Directed Self-Assembly with Sub-100 Degrees Celsius Processing Temperature, Sub-10 Nanometer Resolution, and Sub-1 Minute Assembly Time

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Since the 1960s, the number of transistors placed on an integrated circuit has roughly doubled every two years, showing exponential growth in the capabilities of electronic devices.[1] This tendency has been sustained over the past several decades on the basis of continuing advancements in manufacturing technologies including optical lithography.[2–5] However, photolithography is reaching a physical limit in resolution,[3,6] and alternative technologies such as extreme ultraviolet (EUV) lithography, nanoimprint lithography, interference lithography, and directed self-assembly (DSA) are emerging rapidly. DSA of block copolymers (BCPs) has recently attracted much attention as a promising candidate for next-generation lithography due to its capacity to provide excellent resolution and scalability.[5,17–25] The self-assembly of a BCP, where two mutually incompatible polymer chains are connected via covalent bonding, can create sub-20 nm periodic patterns with different geometries such as dots, lines, holes, and rings,[17,18,26–28] while even more complex features such as bends, T-junctions, and jogs have already been demonstrated.[29] Based on these promising results, recent research efforts have focused on resolving remaining challenges for DSA such as control over defects, resolution, and throughput.[30–33]

To generate well-registered patterns within guiding templates by accelerating chain movements, thermal annealing or solvent annealing is typically used.[13,14,17,18,26,29] Thermal annealing increases the temperature of BCPs over their glass transition temperatures \( (T_g) \), and is widely employed due to simplicities in processing.[17,24–36] It has previously been reported that very short annealing time of less than 5 minutes is sufficient for the self-assembly of poly(styrene-b-methylmethacrylate) (PS-b-PMA) BCP.[28,29,37–39] On the other hand, further reduction of the critical dimension (CD) and line edge roughness may require the use of BCPs with a larger Flory-Huggins interaction parameter \( (\chi) \).[33] Poly(styrene-b-ethylene oxide) (PS-b-PEO), poly(styrene-b-dimethylsiloxane) (PS-b-PDMS), poly(dimethylsiloxane-b-2vinylpyridine) (PDMS-b-P2VP), poly(styrene-b-lactide) (PS-b-PLA), and polyhedral oligomeric silsesquioxane (POSS) containing BCPs (PS-b-PMAPOSS and PMMA-b-PMAPOSS) have been suggested as BCPs with large \( \chi \) values, and improved resolution and edge roughness have been demonstrated.[23,26,39–42] However, the applicability of BCP with a high \( \chi \) is hindered by slow self-assembly kinetics, which results from the exponential decrease of the chain diffusivity in the BCP with \( \chi \).[43] Thus, for such BCPs, solvent annealing, which can provide better chain flexibility compared to thermal annealing, has been more commonly used, with the aim of realizing good ordering of BCP microdomains.[23,44,45] Another advantage of solvent annealing is the capability to control the orientation and morphologies of BCP microdomains.[23,26,39,42,46]

Despite the significant role of solvent molecules incorporated in BCPs, the self-assembled pattern generation of high-\( \chi \) BCPs generally takes a few to tens of hours, thus detrimentally affecting the throughput of DSA.[26,36,42,45,47–49] Considering the high throughput (~200 wafers per hour) of commercial ArF scanners, the self-assembled pattern generation time may need to be reduced significantly. Recently, Buriak and coworkers reported that the self-assembly processing time can be significantly shortened by the application of microwave annealing of BCP samples contained in closed vessels filled with a solvent.[50] They comprehensively analyzed the effects of annealing temperature and time, BCP molecular weight, and substrate resistivity. They found that for the formation of well-ordered patterns with a minimum defect density, an annealing temperature higher than 140 °C and Si substrates with a low resistivity (<0.02 Ω-cm) were dispensable. These findings imply that, in order to extend the versatility of solvothermal treatment for DSA, it is very
important to develop a more practical and simpler strategy that can work with diverse substrates and that can be more easily implemented in semiconductor production lines. Here, we show how sub-10 nm resolution and sub-1 min self-assembly can be simultaneously achieved for more practical DSA technology. We conducted a systematic study on the effects of simple low-temperature thermal assistance for solvent vapor treatment on BCPs with a large $\chi$ parameter, and on the basis of these results, we demonstrate how the pattern formation time can be effectively reduced by the strategy. By optimizing the temperature and other parameters of solvent vapor treatment, well-ordered sub-10 nm half-pitch patterns were obtained via short annealing for 1 min. We demonstrate that low-temperature thermal assistance to solvent vapor treatment is widely effective for realizing various morphologies of BCPs, such as spheres, cylinders, and perforated lamellae.

