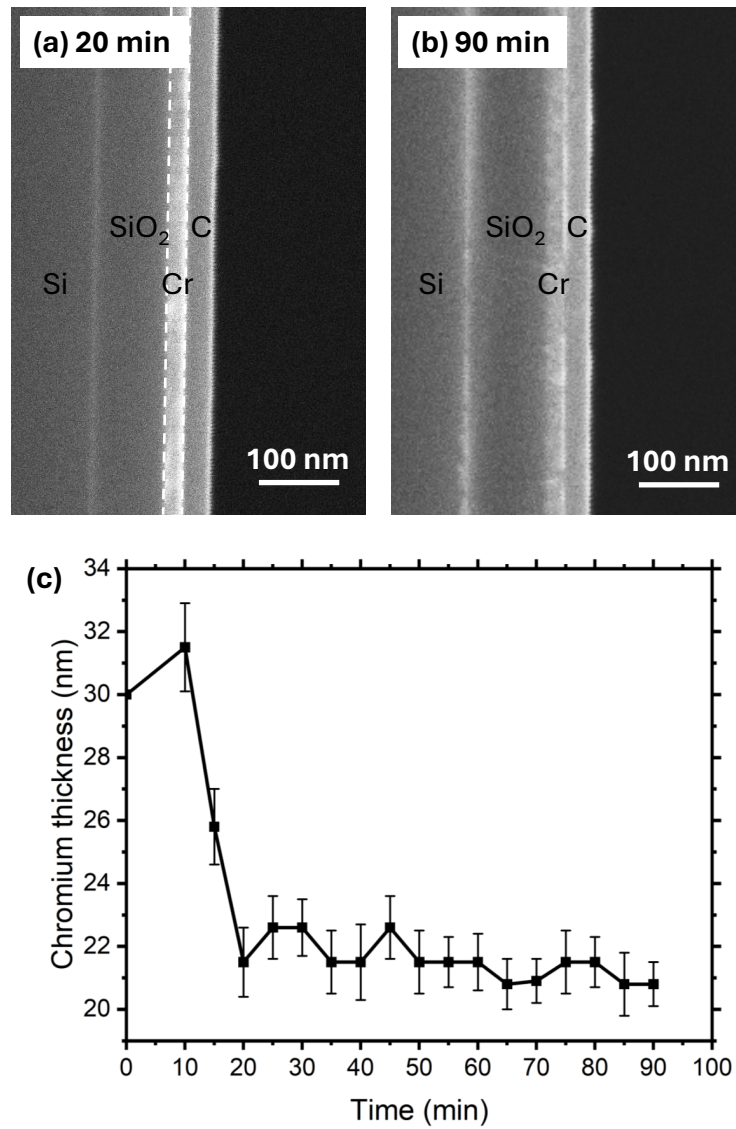


Figure 5.8. Thickness evolution study of chromium with respect to vibropolishing time. Cross-section SEM images after (a) 20 minutes and (b) 90 minutes of vibratory polishing, along with (c) a plot depicting chromium thickness as a function of polishing time.

These results demonstrate that the chromium on the planar substrate can be thinned by vibropolishing at a controlled rate. However, on patterned substrates, the process is self-limited after a certain thickness, indicating that the sacrificial film approach based on vibratory polishing is not a reliable method for pattern inversion in the present system. These results highlight the challenges associated with mechanical planarization at the nanoscale and emphasize the need for alternative material removal approaches such as ion beam milling or atomic layer etching for precise and controllable pattern inversion along a process chain using sacrificial layers, as shown in Figure 5.5.

5.3.2 Structure inversion via selective swelling

This section focuses on a solvent-mediated approach for pattern inversion which does not require mechanical material removal. Dynamic solvent vapor annealing (SVA) was explored as an alternative route to enable controlled reorganization of polymer domains through selective swelling. By selectively swelling one polymer domain, the effective volume fraction is modified and thereby the transformation of the resulting morphology is enabled.

As explained in Section 2.4.2, in SVA, the morphology after phase separation is strongly influenced by the swelling solvent species. This approach was investigated in collaboration with J. Freibel [158] in her master thesis. In Chapter 4, PS-*b*-PDMS (16 kg/mol) thin films were swelled by the neutral solvent acetone, and a toluene-heptane mixture in 5:1 proportion, resulting in approximately equal swelling of PS and PDMS domains. Among these, toluene and heptane are particularly interesting as heptane is PDMS selective and toluene behaves as a neutral solvent, and varying the solvent ratio enables selective swelling. By selectively swelling the PDMS in the 21 kg/mol PS-*b*-PDMS BCP, the effective volume fraction is enlarged, thereby driving a morphology transition in the system as indicated in the phase diagram shown in

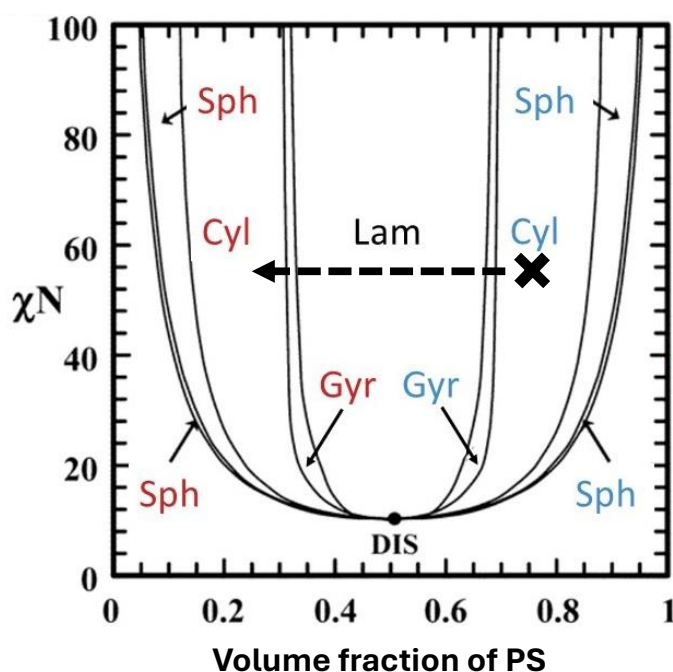


Figure 5.9. Phase diagram of block copolymer morphologies as a function of the volume fraction of block PS and segregation strength (χN), illustrating the effect of selective swelling. The proposed trajectories of a toluene/*n*-heptane solvent mixture during selective swelling are indicated, showing how the effective volume fraction is altered. The marker (X) represents the equilibrium position of the studied PS-*b*-PDMS system. Selective swelling shifts the effective composition, enabling transitions from cylindrical to lamellar or inverse morphologies.

Figure 5.9. The aim is to reduce the effective volume fraction of the PS block such that the system approaches the regime that promotes PS cylinders, as shown in the phase diagram (Figure 5.9).