As shown in Figure 1, the annealing experiments were performed in a stainless steel chamber containing a solvent at the bottom of the chamber. Stainless steel was chosen for...
faster stabilization of temperature due to its higher thermal conductivity compared to glass or plastics. The chamber was preheated at designated temperatures before placing BCP samples inside of it. Solvent annealing was then performed at controlled temperatures between room temperature and 100 °C. As a previous study pointed out, solvothermal treatment at a high temperature can cause serious solvent condensation on BCP films,[50] and therefore we focused on a lower temperature range (<100 °C), where a solvent vapor with a relatively low vapor pressure is produced. As will be discussed in detail in the latter part of this paper, such low-temperature solvothermal treatment can effectively facilitate self-assembly without solvent condensation. This simple solvothermal annealing method can be performed on a typical hot plate and does not need a closed environment or a sophisticated heating mechanism, and thus may be more advantageous for implementation in production lines. We used PS-b-PDMS BCPs, which has a known γ of ~0.26. The γ of PS-b-PDMS is several times larger than that of PS-b-PMAA, and thus PS-b-PDMS is an appropriate model BCP material with a large γ.[26,42,51,52] Our previous reports showed that typical annealing time for achieving good ordering is 3–18 h.[26,42,52]

To begin with, in order to investigate the effectiveness of thermal assistance to solvent annealing, conventional solvent vapor and thermal treatments were performed in the same chamber. PS-b-PDMS BCPs with different molecular weights (MW) of 16 kg mol⁻¹ (SD16, Figures 1c-e), 45.5 kg mol⁻¹ (SD45, Figures 1f-h), and 51.5 kg mol⁻¹ (SD51, Figures 1i-k) were spin-coated on PS-brush-treated trench substrates. (See the details pertaining to the overall processing procedure, including the trench fabrication, brush treatment, BCP self-assembly, and plasma treatment steps in the Experimental Section.) When PS-b-PDMS BCPs were treated by a solvent (toluene) vapor or thermally annealed at 85 °C, uniform ordering in 1-μm-wide trenches was not observed during the given treatment times (5, 10, and 30 min for SD16, SD45, and SD51, respectively). However, the solvent vapor treatment at 85 °C accomplished a good ordering of the BCPs with a low defect density less than 1 μm⁻² in the same trenches. Well-ordered 8-mm-wide line (Figure 1e), 16-mm-wide line (Figure 1h), and 20-mm-sized dot (Figure 1k) patterns were obtained after the same duration of treatment times. The given treatment times of 5, 90, and 30 min were the minimum annealing times to achieve a good ordering of the SD16, SD45, and SD51 BCPs, respectively. In 1-μm-wide trench templates. For comparison, we confirmed that, for the uniform assembly of SD16 BCP in the same trench patterns, solvent annealing at room temperature required treatment longer than 1 h,[52,55] and simple thermal annealing alone could not achieve good ordering in such wide trench templates. Even when the PS-b-PDMS BCPs were thermally annealed at higher temperature above 200°C (≫Tg) for 10 h in a vacuum oven, perfectly ordered structures in the trenches could not be obtained (Figure S1). These results suggest that thermal-assisted solvent annealing is highly effective for accelerating the kinetics of self-assembly despite the much lower temperature employed compared to a previous study.[50] Due to higher chain mobility for a smaller MW, sub-10 nm patterns with good alignment could be obtained in shorter time compared to the BCP with a line width of 16 nm, which will be discussed in detail below.