PS-*b*-PDMS (21 kg/mol) thin films were annealed using dynamic SVA without a PVA top coat, because preliminary experiments with a 300 nm thick PVA film did not show structure inversion. The presence of the PVA top layer is assumed to slow down the deswelling process such that the initially inverted structure (anticylinder) has enough time to return to the equilibrium structure (cylinders) in the unswollen state. In addition, several studies have reported the SVA of PS-*b*-PDMS thin films without a top coat, where an additional plasma etching is done for the removal of the PDMS wetting layer.

Unlike the systematic variation of each parameter as in the previous sections, in this section only the selected processing conditions that yielded the morphology inversion will be treated, as a detailed description has already been given elsewhere [158]. To find suitable processing conditions, parameters like solvent mixture ratio, temperature, and annealing duration were varied. Out of these, the solvent mixture ratio plays a significant role, and it has been reported that a toluene-heptane mixture with a toluene fraction from 55-66% promotes antidot formation [150, 163, 164]. Thus, a toluene-heptane mixture with a toluene concentration of 60% was utilized for dynamic SVA. Thin films with a thickness of 20 nm were annealed at different temperatures of 25–65 °C and the annealing duration was varied from 30 min to 150 min. Nitrogen gas was used as the carrier gas, and the film was deswelled by purging the chamber with 10 sccm nitrogen for 10 minutes. An annealing duration of 120 min at a temperature of 45 °C resulted in antidot structures, as shown in Figure 5.10.

The low magnification image in Figure 5.10 (a) shows a morphology overview across the surface, where darker and brighter regions across the substrate appear. These variations indicate that the morphology is not uniform over the entire surface. To investigate the nanostructure in these regions, a representative region from Figure 5.10 (a) is selected and investigated at higher magnification to reveal the nanostructure morphology. A transition in morphology is visible across the highlighted region from red to green (Figure 5.10 b). Three different morphologies are observed: antidots (red region), in-plane cylinders (white region), and short-range ordered polymer domains (green region). In the regions appearing dark in the low-magnification image in Figure 5.10 (a), hexagonally arranged antidot features are observed (Figure 5.10 c).

The variations in the nanostructure morphology are correlated to local differences in the film thickness, which have been observed by AFM [158] on these regions. The AFM investigation revealed that the regions with antidot-like structures have a higher film thickness of approximately 10 nm, compared to the short-range ordered structures. In addition, it has been observed [158] that the width and pitch of these antidot structures are larger than those of

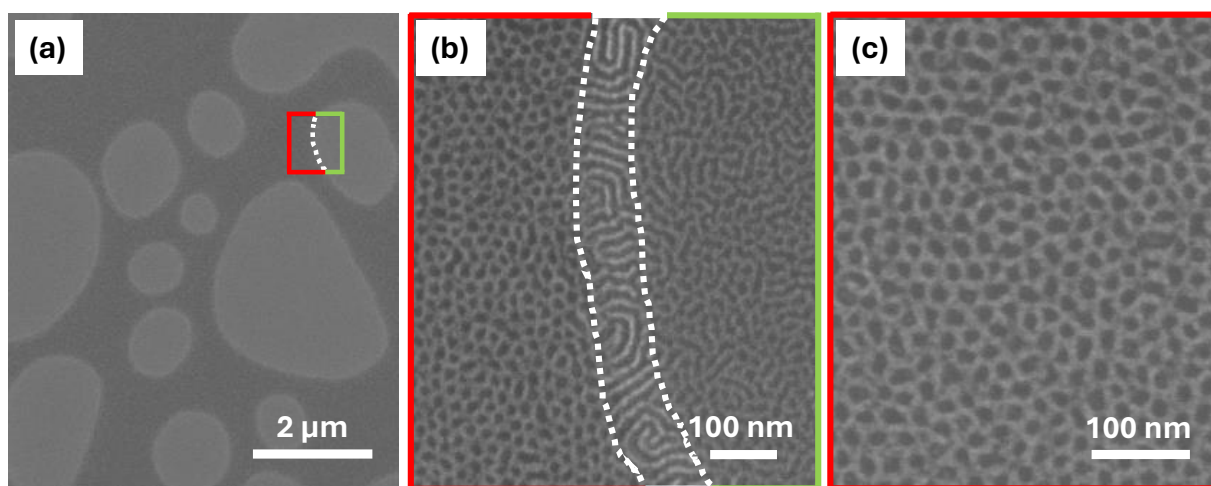


Figure 5.10. Top-view SEM images of the PS-*b*-PDMS thin films subjected to selective swelling with dynamic SVA. A toluene concentration of 60% out of the heptane mixture is employed for selective swelling.

perpendicular cylindrical domains. The pitch of the anticylinders were 25 nm, while the cylinders were 21 nm, and the anticylinder diameter was 15 nm instead of 10 nm for the cylindrical (PDMS) domains. The increased pitch reflects the swelling of the PDMS block by the heptane-rich solvent, which expands the effective domain size of the inverted phase. Thus, for the antidot structures, the spin-coated film thickness of 20 nm is not commensurate with the natural domain spacing (25 nm), resulting in polymer redistribution and consequently leading to local thickness variations. This shows that the morphology of the polymer blocks is highly sensitive to both film thickness and effective volume fractions; even small variations across the sample can lead to different equilibrium or metastable structures.

Figure 5.10 (c) shows a higher magnification image of a well-ordered region where the antidot morphology is clearly visible. Both structures, cylinders and anti-cylinders, exhibit similar ordering, with the cylindrical domains appearing slightly more ordered based on qualitative observation. Altogether, the surface is covered by two different types of structures with comparable surface coverage fractions. Nevertheless, the study shows that in principle it is possible to create ordered antidot structures by dynamic SVA, even though some optimization is required to obtain homogeneous morphologies on the entire surface. In the following section, a potential application of the BCP patterns described above will be presented: memristors.

5.4 Proposed memristor architecture based on BCP-derived nanopatterns

The block copolymer-derived nanopatterns developed in this work provide a promising platform for memristive device applications, where geometric confinement of the active region can reduce the unpredictability of conductive filament formation that limits RRAM device uniformity. The underlying physics of resistive switching, the relevant electrochemical metallization (ECM) and valence change memory (VCM) mechanisms, and the role of nanopatterning in controlling filament formation are described in Section 2.6. In this section, the advantages of using the PS-*b*-PDMS system from this work for memristor applications are discussed, and a conceptual device architecture is proposed.

The fabrication of a memristor system by exploiting PS-*b*-PDMS block copolymer lithography offers several advantages. The nanopatterned SiO_x obtained by the lithography process aids in spatial control over filament formation. In the studied PS-*b*-PDMS system, the ordered antidot-like pores, if filled with suitable switching material, may act as sites for electric field concentration. As a result, this reduces uneven filament formation behavior, thereby improving the device uniformity. Furthermore, the feature size in the sub-20 nm regime achieved in this work is beneficial for high-density memory applications. By implementing a small feature size, it enables a high packing density of memory cells, increasing the storage capacity. In addition, the nanoscale features enable local confinement of the electric field, which reduces the operating voltage and improves the switching efficiency [98]. Thus, a SiO₂-based nanopatterning derived from block copolymer lithography offers a scalable and effective pathway towards energy-efficient and high-density RRAM devices.

Recent studies have demonstrated that block copolymer (BCP) lithography can be exploited in various ways to fabricate memristive devices, enabling controlled electric field localization by nanopatterning the dielectric layer [12–16]. Among these, a study reported in [15] demonstrated an ECM-based memristive device composed of silver nanocones embedded in a SiO₂ nanomesh to enhance the resistive switching (Figure 5.11). PS-*b*-PDMS block copolymers are employed to form line patterns by DSA, which are first converted into SiO_x line templates. These are then replicated as Cr nanowires via nano-transfer printing. By performing a second printing step with a 90° rotation, an orthogonal Cr nanowire array is formed, creating a mesh structure. This mesh serves as an etching mask, enabling the fabrication of square-shaped nanopatterns. The incorporation of the nanomesh within the oxide layer enables local confinement of the electric field, which promotes preferential filament formation at the tip of the nanocones, as shown in Figure 5.11. In particular, the well-arranged nanomesh with a width of approximately 26.5 nm and 9.8 nm acts as a predefined site for filament formation, thereby

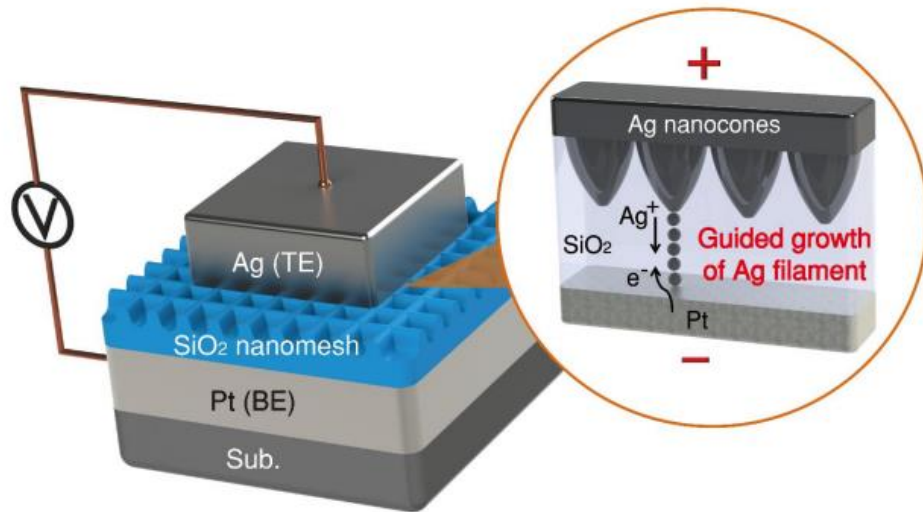


Figure 5.11. Schematic showing a nanomesh patterned memristor device based on electrochemical metallization (ECM) [15]. BE, and TE correspond to the bottom and top electrodes.

improving uniformity with high-density memory cells. The electrical characteristics demonstrated improved switching speed along with enhanced uniformity and reduced cycle-to-cycle variation, which is critical for practical applications.

While such nanostructured systems demonstrate the importance of geometric confinement in memristive devices, achieving these with multi-step fabrication routes remains a challenge for scalable implementation. These challenges could be addressed by patterning the dielectric layer with the PS-*b*-PDMS system (21 kg/mol) used in this work, which produces hexagonally ordered 15 nm antidot structures in a single block copolymer self-assembly step, without the need for nano-transfer printing. Although the 15 nm antidot pore size in this work is larger than the 9.8 nm features achievable with the orthogonal nano-transfer printing approach [15], the hexagonal arrangement of the antidot array compensates for the larger pitch. The resulting areal density of switching sites is approximately 1850 pores/ μm^2 , which is comparable to the 1890 pores/ μm^2 density of the square nanomesh architecture at 23 nm pitch. The contribution lies in process simplicity rather than feature size, offering a single-step alternative with comparable density of switching sites that may be easier to integrate at large scale.

Based on these findings, a conceptual memristive system architecture based on the existing nanostructured system (Figure 5.11) is proposed, as illustrated in Figure 5.12. The concept utilizes nanopatterned SiO_x structures (antidots) developed in this work. The fabrication process starts by depositing the bottom electrode on the silicon substrate (Figure 5.12 a) with subsequent deposition of the SiO_2 layer on the bottom electrode (Figure 5.12 b). BCP lithography is performed using the 21 kg/mol PS-*b*-PDMS system to produce hexagonally arranged pores (antidot-like structures) (Figure 5.12 c). Finally, the top electrode is deposited on the