As expected, the self-assembly kinetics of the solvent-annealed BCP samples depends on treatment temperature. The morphologies of the BCPs annealed at various temperatures (25–85 °C) for a fixed time (5 min) are shown in Figure 2a-d. Uniform alignment of the 8-mm-wide line patterns could not be obtained in 5 min by annealing the BCPs at a temperature lower than 85 °C. A higher annealing temperature in a range between 25–85 °C rapidly decreased both the defect density and the minimum annealing time to achieve well-ordered patterns (Figure 2e,f) with a low defect density of less than 1 μm⁻², confirming the effectiveness of thermal activation for higher chain mobility. However, a higher annealing temperature above 100 °C caused dewetting of the BCP films, as shown in Figure S2, due to condensation of the solvent on the surface of the BCP films. Thus, the solvent condensation determines the upper limit of the processing temperature. Using the temperature-dependent defect density data and the analytical model in a previous study,[50] the defect diffusion activation energy (Ea) of the SD16 BCP was calculated to be ~2.06 kJ/mol, which is orders of magnitude smaller than the reported value for cylinder-forming PS-b-PMAA with a MW of 84 kg/mol. The significantly smaller Ea can be attributed to the highly effective plasticization caused by the solvothermal treatment as we well as the relatively small MW of SD16 as compared to the PS-b-PMAA BCP. We also investigated whether thermal assistance (85 °C) facilitates the realization of BCPs with various morphologies and molecular weights. PS-b-PDMS BCPs with MW = 16, 45.5, 55, and 51.5 kg mol⁻¹, respectively, were used for the experiments. Figure 3 shows the time evolution of the BCP morphologies treated at the same conditions. The molecular weight significantly affected the rates of alignment along the topographic trench walls and defect annihilation. Longer annealing time was required to obtain uniform good ordering for BCPs with a large molecular weight due to kinetically slower chain mobility.[50] For example, for cylinder-forming BCPs, as presented in Figure 3a,b, the ordering process of the BCP with a MW of 16 kg mol⁻¹ was completed in 5 min, while a higher MW (45.5 kg mol⁻¹) case needed 90 min. As shown in Figure 3e, the decline of defect density (D) with annealing time (t) was steeper for the SD16 BCP. The correlation length of the BCP self-assembly patterns is known to grow according to a power law; thus, the defect density (D) can be expressed using the formula, D ≡ t⁻α. The time-decay exponent (n) for SD16 was estimated to be 2.5, while that for SD45 was 1.74.

A similar tendency was observed for spherical morphologies (Figure 3c,d). On the other hand, the minority volume fraction of BCPs also influences the self-assembly kinetics. A faster decrease of defect density with annealing time for SD55 (minority volume fraction = 9.8%) compared to SD51 (minority volume fraction = 17.7%) was observed, as shown in Figure 3f. Despite the larger MWs
of SD51 and SD55 compared to SD45, the sphere-forming BCP more rapidly self-assembled compared to the cylinder morphology. The estimated time-decay exponents (n) for SD51 and SD55 were 3.09 and 3.37, respectively, which are significantly larger than that of SD16. This is likely due to the relaxed requirement of perpendicular diffusion in the spherical morphology compared to the cylindrical morphology, which leads to a smaller activation barrier for chain diffusion.[54]

The proposed thermally assisted solvent annealing is also applicable to treatment with mixed solvent vapors. Our previous study reported the geometrical tunability of PS-b-PDMS BCPs through treatment with a mixed vapor of partially and fully selective solvents.[24] A morphological transition from cylindrical patterns to hexagonally perforated lamellar (HPL) patterns was observed by selectively swelling the PDMS block using heptane. Solvent annealing at an elevated temperature (85 °C) can also expedite the formation of well-ordered HPL morphologies (Figure S3c) to within 25 min, which is much faster than the time (3 hours) reported previously.[26] This result indicates that thermal assistance is also effective for treatment with mixed solvent vapors and is compatible with the solvent annealing process employed to tune self-assembled morphologies in a wide range.