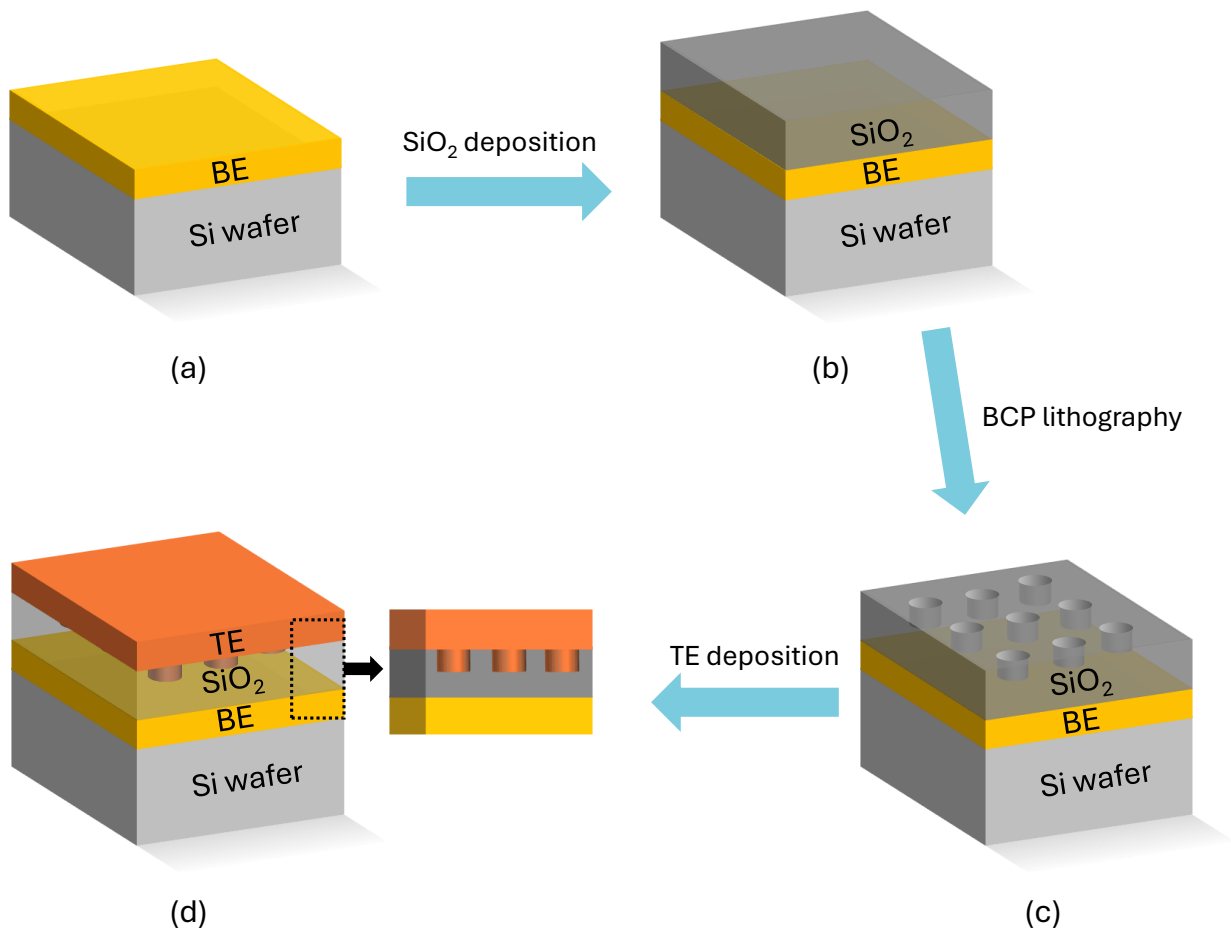


Figure 5.12. Schematic illustration of the fabrication of the proposed memristive design based on block copolymer-derived SiO_x antidot-like structures.

surface, resulting in a top electrode film that partially fills the nanopores in SiO₂ as shown in Figure 5.12 (d).

Despite the promising potential of the proposed memristive system, the fabrication and experimental realization of such a device are beyond the scope of the present study. Thus, the proposed concept requires experimental validation and electrical characterization. Furthermore, the uniformity and reproducibility of the antidot-like structures in the BCP thin film directly influence the device performance. Overall, the presented concept highlights the potential of the block copolymer-derived nanopatterning as a viable approach for the fabrication of a high-density memristive system.

5.5 Summary

This chapter explored the self-assembly behavior of a PS-*b*-PDMS BCP (21 kg/mol), aiming at the formation of perpendicularly oriented cylindrical structures and the inversion of this pattern for potential applications. The study began with a static solvent vapor annealing (SVA) system using parameters adapted from the previously studied polymer with the same polymers, but shorter chains and similar composition (Chapter 4). Perpendicularly oriented nanostructures were not fully achieved when the film thickness was varied within the natural domain spacing (L_0) range. To overcome this limitation, the film thickness was reduced to the sub- L_0 regime and a thickness of 13 nm resulted in well-ordered dot-like (perpendicular cylindrical) PDMS domains, which convert into approximately 8 nm tall, 10 nm diameter SiO_x cylinders, hexagonally arranged with 21 nm pitch.

The uniform arrangement of hexagonally packed cylinder structures motivated us to investigate the influence of directed self-assembly. The structures confined within 110 nm wide trenches did not exhibit long-range alignment, while the mesa regions in between were covered with dot-like structures due to locally reduced BCP film thickness.

The second part of this chapter focused on pattern inversion, aiming to convert the dot-like structures obtained from the PS-*b*-PDMS BCP into antidot (pore) morphologies. Two different approaches were implemented and investigated. Firstly, pattern inversion using a sacrificial chromium film as a hard mask combined with vibratory polishing was explored, which showed a controlled removal of the chromium on the planar sample. However, on the patterned sample, the material removal stopped after the surface became more planar. This approach is considered to be challenging because it involves precision planarization in the single-digit nanometer regime.

In contrast, selective swelling-driven inversion using dynamic SVA was explored as a simpler approach and achieved promising results. The PDMS block was selectively swollen by increasing the heptane fraction in a toluene-heptane mixture, thereby modifying the effective volume fraction. At a toluene concentration of 60%, a 20 nm thick PS-*b*-PDMS thin film annealed at 45 °C for two hours resulted in mixed morphology consisting of hexagonally arranged antidot-like structures at about 50% of the sample and short-range ordered domains at the other 50%. The comparable fraction of these morphologies highlights local thickness variation across the film, leading to mixed morphologies in different regions.

Finally, based on nanostructures obtained in this work, a conceptual memristive device architecture was proposed. The proposed concept is inspired by recent works on SiO_2 based memristive systems, where the resistive switching occurs by ion transport induced filament formation, described by the electrochemical metallization mechanism (ECM). The block copolymer-derived SiO_x antidot structures act as predefined sites for localized electric field confinement.

Compared to the literature system, where multiple lithography steps are employed, the proposed architecture offers a simpler and potentially scalable route to achieve sub-20 nm feature sizes. The proposed system is expected to demonstrate advantages in terms of process simplicity, achievable feature density, and spatial control over filament formation through the hexagonally ordered antidot template.

Overall, this chapter demonstrates that block copolymer self-assembly serves as a versatile platform for nanoscale pattern formation and inversion. This highlights its potential for enabling next-generation memory devices through controlled nanopatterning.

6 Conclusion and Outlook

6.1 Conclusion

In this work, block copolymer (BCP) lithography is demonstrated as a versatile and scalable platform for nanopatterning large surface areas at low cost and short processing times. High- χ PS-*b*-PDMS block copolymers were employed in this work due to their high etch contrast and ability to achieve sub-10 nm feature sizes. The self-assembly behavior and nanopatterning capabilities of these polymers under solvent vapor annealing (SVA) were systematically investigated. The studies focused on achieving nanoscale morphologies in the sub-10 nm regime with particular emphasis on morphology control, pattern orientation, and integration into device architectures for advanced applications. Two different molecular weight systems were systematically studied, and their response to solvent vapor annealing, geometric confinement, and pattern inversion strategies was examined.

Firstly, the 16 kg/mol cylinder-forming PS-*b*-PDMS system was studied. Two different annealing approaches, namely static and dynamic SVA, with extensive optimization of annealing conditions, revealed a strong tendency to form in-plane cylindrical morphologies. Despite extensive optimization, including the use of a PDMS brush layer for surface neutralization, different substrates, and directed self-assembly approaches, perpendicular cylinder orientation could not be achieved. This behavior is attributed to the influence of interfacial interactions and preferential wetting effects, which limit the polymer domain reorganization, hindering their ability to orient perpendicularly under confinement.

To overcome this limitation, a higher molecular weight PS-*b*-PDMS system (21 kg/mol) was investigated. The optimization of the film thickness revealed the formation of mixed morphologies consisting of perpendicular-oriented and in-plane cylindrical domains. A key finding of this study is that reducing the film thickness to the sub- L_0 regime enabled the formation of uniformly distributed, hexagonally ordered perpendicular cylinders across the substrate. This indicates that the in-plane orientation of the cylindrical domains can be effectively suppressed by geometrical confinement through thickness reduction.

In addition, the pattern transfer process was investigated as a crucial step in block copoly-

mer lithography. Selective removal of PS and conversion of PDMS into silicon oxide (SiO_x) were achieved using a two-step oxygen plasma process, as confirmed by DRIFT spectroscopy. The resulting material contains residual carbon, which does not adversely affect pattern transfer fidelity and may contribute to enhanced mechanical stability of the nanostructures. For the 16 kg/mol BCP, detailed morphological analysis revealed 9 nm feature sizes with a domain spacing of 18 nm. Cross-sectional TEM investigations showed dome-like nanostructures corresponding to horizontally aligned half-cylinders. This geometry is attributed to asymmetric wetting effects and plasma-induced densification, providing insight into the nanoscale structure after pattern transfer.

For the pattern inversion, to transform perpendicular cylindrical domains into antidot-like nanostructures two different approaches were employed. The deposition of a sacrificial chromium film, followed by vibratory polishing to expose the embedded SiO_x nanocylinders, was explored. The mechanical planarization approach for the controlled removal of the chromium hard mask was successful for planar substrates. However, the nanopatterned substrates exhibited a self-limiting behavior, preventing the exposure of the SiO_x cylinder tops. This indicates a limitation of the vibratory polishing process in nanoscale pattern inversion with the investigated process chain.

On the other hand, dynamic solvent vapor annealing with selective swelling enabled the formation of anticylinder features using the cylinder-forming polymer. This process involved the selective swelling of PDMS with heptane, which enhances the effective volume fraction of the PDMS and induces the formation of PS cylinders within the swollen PDMS. This results in the formation of an empty cylinder upon removal of PS, i.e., the creation of an inverted SiO_x structure. Although the resulting morphology exhibits local variations in nanostructure morphology, hexagonally arranged antidot-like morphology in the sub-20 nm regime was successfully achieved, covering approximately 50% of the surface. It is likely that this surface fraction can be extended to a full coverage by optimizing the BCP film thickness with otherwise unchanged processing parameters.

Finally, based on the results obtained in this work, a conceptual memristor device architecture was proposed. The obtained SiO_x antidot morphology can be used as a mask to create well-arranged pores in the dielectric SiO_2 . By the implementation of a top electrode, the columns of the top electrode are embedded in the SiO_2 , which acts as preferential sites for electric field localization, thereby potentially enabling improved control over filament formation during resistive switching. As this approach does not involve multiple lithographic steps, the presented approach is expected to offer a scalable and simpler route for creating high-density memory devices than present technologies.

To conclude, this thesis demonstrates that block copolymer lithography utilizing the self-assembly of polymer domains to create ordered nanopatterns in the sub-10 nm regime can be

tailored through various processing strategies to create a wide range of nanoarchitectures. The results highlight both the opportunities and the limitations associated with achieving perpendicular orientation, directed self-assembly, pattern inversion, and integration of block copolymer-derived nanopatterns into future electronic applications. Thus, block copolymer lithography is proven once again as a versatile nanopatterning technique and holds significant potential in the fabrication of next-generation electronic devices.

6.2 Outlook

While this work provides important insights into BCP lithography, several open questions remain for further investigation to enable their application in practical devices. This section discusses some key directions for further research and potential improvements.

First, the self-assembly behavior investigation of the 16 kg/mol PS-*b*-PDMS BCP suggests the formation of a PS wetting layer at the surface. In addition, the TEM investigation after PS etching and PDMS conversion by the two-step oxygen plasma treatment reveals a half-cylinder morphology of the in-plane fingerprint domains. To obtain a conclusive understanding, cross-section TEM analysis after SVA is required prior to the plasma treatments. This would give further insight into the possible plasma erosion effect and into the conversion of PDMS into SiO_x.

Secondly, further optimization of the brush layer could be implemented to favor perpendicular domain orientation of the cylinder-forming shorter chain PS-*b*-PDMS. The implementation of a random copolymer brush, PS-*r*-PDMS, which provides equal affinity to both PS and PDMS should lead to perpendicular oriented cylindrical PDMS nanodomains. This could not be implemented in the current work, as such a random copolymer was not commercially available. The synthesis would be the next viable approach, which, however, requires expertise in polymer synthesis.

Further studies on the directed self-assembly are required to achieve long-range alignment of nanostructures within the trenches. This may involve optimizing the trench width in steps of a fraction of L_0 , i.e., in steps of 18 nm and 22 nm, to obtain commensurable trench widths after trench etching. Improving sidewall roughness and controlling sidewall slopes by tuning the etching recipe, as well as tuning interfacial energies to guide the domain orientation, would be leveraged to achieve well-aligned patterns.

In the case of the pattern inversion approach by dynamic SVA on 21 kg/mol, the influence of film thickness requires further investigation to obtain homogeneously covering antidot structures at the surface. Further optimization of the SVA parameters might lead to greater control over the ordering of the antidot-like morphology. Furthermore, applying the pattern inversion

approach to the 16 kg/mol PS-*b*-PDMS studied in Chapter 4 would be an extension of this work, as the smaller natural domain spacing might yield smaller antidot features.

Finally, for the proposed memristor design, the most critical step is the experimental implementation and electrical characterization. This would provide insight into whether the expected advantages over the existing memristive systems can be achieved. Additionally, different electrode materials, including the substrate explored in this work, such as ruthenium or graphene, may be explored to improve device performance.

Addressing these aspects will provide a deeper understanding of the fundamental questions to achieve device-level integration of high- χ BCP lithography.