The self-assembly processing time can be further reduced by using narrower guiding templates. Figure 4 shows highly ordered linear patterns assembled in 200-nm-wide linear and 360-nm-wide circular trenches. Notably, linear and concentric ring patterns with a line width of 8 nm were well ordered (defect density <1 μm−2) after a treatment lasting only one minute. The self-assembly of SD45 BCP forming 16-nm-wide lines was completed within 20 min, which is much faster compared to the case of 1-μm-wide trenches. The time evolution of the morphology of SD45 in the narrow trenches are shown in Figure S4. Considering the
patterning capability of a commercial ArF scanner that can provide sub-100 nm guiding templates, the DSA processing time by this solvothermal treatment has potential to be further shortened to a few tens of seconds in the case of SD16 BCP. The line edge roughness (LER) and line width roughness (LWR) of the SD16 BCP were estimated to be 2.57 and 2.18 nm respectively. (See the details in Figure S5 in the Supporting Information.)

In summary, we demonstrated a facile and simple methodology to achieve both ultrahigh resolution and short processing time of DSA by applying thermally-assisted solvent vapor annealing to PS-\(b\)-PDMS with a large \(\chi\) parameter. BCP pattern generation with sub-10 nm resolution, sub-100 °C processing temperature, and sub-1 min annealing time was successfully achieved. This method is applicable to different geometries such as dots, lines, and hole patterns with substantially reduced processing time compared to previous studies. This practical and useful method will provide new opportunities for next-generation sub-10 nm lithography applications.

Figure 3. Time evolution of self-assembled morphologies for BCPs with different MW. MW = (a) 16 kg mol\(^{-1}\), (b) 45.5 kg mol\(^{-1}\), (c) 55 kg mol\(^{-1}\), and (d) 51.5 kg mol\(^{-1}\). The annealing temperature was fixed at 85 °C, while its annealing time was varied. (e)–(f) Time evolution of defect density as a function of (e) MW and (f) minority volume fraction \(f_{PDMS}\).

Figure 4. Self-assembled pattern formation in narrow trenches by the optimized treatment. (a,b) 8-nm-wide line patterns made from SD16 treated at 85 °C for 1 min. (c,d) 16-nm-width line patterns made from SD45 (at 85 °C for 10 min and 20 min, respectively). Trench width = (a,c) 200 nm, (b) 360 nm, and (d) 360 nm.
**Experimental Section**

*Self-Assembly of Block Copolymers*: In order to guide the self-assembly of BCPs, Si substrates with periodic trenches with a depth of 40 nm and a width of 1 μm were fabricated using Krf lithography. The surface of the Si substrate was treated by hydroxy-terminated PS homopolymers with a molecular weight of 38 kg mol⁻¹, which was spin-coated on the substrates and annealed at 150 °C for 2 h in a vacuum oven and then washed with toluene to remove unreacted polymer residues. The PS-brush treatment on annealing vapor, toluene of 15 mL was added to the chamber (full and annealed by solvent vapor. For the generation of the solvent and 17.5%, respectively were used. All of the BCPs were purchased terminated PS homopolymers with a molecular weight of 38 kg

**Image Analysis**: The defect density was counted with the assistance of image analysis software (Image J). In order to quantify the line width, line-edge roughness (LER), and line-width roughness (LWR) of the self-assembled patterns, a commercial image analysis software (SuMMIT) was used.

**Supporting Information**

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

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