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Appendix

A.1 Experimental data from measurements

Table A.1. Process steps and optimized parameters for transferring single-layer graphene

No:	Process	Process parameter	Reference
1	Copper cutting and flattening	• Cut Cu to $1 \times 1 \text{ cm}^2$ • Flatten Cu piece using glass slides	
2	Copper etching	• 2 g sodium persulfate in 20 ml DI water • Cu etched for 3 h at 25 °C	
3	DI water rinse	• Graphene/PMMA film transferred to DI water • 5 min at 25 °C for residual removal	
4	Graphene transfer	• Transferred onto the substrate by scooping the film • Film dried using N_2	
5	Moisture removal	• Heated at 40 °C for 30 min	
6	Adhesion improvement	• Annealed at 140 °C for 1 h at 1×10^{-3} mbar	
7	PMMA removal	• Acetic acid bath for 3 h at 25 °C • Isopropanol rinse for acid removal • Film dried using N_2 • Annealed at 140 °C for 2 h at 1×10^{-3} mbar	Figs. 4.9, 4.10, and 4.11a

Table A.2. Process steps and optimized parameters for achieving SiO_x cylinders on silicon substrates using static and dynamic SVA, with corresponding references.

No:	Process	Process parameter	Reference
1	Ultrasonic cleaning	100 W, 40 °C, 1 min in cyclohexane	
2	BCP spin coating	0.5 wt% for 16 kg/mol PS-<i>b</i>-PDMS in cyclohexane 0.2 wt% and 0.5 wt% for 21 kg/mol PS-<i>b</i>-PDMS in cyclohexane	Section A.2.1 for thickness calibration curve
3	PVA spin coating	5 wt% partially hydrolyzed PVA (40%) in water/methanol (1:1) 2000 rpm for a 300 nm PVA film	
4	Drying of PVA film	Sample placed in a desiccator for 24 h	
5	Solvent vapor annealing	SVA setup: - Annealing beaker preheated to 100 °C for 5 min to remove residual moisture - Annealing solvents: toluene:heptane (5:1) or acetone - Annealing performed at 35 °C for 1 h Dynamic setup: - N₂ purging at 200 sccm for 10 min for air/moisture removal - Swelling at flow rate of 37 sccm, solvent: toluene/heptane (5:1) - Deswelling by 10 sccm N₂ for 10 min - SVA performed at 35 °C for 1 h	
6	Solvent removal	Sample placed in a desiccator for 24 h	
7	PVA removal and low-power plasma treatment	- Immersion in water for 1 min - Low-power O₂ plasma 30 W, 6 sccm O₂, 220 mTorr, 2 min	Static SVA: Figs. 4.1c , 4.2b , and 4.3b ; Dynamic SVA: Figs. 4.6b , and 4.7c Morphology: Figs. 4.16a and 4.17a
8	PS removal and PDMS conversion	- High-power O₂ plasma 80 W, 20 sccm O₂, 75 mTorr, 20 s	Fig. 4.15b , 4.16c , and 4.17c

A.2 Supplementary information

A.2.1 Thickness calibration

The relationship between spin speed and film thickness for the BCP thin films used in this work was investigated by spin coating BCP solutions onto silicon wafers at different spin speeds. The resulting film thicknesses were measured by ellipsometry at three spatially separated positions on each sample. The average film thickness was calculated, and the associated error was determined from the standard deviation of the three measurements. The dependence of film thickness on spin speed was analyzed using a power-law fit.

For the 16 kg/mol PS-*b*-PDMS, a 0.5 wt% solution was used to obtain the investigated film thickness range, whereas for the 21 kg/mol BCP, two different concentrations (0.2 wt% and 0.5 wt%) were employed to achieve a broader range of analyzed film thicknesses. Figure A.1 shows the spin speed–thickness relationship for the BCP systems used in this work.

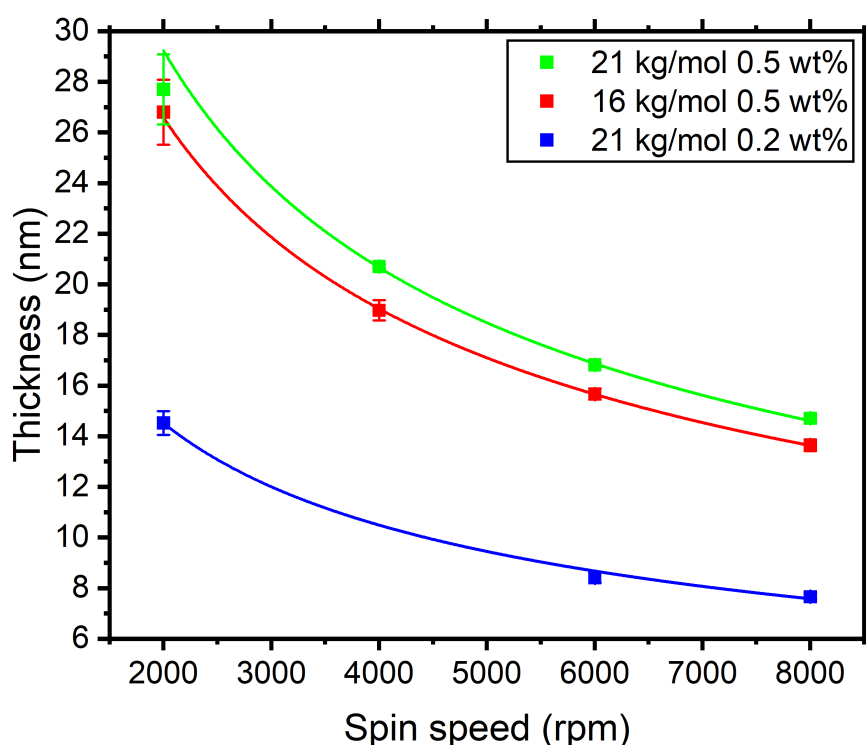


Figure A.1. Dependence of the PS-*b*-PDMS film thickness on spin speed for different molecular weights and solution concentrations. Film thicknesses were measured by ellipsometry at three different positions on each sample, and the error bars represent the standard deviation. Solid lines correspond to power-law fits of the experimental data.

A.2.2 Calculation of chain dimensions

The chain dimensions of the 21 kg/mol PS-*b*-PDMS were estimated using the mean-square end-to-end distance per molar mass, $\langle R^2 \rangle_0 / M$, tabulated for each homopolymer by Fetters et al. [165]. This ratio is a chemistry-specific constant that follows from the Gaussian chain model $\langle R^2 \rangle_0 \propto M$ [40, 43]. For each block, the end-to-end distance is:

$$\langle R^2 \rangle_0^i = \left(\frac{\langle R^2 \rangle_0}{M} \right)_i \cdot M_i, \quad (\text{A.1})$$

and the radius of gyration is $R_g^i = \sqrt{\langle R^2 \rangle_0^i / 6}$. For a diblock chain end-to-end distance follows from the additivity of mean-square end-to-end distances of the two blocks [40, 166]:

$$\langle R^2 \rangle_0 = \langle R^2 \rangle_0^{\text{PS}} + \langle R^2 \rangle_0^{\text{PDMS}}. \quad (\text{A.2})$$

Using $(\langle R^2 \rangle_0 / M)_{\text{PS}} = 0.434$ and $(\langle R^2 \rangle_0 / M)_{\text{PDMS}} = 0.457 \text{ \AA}^2 \text{ mol g}^{-1}$ from [165], with $M_{\text{PS}} = 15.5 \text{ kg/mol}$ and $M_{\text{PDMS}} = 5.5 \text{ kg/mol}$, the per-block end-to-end distances are $R_{\text{PS}} \approx 8.2 \text{ nm}$ and $R_{\text{PDMS}} \approx 5.0 \text{ nm}$. The total unperturbed end-to-end distance of the diblock chain is $R \approx 9.6 \text{ nm}$.

A.2.3 Image analysis methods

Quantitative analysis of the SEM images was performed using ImageJ [152], with pixel-to-length conversion calibrated from the SEM scale bar of each image using the Set Scale function. Three complementary analyses were carried out: Fourier transform analysis for domain spacing, particle analysis for individual domain size, and density counting for areal dot density. Each is described below.

Domain Size Analysis

For the domain size analysis, the SEM images were converted to binary images by thresholding. To ensure accurate quantification, only regions containing well-defined perpendicular cylindrical domains were selected, excluding areas with defects such as lying cylinders or grain boundaries. Particle analysis was performed using size filtering ($30\text{--}300 \text{ nm}^2$) and circularity constraints ($0.70\text{--}1.00$) to remove noise and irregular features.

For each detected domain, the major and minor axes were obtained by fitting an ellipse to each binary particle, where the major and minor axes correspond to the longest and shortest diameters of the fitted ellipse. The effective domain diameter d was calculated as:

$$d = \frac{d_{\text{major}} + d_{\text{minor}}}{2}$$

Statistical analysis was performed over detected domains within representative regions. The average domain diameter was determined with the standard deviation of the measured distribution. This approach ensures reliable estimation of intrinsic domain size while minimizing contributions from morphological defects and segmentation artifacts.

Determination of domain spacing by Fourier Transform analysis

The characteristic domain spacing (L_0) was determined using two-dimensional fast Fourier transform (FFT) analysis of the SEM images. The FFT provides a reciprocal-space representation of the spatial periodicity of the nanostructures.

For structures exhibiting well-ordered arrangements, the FFT displays discrete spots, whereas weakly ordered structures produce a diffuse circular ring. The radial position of this feature corresponds to the dominant spatial frequency q . To quantitatively extract this, the radially averaged intensity profile of the FFT was computed using the Radial Profile plugin in ImageJ, yielding the intensity as a function of radial distance from the center.

The position of the first-order peak in the radial profile (R_{peak} , in pixels) was identified as the dominant spatial frequency. The corresponding real-space domain spacing L_0 was calculated using:

$$L_0 = \frac{N \cdot \Delta x}{R_{\text{peak}}}, \quad (\text{A.3})$$

where N is the image size in pixels and Δx is the real-space pixel size (nm/pixel). For dot-like domains, L_0 corresponds to the nearest neighbor center-to-center distance of the hexagonal arrangement. For fingerprint morphologies, L_0 corresponds to the row-to-row spacing of the parallel cylinders. To minimize the influence of mixed morphologies, the analysis was performed on selected regions of interest containing either fingerprint-like or dot-like domains.

The accuracy of the domain spacing determination is primarily limited by the finite width of the first-order peak in the radial intensity profile. Structural disorder, finite domain size, and instrumental resolution all contribute to peak broadening. Consequently, the uncertainty in R_{peak} was estimated from the full width at half maximum (FWHM) of the peak. Assuming a Gaussian peak shape, the FWHM was converted to a standard deviation via $\sigma_R = \text{FWHM}/(2\sqrt{2\ln 2})$, and the corresponding uncertainty in L_0 was obtained from error propagation:

$$\frac{\sigma_{L_0}}{L_0} = \frac{\sigma_R}{R_{\text{peak}}}. \quad (\text{A.4})$$

Image Analysis and Dot Density Calculation

Density analysis of the dot-like structures was performed on SEM images of 21 kg/mol PS-*b*-PDMS thin films. The images were converted to 8-bit grayscale, cropped, and thresholded to obtain binary representations of the morphology, as shown in Figure A.2 (a).

Particle analysis was carried out using defined size (40–120 pixel²) and circularity (≥ 0.9) criteria to selectively identify dot-like perpendicular cylindrical domains while excluding elongated structures. The detected domains are indicated as red markers in Figure A.2 (b).

The areal dot density was calculated by normalizing the number of detected particles (N) with the analyzed area (A):

$$\rho = \frac{N}{A}$$

The image area was determined using calibrated pixel-to-length conversion obtained from the scale bar of each image. The pixel area was converted into physical units (nm²) and subsequently expressed in μm^2 to report the dot density in units of dots/ μm^2 .

To enable direct comparison between samples, identical analysis parameters (size filter, circularity threshold, magnification) were applied across all SEM images. The resulting dot density values were used to quantitatively compare the extent of perpendicular domain formation as a function of film thickness.

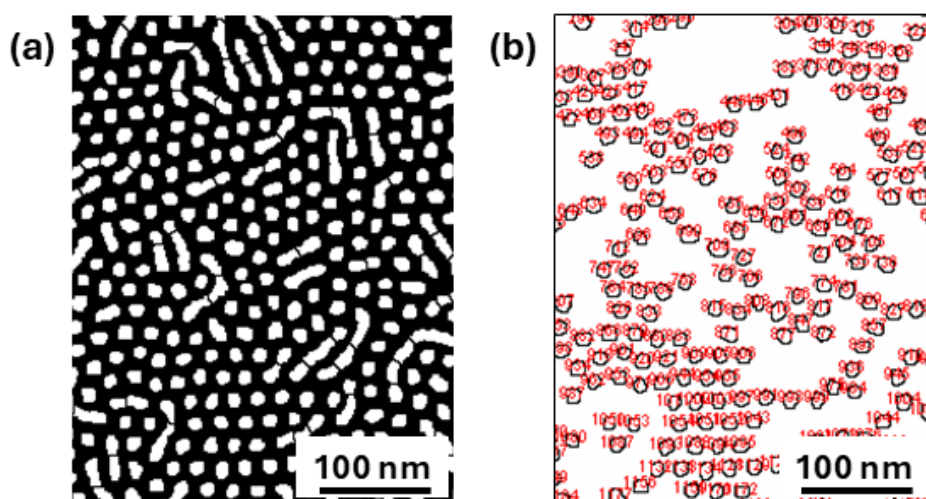


Figure A.2. (a) Binary image obtained from the SEM top-view image after thresholding. (b) Corresponding particle detection output, where red markers indicate detected cylindrical domains used for dot density calculation.

List of Publications

Contributions in Peer-Reviewed Journals

(* authors equally contributed)

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

Julius Bürger*, **Harikrishnan Venugopal***, Daniel Kool, Teresa de los Arcos, Alejandro Gonzalez Orive, Guido Grundmeier, Katharina Brassat, Jörg K. N. Lindner,

Adv. Mater. Interfaces 2022, 9, 2200962, DOI:10.1002/admi.202200962

Conference Contributions

(Presenting author underlined)

Oral Contributions

- Morphological characterization of sub-10 nm surface patterns created by block-copolymer self-assembly on graphene and metallic substrates,

Harikrishnan Venugopal, Janna X. Friebe, Jörg K. N. Lindner,

17th International Conference on Physics of Advanced Materials (ICPAM-17), Shizuoka University, Hamamatsu Campus, Japan, November 16–23, 2025.

- Morphology inversion in thin films of a cylinder-forming PS-*b*-PDMS block copolymer,

Janna X. Friebe, **Harikrishnan Venugopal**, Jörg K. N. Lindner,

17th International Conference on Physics of Advanced Materials (ICPAM-17), Shizuoka University, Hamamatsu Campus, Japan, November 16–23, 2025.

- Morphological characterization of sub-10 nm surface patterns created by block-copolymer self-assembly,

Harikrishnan Venugopal, Janna X. Friebe, Julius Bürger, Jörg K. N. Lindner,

Annual Meeting of DPG and DPG-Frühjahrstagung (DPG Spring Meeting) of the Condensed Matter Section (SKM), Regensburg, Germany, March 16–21, 2025.

- Sub-10 nm nanostructures in thin films of a cylinder-forming PS-*b*-PDMS block copolymers,

Janna X. Friebe, **Harikrishnan Venugopal**, Julius Bürger, Jörg K. N. Lindner,

Annual Meeting of DPG and DPG-Frühjahrstagung (DPG Spring Meeting) of the Condensed Matter Section (SKM), Regensburg, Germany, March 16–21, 2025.

- Invited talk: Progress in the nanopatterning of silicon surfaces with block copolymer lithography,

Harikrishnan Venugopal, Janna X. Friebe, Felix Lohmeyer, Julius Bürger, Jörg K. N. Lindner,

DSA 2024, Grenoble, France, October 17–18, 2024.

- Microphase Separation in Thin Films of a Sphere Forming PS-*b*-PDMS Block Copolymer, Janna X. Friebe, Alexander Stratmann, **Harikrishnan Venugopal**, Jörg K. N. Lindner, ICPAM-16, Antalya, Turkey, September 7–15, 2024.

- High-resolution study of changes in morphology and chemistry of microphase separated PS-*b*-PMMA thin films after selective removal of PMMA,

Harikrishnan Venugopal, Julius Bürger, Daniel Kool, Teresa de los Arcos, Alejandro González Orive, Guido Grundmeier, Katharina Brassat, Jörg K. N. Lindner,

Future-Materials-2023, Valencia, Spain, October 23–27, 2023.

- Revealing interfacial widths and line-edge roughnesses in cylinder-forming block copolymers using low keV analytical transmission electron microscopy,

Julius Bürger, **Harikrishnan Venugopal**, Daniel Kool, Teresa de los Arcos, Alejandro González Orive, Guido Grundmeier, Katharina Brassat, Jörg K. N. Lindner,

Microscopy Conference 2023, Darmstadt, Germany, Feb 26 – Mar 02, 2023.

- Ultra-high-resolution characterization of cylindrical mask openings created by microphase separation in PS-*b*-PMMA,

Julius Bürger*, **Harikrishnan Venugopal***, Daniel Kool, Teresa de los Arcos, Alejandro Gonzalez Orive, Guido Grundmeier, Katharina Brassat, Jörg K. N. Lindner,

The 6th DSA Symposium at KAIST, Daejeon, Korea, October 19–21, 2022.

Poster Contributions

(Presenting author underlined)

- Nanophase separation in cylinder forming PS-*b*-PDMS block copolymer thin films,
Harikrishnan Venugopal, Alexander Stratmann, Janna X. Friebe, Jörg K. N. Lindner,
EMRS Spring Meeting 2024, Strasbourg, France, May 27–31, 2024.
- Microphase separation in thin films of a sphere-forming PS-*b*-PDMS block copolymer,
Janna X. Friebe, Alexander Stratmann, **Harikrishnan Venugopal**, Jörg K. N. Lindner,
Annual Meeting of DPG and DPG-Frühjahrstagung (DPG Spring Meeting) of the Condensed Matter Section (SKM), Berlin, Germany, March 17–22, 2024.
- Microphase Separation in Thin Films of a Sphere Forming PS-*b*-PDMS Block Copolymer,
Janna X. Friebe, Alexander Stratmann, **Harikrishnan Venugopal**, Jörg K. N. Lindner,
15th International Conference on Physics of Advanced Materials (ICPAM-15), Sharm El Sheikh, Egypt, November 19–26, 2023.
- Investigation of interfacial widths and line-edge roughnesses in microphase separated cylindrical block copolymer films,
Julius Bürger, **Harikrishnan Venugopal**, Daniel Kool, Teresa de los Arcos, Alejandro González Orive, Guido Grundmeier, Katharina Brassat, Jörg K. N. Lindner,
EMRS Spring Meeting 2022, May 30–June 03, 2022.
- Arrangement and alignment of lamellar block copolymer nanodomains in metallic antidot film,
Daniel Kool, **Harikrishnan Venugopal**, Jörg K. N. Lindner,

14th International Conference on Physics of Advanced Materials (ICPAM-14), Dubrovnik, Croatia, September 8–15, 2022.

- XPS study of the selective removal of PMMA from microphase separated PS-*b*-PMMA thin films,

Harikrishnan Venugopal, Teresa de los Arcos, Alejandro González Orive, Julius Bürger, Daniel Kool, Katharina Brassat, Guido Grundmeier, Jörg K. N. Lindner,

13th International Conference on Physics of Advanced Materials (ICPAM-13), Sant Feliu de Guíxols, Spain, September 24–30, 2021.

- Analytical high-resolution STEM investigations of interfacial widths and line-edge roughnesses in microphase separated cylindrical block copolymer thin films,

Julius Bürger, **Harikrishnan Venugopal**, Daniel Kool, Teresa de los Arcos, Alejandro González Orive, Guido Grundmeier, Katharina Brassat, Jörg K. N. Lindner,

13th International Conference on Physics of Advanced Materials (ICPAM-13), Sant Feliu de Guíxols, Spain, September 24–30, 2021.

- Order and arrangement of block copolymer domains in metallic antidot films,

Daniel Kool, Julius Bürger, **Harikrishnan Venugopal**, Katharina Brassat, Jörg K. N. Lindner,

13th International Conference on Physics of Advanced Materials (ICPAM-13), Sant Feliu de Guíxols, Spain, September 24–30, 2021.